Stantec

Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan

East Palestine Train Derailment Site
East Palestine, Ohio
Norfolk Southern Railway Company

June 28, 2023

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Prepared for:

Norfolk Southern Railway Company
East Palestine, Ohio

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SENTINEL MONITORING WELL INSTALLATION AND GROUNDWATER SAMPLING WORK PLAN
NORFOLK SOUTHERN - EAST PALESTINE, OHIO
June 26, 2023

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ACRONYM LIST

ASTM	ASTM International
bgs	Below ground surface
°C	Degrees Celsius
CCHD	Columbiana County Health District
CoC	Chain-of-Custody
COC	Contaminants of Concern
DDAGW	OEPA Division of Drinking and Ground Waters
DERR	OEPA Division of Environmental Response and Revitalization
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DQO	Data Quality Objective
EUL	Environmental Unit Leader
FOC	Fraction Organic Carbon
FSOP	Field Standard Operating Procedure
GIS/GPS	Global Information System/Global Positioning System
HASP	Health and Safety Plan
HCL	Hydrochloric Acid
ID	Identification
IDW	Investigation Derived Waste
JSA	Job Safety Analysis
LNAPL	Light Non-Aqueous Phase Liquid
MCL	Maximum Contaminant Levels (US EPA)
ug/L	micrograms per liter
µS/cm	MicroSiemens per Centimeter
mg/L	Milligrams per Liter
MS/MSD	Matrix Spike/Matrix Spike Duplicate
mV	Millivolts
NAPL	Non-Aqueous Phase Liquid
NSRC	Norfolk Southern Railway Corporation
NTU	Nephelometric Turbidity Units
OAC	Ohio Administrative Code
ODH	Ohio Department of Health

OEPA	Ohio Environmental Protection Agency
OEPA TGM	OEPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring
ORP	Oxidation Reduction Potential
PADEP	Pennsylvania Department of Environmental Protection
PADEP TGM	PADEP Land Recycling Program Technical Guidance Manual
PFAS	Per- and Polyfluorinated Substances
Plan	Sentinel Monitoring Well Installation and Sampling Work Plan
PID	Photoionization Detector
PPE	Personal Protective Equipment
PVC	Polyvinyl Chloride
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
Responders	NSRC, its Consultants, or Contractors
RSL	Regional Screening Levels (US EPA)
SOP	Standard Operating Procedure
s.u.	Standard Unit
Stantec	Stantec Consulting Services Inc.
SVOC	Semi-Volatile Organic Compound
UAO	Unilateral Administrative Order
UC	Unified Command
USCS	Unified Soil Classification System
US EPA	United States Environmental Protection Agency
VAP	OEPA Voluntary Action Program
VOC	Volatile Organic Compound

Revision	Description	Date
0	Issued for internal review	Report Date
1	Update of Document	March 6, 2023
2	Updated	April 14, 2023
3	Updated based on 4/18/23 Comments	April 30, 2023
4	Updated based on 5/13/23 Comments	June 2, 2023
5	Updated based on 6/9/23 Comments	June 13, 2023
6	Updated criteria based on 6/17/23 Comments	June 20, 2023
7	Updated criteria for PFAS and added Compound to Table 5 based on Comment	June 26, 2023
8	Updated RSL criteria for VC per comment	June 28, 2023

1.0 INTRODUCTION

On February 3, 2023, a derailment occurred near the North Pleasant Drive crossing in East Palestine, Columbiana County, Ohio (the Site). The derailment involved 51 rail cars and resulted in a fire and breaches to tank cars that contained hazardous materials (i.e., vinyl chloride, butyl acrylate, ethylene glycol, monobutyl ether, ethylhexyl acrylate, isobutylene) and non-hazardous materials. The release of hazardous materials from the damaged cars affected environmental media in the area of the derailment.

Norfolk Southern Railway Company (NSRC) immediately mobilized response personnel to the incident. Response crews established operations to stop, contain, and recover the releases. That work continues and has expanded to include efforts to assess the nature and extent of potential impacts and to conduct additional removal activities to protect human health and the environment.

This Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan (Plan) has been developed to monitor groundwater quality in the vicinity of the Site in accordance with the Unilateral Administrative Order for Removal Actions (UAO) issued by the United States Environmental Protection Agency (US EPA) Regions 3 and 5, signed on February 21, 2023. As part of a larger group of plans collectively making up the project Removal Work Plan, the work described in this Plan will be conducted in accordance with the Sentinel Water Well Sampling Quality Assurance Project Plan (QAPP), Site Health and Safety Plan (HASP), and other overall documents that provide procedures for sample collection, identification, analysis, and reporting. Media-specific sampling and analysis procedures are presented below to support the scope of work discussed in the plan.

This Plan was developed on behalf of Norfolk Southern Railway Company (NSRC) by Stantec Consulting Services Inc. (Stantec).

2.0 OBJECTIVE

This Plan has been developed to provide methodologies used to monitor potential migration of contaminants of concern (COC) in groundwater at sentinel wells prior to reaching potential receptors that include private potable wells in Ohio and Pennsylvania and the Village of East Palestine municipal supply wells. The sampling program was initially developed in coordination with Site stakeholders (US EPA, Ohio Environmental Protection Agency (OEPA), Columbiana County Health District (CCHD), Ohio Department of Health (ODH), and the Pennsylvania Department of Environmental Protection (PADEP). Currently, co-located samples are collected by NSRC consultants, OEPA, and PADEP from sentinel wells, when requested. Co-located sampling can change upon request with approval by the Environmental Unit Leader (EUL). Further details on co-located sampling are provided in Section 6.2.4.1.

Sentinel monitoring wells have been installed between the derailment area and private and public drinking water wells. The objective of the sentinel wells is to monitor potential impacts to groundwater, specifically the drinking water aquifer or aquifers, between the derailment area and potential groundwater receptors near the Site in Ohio and Pennsylvania. Furthermore, groundwater analytical data along with other site-specific data may be used in the development of a preliminary groundwater fate and transport model to evaluate and estimate flow pathways and travel distances of COCs. As of the date of this Plan, 14 permanent sentinel monitoring wells (11 in Ohio and three in Pennsylvania) have been installed and the locations of the sentinel monitoring wells are presented on **Figure 1**. Initial sentinel monitoring wells (SMW-01, 02, 03, 04, and 05) were installed utilizing hollow-stem auger drilling technology and all subsequent sentinel monitoring wells were installed utilizing roto-sonic drilling technology. These wells are currently being monitored on a weekly basis.

Additional sentinel wells are not currently proposed. The need for installation of additional sentinel wells will be based on the results of groundwater quality as it relates to the incident and the risk of impacts to potable wells or identified data gaps. If additional sentinel monitoring wells are proposed, locations and screen depths will be determined by stakeholders and approved by the EUL. At the selected additional sentinel monitoring well locations, exploratory soil borings will be drilled and sentinel monitoring wells will be installed, wells will be developed, and groundwater samples will then be collected from the sentinel groundwater well monitoring network for chemical analysis, in accordance with the procedures provided in this Plan. Implementation of this Plan will be completed by NSRC, its consultants, or contractors (collectively referred to as Responders). Initial installation and sampling activities for each sentinel monitoring well location is described in Section 5.0.

Investigations in the vicinity of the derailment area coinciding with this Plan have identified shallow groundwater (possibly perched) within 6 to 12 feet below ground surface (bgs). No sentinel monitoring wells are screened in this zone, and further investigation and characterization is to be completed as part of other work plans and is not considered part of this Plan.

The protocols established in this Plan have been prepared to assist in sampling groundwater by defining sampling procedures and schedules, refining the COCs, and defining how results will be communicated to NSRC, US EPA, and other responding agencies to meet the requirements of the UAO.

The associated OEPA Division of Environmental Response and Revitalization (DERR) Field Standard Operating Procedures (FSOPs) and OEPA Voluntary Action Program (VAP) Technical Guidance Compendium VA30007.14.22 (**Appendix A**), OEPA DERR Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) *Chapters 4, 7, 10, and 14* (**Appendix B**), PADEP Land Recycling Program Technical Guidance Manual (PADEP TGM) *Section III and Appendix A* **(Appendix C),** OEPA Division of Drinking and Ground Waters (DDAGW) SOP for Per and Polyfluorinated Alkyl Substances (PFAS) and US EPA SOPs **(Appendix D)** are utilized as guidance documents for all investigation activities of this Plan

Table 1 - Standard Operating Procedures References

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
OEPA TGM	Technical Guidance Manual (2009)	OEPA DERR	This manual describes standard hydrogeologic investigations and groundwater monitoring practices.
PADEP TGM	Land Recycling Program Technical Guidance Manual (2019)	PADEP	Selections from this manual describe standard hydrogeologic investigations and groundwater monitoring practices.
OEPA VA30007.14.22	Sampling and Analysis of Fraction Organic Carbon (FOC) in Soils (January 2014)	OEPA VAP	This procedure describes standard practices for sampling and analysis of fraction organic carbon in soils.
FSOP 1.3	Field Documentation (April 29, 2020)	OEPA DERR	This procedure describes standard practices for field documentation of sampling and other field activities.
FSOP 1.5	Sample Custody and Handling (May 6, 2020)	OEPA DERR	This procedure describes standard practice for custody and handling of environmental samples

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
			(water, soil, sediment, soil gas, or air).
FSOP 1.6	Sampling Equipment Decontamination (May 12, 2020)	OEPA DERR	This procedure describes standard practices of decontamination of sampling equipment.
FSOP 1.7	Investigation Derived Waste (May 21, 2020)	OEPA DERR	This procedure describes standard practices for management and disposal of investigation derived waste (IDW) generated during site assessments.
FSOP 2.1.1	Discrete Soil Sampling (May 26, 2020)	OEPA DERR	This procedure describes standard practices for discrete soil sampling and sample collection.
FSOP 2.1.4	Sample Headspace Screening	OEPA DERR	This procedure describes standard field practices for headspace screening of soil or other solid or liquid samples to provide a basis for laboratory sample selection.
FSOP 2.1.5	Soil Description Classification and Logging (June 30, 2020)	OEPA DERR	This procedure describes standard field soil description, classification, and logging practices.
FSOP 2.2.1	Well Development (July 14, 2020)	OEPA DERR	This procedure describes standard monitoring well development practices.

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
FSOP 2.2.2	Ground Water Level Measurement (July 20, 2022)	OEPA DERR	This procedure describes the measurement of groundwater levels from wells or piezometers.
FSOP 2.2.4	Ground Water Sampling (General Practices) (August 4, 2020)	OEPA DERR	This procedure describes general practices for decontaminating non-dedicated sampling equipment.
FSOP 2.2.6	Low-Flow Groundwater Sampling (August 19, 2020)	OEPA DERR	This procedure describes the applicability of low-glow ground water sampling.
FSOP 2.2.8	Groundwater Sampling Using a Bladder Pump (December 3, 2020)	OEPA DERR	This procedure describes the utilization of a bladder pump.
FSOP 2.2.10	Groundwater Sampling Using an Electric Submersible Pump (December 10, 2020)	OEPA DERR	This procedure describes the utilization of an electric submersible pump.
PFAS SOP	SOP for Per- and Polyfluorinated Alkyl Substances Sampling at Public Water Systems (March 3, 2020)	OEPA DDAGW	This procedure provides general information for the collection of PFOS/PFAS water samples from a water supply system tap.
EPA 524.2	Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (1995)	US EPA 524.2-1	Method for analysis of VOCs in water.

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
EPA 525.2	Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (1995)	US EPA 525.2-1	Method for analysis of SVOCs in water.
EPA 533	Determination of Per- and Polyfluoroalkyl Substances in drinking water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/ Tandem Mass Spectrometry	US EPA 533	Method for analysis of PFAS in water.

3.0 HEALTH AND SAFETY

This work will be conducted under an approved, overall project Site HASP, and media specific HASP. Each worker will be responsible for reviewing the HASP. Personnel conducting field activities will have completed required training, understand safety procedures, and be qualified to conduct the field work described in this Plan. The HASP will include a job safety analysis (JSA) for each task described in this Plan and provide control methods to protect personnel. Personal protective equipment (PPE) requirements and safety, security, health, and environmental procedures are defined in the HASP. In addition, authorized field personnel will attend NSRC-required safety orientations and training.

Safety briefings will take place each day prior to beginning work and at mid-shift or after lunch breaks. The briefings will be documented including the names of those in attendance and items discussed. The JSAs will be updated upon a change in conditions.

4.0 PRELIMINARY CONCEPTUAL SITE MODEL

4.1 STUDY AREA

The sentinel monitoring well study area is generally within approximately 0.5 to 1.5 miles of the Site, but currently excludes the immediate vicinity of the incident area. These initial areas may be expanded in the future if groundwater analytical results from the sentinel monitoring wells indicate impacts to groundwater that could be associated with derailment and migrating outside of the initial study area. The areas were defined in part based on the regional inferred groundwater flow direction, surface water flow, and the watershed basin. Information shown on **Figure 2** is preliminary and based on a small, incomplete data set.

4.2 LAND USE

The sentinel monitoring well study area is located within a mixed-use residential, commercial, and industrial area, with residential properties northwest, southeast, and south of the derailment area. The nearest residences are less than 1,000 feet from the incident area. Residential properties are also located along waterways which became contaminated following the derailment and are within the affected area. The Ohio-Pennsylvania border is located less than 1 mile from the derailment location. (Arcadis, 2023).

4.3 PHYSICAL SETTING

4.3.1 Site Topography and Drainage

East Palestine is located in the northeast portion of Columbiana County, approximately 0.25 miles from the Pennsylvania border. Columbiana County lies within the Appalachian Plateau physiographic province. The northern portion of the county lies within the Glaciated Allegheny Plateau, where the general topography is characterized as hummocky to rolling uplands associated with numerous glacial end moraines, with elevations ranging from 600 to 1,505 feet above mean sea level (amsl) and moderate relief (Brockman 1998). Valleys tend to be broad and relatively flat lying. East Palestine is generally within a valley where the ground surface gently slopes to the west along Sulphur Run and intersects narrow valleys along Leslie Run trending northeast to the south. The topography within the town is generally sloping to the west with an average grade of 0-2 percent (%) (Angle 1994) [Arcadis, 2023].

The ground surface in the derailment area is at an approximate elevation of 1,000 feet above mean sea level. Just west of the derailment area, stormwater runoff tends to flow west towards Sulphur Run. As Sulphur Run flows to the west/southwest through East Palestine, numerous storm drains exist which generally flow toward Sulphur Run. On the west side of East Palestine, surface runoff tends to flow west, southwest, or south toward Leslie Run, which flows to the east-southeast and then to the south after converging with Sulphur Run.

4.3.2 Regional Geology and Hydrogeology

Relevant information on area hydrogeology is provided in the Ohio Department of Natural Resources (ODNR) Ground Water Pollution Potential Report No. 35, Ground Water Pollution Potential of Columbiana County, Ohio, published in 1994. This publication indicates East Palestine is in a buried valley hydrologic setting where topology is typically associated with end moraines and rolling hills. Soils are typically clay loam with a thickness up to 140 feet. Sand and gravel aquifers are present but may be thin and isolated from each other. Yields of these aquifers tend to average from 10 to 20 gallons per minute. There are areas where 25-500 gallons per minute can be achieved from interbedded and interlinked sand lenses, gravel, and silt deposits which extend up to 300 feet bgs (Crowell 1978). Recharge is reportedly high (7-10 inches per year due to the permeable soils in the vadose zone), the shallow to moderate depth to water (15-30 feet bgs), and the topography is relatively flat. Information from the ODH and interpretation of available information on the East Palestine water supply wells indicates that the deeper portions of the valley deposits include productive, high-conductivity sand and gravel zones.

Shallow groundwater is expected to flow toward Sulphur Run and Leslie Run. Based on a groundwater potentiometric map published by ODNR (ODNR 2007), deeper regional groundwater in bedrock flows toward the valley in which the Village of East Palestine is located. From the confluence of Sulphur Run and Leslie Run, the deeper regional groundwater flows to the south. Contours of the potentiometric surface based on the May 10, 2023, comprehensive groundwater gauging event are presented on Figure 3. Well construction details and groundwater level data for the sentinel wells from the May 10, 2023 gauging event are presented in Table 2.

4.3.3 Site Geology and Hydrogeology

Subsurface geology observed near the Site consists of structural fill underlain by silts and clays.

Sentinel wells that were installed within approximately 0.5 to 1.5 miles of the Site indicate that the upper 10 to 15 feet bgs consists of sands, gravels, and fill with inclusions of clays and silts. A predominant clay layer with interbedded silty sand is encountered to depths of approximately 50 to 60 feet bgs. The clays and silts were described as predominantly dry and potentially act as a confining layer between the shallow (perched) and deeper aquifers.

Below the confining silts and clays, coarser grained materials begin to appear. The coarser grained materials consist of fine to coarse sands and loose gravels that were described as wet and may indicate the drinking water aquifer. This zone is characterized by groundwater levels at an elevation between approximately 970 to 980 feet amsl.

Sentinel wells located further downgradient and in the vicinity of the municipal wells do not depict the thick silt and clay layer. Ground surface elevation in this region drops approximately 50 feet from the elevation of the incident area. Due to the lower elevations, the silt and clay layer may thin out or has been eroded. Water levels in these wells are shallower, but elevations are in line with the deeper coarse water bearing zone seen near the incident area. Sentinel wells in this area are screened in these coarser materials as indicated by the static water levels shown on **Figure 3** and provided in **Table 2**.

The thickness of the coarse sand and gravels is unknown. Bedrock underneath East Palestine is comprised of sandstone and shale. Data for bedrock depths in the region is limited to records located on the ODNR water wells database for the potable water wells. Available records indicate that bedrock depths vary from approximately 20 to 130 feet bgs.

4.3.4 Water Resources in the Area

There are surface water ways along with public and private water supply wells in the area downgradient of the derailment. Sulphur Run is downgradient of the derailment, flows to the west and joins Leslie Run, which flows generally to the south. Public water supply wells are located to the west of Leslie Run in the area of East Palestine Park. One transient public water well is located southeast of the incident area and services a local business (**Figure 1**). Private water supply wells are located throughout East Palestine.

Potable water supply wells that have been sampled as part of the Potable Well Work Plan, along with the location of private wells identified on the ODNR Water Wells Database (ODNR 2023) are shown on **Figure 4**. Available data indicating the total depth for these wells are included in **Table 3**.

4.4 INTENDED REUSE

There is no anticipated change in land use. Sampling and characterization efforts have been and will continue to be carried out across various environmental media to understand potential impacts to residential, agricultural, commercial, and special use properties (Arcadis 2023).

4.5 PATHWAY-RECEPTOR NETWORK

The potential pathways being evaluated as part of the sentinel well investigation includes contaminant migration of groundwater to a potential human receptor and interaction of groundwater with surface water. Contaminant migration from soils to groundwater is being investigated under a separate work plan.

Groundwater in this region is used as a drinking water source via potable water wells and municipal water wells. In the vicinity of the sentinel well network and in the direction of groundwater flow, a majority of residents' potable water is supplied by the municipality. The municipal wells that service the public water supply are set at an average depth of 79 feet bgs (approximately 935 feet amsl) in the sand and gravel layer with an average depth to groundwater of 44 feet bgs (approximately 968 feet amsl).

Sentinel wells SMW-01 through SMW-04 were installed between the municipal wells and Leslie Run in the same sand and gravel layer at an average depth of approximately 40 feet bgs with an average depth to groundwater of 6 feet bgs.

Generally, the potable wells sampled to date closest to the derailment area are located approximately one mile northwest and 0.5 to one mile southwest of the Site. Based on the information gathered from the ODNR Water Well database and interviews with the residents, the average depth of these potable wells is approximately 170 feet bgs, and the wells are set in the shale or sandstone bedrock aquifer. The average depth to groundwater is approximately 50 feet bgs.

At present, groundwater quality data from the sentinel wells and municipal wells have shown limited to no detections of the COCs related to the incident with no detections above the drinking water standard screening level. Given what is known about the site geology and hydrogeology and the nature of the release of contaminants, the following bullets provide a preliminary conceptual site model that will be updated as additional data are collected and evaluated:

- The low permeability silt and clay layer that has been documented at depths from 15 to 65 feet bgs (approximately 1,040 to 980 feet amsl) near the Site becomes shallower and thinner in the direction of groundwater flow.
- According to the monitoring well logs, approximately 20 to 30 feet of low permeability till, which is largely described as dry, are present between the upper and lower water bearing units (Arcadis, 2023).
- The low permeability silt and clay layer impedes downward vertical flow of groundwater.
- The deeper groundwater system is separated from the shallow groundwater system by the silt and clay layer.
- The groundwater elevations in wells SMW-07 and SMW-08 suggest an intermediate coarse-grained water bearing zone between the shallow zone near the derailment area and the deeper drinking water aquifer.
- COCs released during the train derailment have not exceeded the drinking water standard screening levels in the deeper coarse-grained water bearing zone where the sentinel well network has been installed.

4.6 DATA GAPS

This preliminary conceptual site model focusing on hydrogeology is part of the development of an overarching conceptual site model that will assess human and ecological risks associated with air, surficial and subsurface soils, sediments, surface water, and groundwater exposure media and pathways. Based on the data collected to date, Stantec has identified the following data gaps that will be the focus of this Plan:

- Detailed understanding of composition of the stratigraphic units including their lateral and vertical extent, saturated zones, aquifers, and aquitards.
- Groundwater flow characteristics and directions, hydraulic conductivity, velocity, recharge and discharge and areas of influence near the drinking water supply wells.
- Presence, migration rate, lateral and vertical extent of groundwater contaminants and their potential impacts on groundwater receptors.
- Groundwater impacts and flow direction of the deeper drinking water aquifer system is unknown in the direction north and northwest of the incident,

- Surface water elevations near the municipal wells need to be better understood to evaluate if the streams and creeks are gaining or losing,
- The sentinel monitoring wells located near the municipal wells southwest of the incident are not constructed or screened as deep as the municipal wells,
- Groundwater elevations between the municipal wells and the existing sentinel wells are unknown.
- The perched aquifer needs to be evaluated as a potential source for soil vapor migration (vapor intrusion into adjacent buildings).
- Further evaluation is needed to determine if there is a connection between the uppermost water bearing unit and deeper coarse sand layer and whether there is a potential for contaminant migration between the two units.

5.0 SCOPE OF WORK

The scope of work for this Plan primarily includes installation of sentinel monitoring wells, well development, sampling of the wells, and evaluation of the data. As part of the Sentinel Well Program, additional tasks may be conducted as part of a hydrogeologic evaluation in support of fate and transport modeling to inform data evaluation and decision criteria. The scope of work includes the following:

- Review proposed sentinel monitoring well locations for potential access issues or surface obstructions.
- Stake/flag/or paint the boring locations to define the areas for subsurface utility clearance via the OH 811 “Call Before You Dig” service or the PA 811 “One Call System” and private utility locate utilizing ground penetrating radar technology prior to hand clearing.
- Advance drill tooling to collect continuous soil samples to the target depth while screening soils with a photoionization detector (PID) at each boring location.
- Log soil lithology during well installation.
- Collect soil samples for Fraction Organic Carbon (FOC) analysis at various depths at select boring locations. Samples collected for FOC analysis will be photographed.
- Install 2-inch diameter polyvinyl chloride (PVC) well screen and casing in the upper most aquifer.
- Develop well to facilitate the hydraulic connection between the well screen and surrounding aquifer.
- Survey ground surface and top of riser or casing elevations and obtain surveyed coordinates of the sentinel well location.
- Notify US EPA, OEPA, and PADEP of proposed sampling/testing activities.
- Gauge groundwater level in the sentinel monitoring wells.
- Collect a groundwater sample from the sentinel wells via bladder (preferred) or submersible pump.
- Compare groundwater analytical results to selected drinking water standards.
- Conduct instantaneous change in head testing (i.e., slug testing) of selected sentinel wells.
- Calculate site-specific hydraulic conductivity for the tested aquifer.
- Evaluate groundwater fate and transport using a groundwater flow model using site-specific factors, such as hydraulic conductivity, FOC, and lithology.
- Provide data deliverables to stakeholders.

6.0 SAMPLE COLLECTION AND FIELD ACTIVITY PROCEDURES

This section details the procedures that will be used to prepare for field activities, advance exploratory soil borings, install and develop groundwater monitoring wells, collect groundwater samples from the sentinel monitoring well network, document field activities, preserve and handle samples, decontaminate equipment, manage waste, and assist in providing scientifically defensible results.

6.1 PREPARATION FOR FIELD ACTIVITIES

Proposed sentinel monitoring wells will be discussed with Site stakeholders and approved by the EUL. Personnel will coordinate with NSRC should an access agreement for private property be required, otherwise wells are proposed to be installed within the public right-of-way. The location will be reviewed for potential access issues, appropriate traffic control measures will be scheduled (if required), public utility clearance notifications will be completed, and private utility clearance prior to mobilizing the drilling crew will be completed and will utilize ground penetrating radar and hand clearing methods. The final locations will be based on field conditions and coordinated with the appropriate Site stakeholders.

As part of field mobilization activities, the field sampling team will:

- Develop sampling list for the day in coordination with NSRC and Site stakeholders, as necessary.
- Designate a Safety Officer.
- Review the applicable reference documents including (but not limited to) FSOPs, SOPs, TGMs, QAPP requirements, HASP, and this Plan.
- Complete required health and safety paperwork, field readiness checklist, and confirm field team members and contractors have completed all required training.
- Gather appropriate PPE including but not limited to nitrile gloves, safety vest, safety glasses, hard hat, and steel-toed boots.
- Coordinate field activities with NSRC and arrange rail protection or traffic control as needed.
- Coordinate field activities with the Environmental Unit and appropriate stakeholders, order sample bottles and preservatives, coolers, and analyte-free deionized water, and communicate sampling and sample arrival dates to the laboratories.
- Discuss project objectives and potential hazards with project personnel.
- Complete sample paperwork, to the extent practical, prior to deploying to the field, including chain-of-custody (CoC) forms and sample labels.
- Coordinate activities with the private utility clearing contractor and drill crew.

- Clear Access - Proposed boring locations will be marked using a wooden stake, flag, or paint. Suitability of each location will be evaluated for logistical issues including access, grubbing needs, and utility clearance. Access improvements, including clearing and grubbing or road building, will be coordinated with NSRC on an as needed basis.
- Complete Utility Locate(s)– Prior to initiating subsurface activities, subsurface utility clearance will be completed via the public OH 811 “Call Before You Dig” service or the PA 811 “One Call System” and the private utility contractor.
- Identify Water Source – A source of potable water will be required to complete several investigation tasks, including certain drilling methods and decontamination procedures.
- Obtain required functional and calibrated field instruments, including health and safety equipment.
- Obtain preservatives (as applicable) and ice and storage containers daily prior to beginning work for sample preservation.

6.2 WELL INSTALLATION, DEVELOPMENT, AND SAMPLING METHODS AND PROCEDURES

Drilling activities performed at the Site during implementation of this Plan will include advancing subsurface boreholes using roto-sonic drilling or other similar methodology based on field conditions and rig availability. Well installation, development, and sampling activities in Ohio will be conducted according to FSOPs and Chapter 7 of the OEPA TGM Guidelines as identified in **Appendices A** and **B**. Pennsylvania well installation, development, and sampling activities will be conducted in accordance with select sections of the PADEP TGM as identified in **Appendix C**. The following sections present drilling procedures to complete the required tasks.

6.2.1 Well Installation Procedures

6.2.1.1 Soil Borings

Stantec will obtain an appropriate drill rig, three-person drill crew, and a geologist to complete the soil borings. Borings will be advanced using roto-sonic methodology, or other drilling technique if determined necessary, and soil samples will be collected for characterization and logging in general accordance with ASTM D2488-17e and OPEA DERR FSOP 2.1.5. The procedures for drilling, soil sample collection, field documentation, preservation and handling, equipment decontamination, and quality assurance/quality control will follow the methodologies described in OEPA DERR FSOP 2.1.1 of **Appendix A** and the PADEP TGM of **Appendix C**.

Subsurface soil samples are proposed to be collected to develop average background values for FOC in soils. Samples are proposed to be collected from several areas to be representative of site geology. Areas will include the vicinity of the derailment, residential areas of the Village of East Palestine, and throughout the East Palestine Park and the municipal well field. Specific areas and sampling depths will be determined by field observations with the objective of collecting samples that are free of anthropogenic sources of carbon and to be representative of the permeable geologic units. Soil samples will be collected in accordance with OEPA VA30007.14.022 as identified in **Appendix A**. Proposed areas, specific sample locations, and sample depths will be developed with stakeholders and approved by the EUL prior to implementation. Soil sampling for addition chemical analysis is not proposed as part of this Plan.

6.2.1.2 Soil Logging

During sentinel well installation, soil samples will be collected continuously to the total depth of each boring to allow for visual logging of the materials encountered at each monitoring well location in general accordance with OEPA DERR FSOP 2.1.5 (**Appendix A**) and the PADEP TGM (**Appendix C)**. The soil boring logs will provide additional understanding of the subsurface profile including the saturated soils.

At a minimum, the following information will be recorded in accordance with ASTM Standard D2488-17e1 (2020), entered on boring logs for each borehole, and each distinct stratum described according to the Unified Soil Classification System (USCS):

- Name of person completing boring log.
- Boring identification and boring date.
- Soil color and classification, using Munsell soil color charts and modified USCS for unconsolidated materials.
    - Note presence of iron staining or manganese staining (black) or nodules.
- Moisture content (e.g., dry, moist, wet).
- Soil consistency or density, size, shape, dilatancy for silts and plasticity for clays, and angularity of particles (for fine to coarse grained soils).
- Observations of organic carbon content (presence of leafy material, twigs, black organic rich zones).
- Soil headspace will be screened with a calibrated PID for the presence of VOCs in accordance with OEPA DERR FSOP 2.1.4.
- Depth interval represented by stratum observations.
- Additional observations deemed relevant (e.g., presence of groundwater, odor, fractures, fill materials and types, GPS survey data, sedimentary structures)

6.2.2 Well Installation and Surveying

Sentinel monitoring wells will be installed utilizing roto-sonic drilling methods, or similar drilling method if necessary. Actual drilling depths will depend on the location of permeable zones but will target the drinking water-bearing unit of the sand and gravel aquifer. Final well depths will vary based on the well location and geologic conditions in the area. A single monitoring well is proposed at each location; no paired or nested wells are planned as part of the initial sentinel monitoring well network. Upon additional direction from stakeholders, paired or nested well installation may be considered.

Typical well completion will consist of a 2-inch diameter PVC well screen and riser, ten feet of 0.010-inch slotted well screen with sand filter pack, bentonite seal, and grout to land surface.

The sand filter pack, rounded 20/40 silica quartz sand, will extend at least two feet above the top of the screened interval. A minimum 2-foot-thick bentonite pellet seal will then be placed and hydrated in 2- to 3-inch lifts on top of the sand filter pack. After the bentonite pellet seal has sufficiently hydrated according to manufacturer’s specification, the remaining annular space will be backfilled with Type 1 Portland cement and 20% solids bentonite grout.

Grout will be placed by tremie method through 1-inch (minimum) diameter PVC pipe or a hose extending to the top of the bentonite seal. The grout will be placed using pumps gauged to allow the installation crew to monitor pressures during the grouting process. In cased boreholes (i.e., through roto-sonic drilling, hollow-stem augers or temporary casing, the sand filter pack and bentonite pellet intervals may be placed by tremie method or may be slowly poured (to prevent bridging) into the annular space of the drill tooling.

Sentinel monitoring wells will be sealed with an expandable, lockable cap at the top of the riser pipe, and the riser pipe will be surrounded at the surface with orange construction fence anchored to shallow-driven T-posts or equivalent prior to well pad installation. The sentinel monitoring wells will be finished with an 8-inch flush mount vault in a 2-foot by 2-foot concrete pad sloped to drain water away from the vault.

The newly installed sentinel monitoring wells will be surveyed by a licensed Ohio Professional Surveyor at the conclusion of drilling activities at the top of well casing and ground surface elevation. The wells are to be located using GPS methods utilizing the Ohio Real Time Network. Vertical Positioning is based on the North American Vertical Datum of 1988, and the Horizontal Positioning is based on the Ohio State Plane Coordinate System, North Zone, North American Datum 1983 (2011) (epoch 2010.0). The survey data will be added to the final boring logs once available.

Drilling spoils will be containerized for characterization and disposal in accordance with Section 6.3.5.

6.2.3 Well Development

Wells will be developed in general accordance with OEPA DERR FSOP 2.2.1 (**Appendix A**) and the PADEP TGM (**Appendix C**) by a combination of surging and pumping after a minimum of 24 hours following well completion to allow the grout seal set. The static water level will be measured, and the well volume calculated. A submersible pump with surge block will be lowered and raised within the screened interval to create a slight surging action to dislodge particles within the well and sand filter pack. Baseline parameter readings of turbidity, pH, temperature, specific conductance, oxidation reduction potential (ORP), and dissolved oxygen (DO) will be measured using calibrated equipment. If the well contains heavy sediment, further surging and pumping will be performed. Well development is complete following removal of a minimum of three well volumes and parameter stabilization as demonstrated by three consecutive recorded readings for each parameter are within the following limits:

pH	+/- 0.2 Standard Units (S.U.)
temperature	0.5 degrees Celsius
conductivity	+/- 3 percent
ORP	+/- 20 millivolts (mV)
DO	+/- 10 percent or 0.2 mg/L, whichever is greater
turbidity	+/- 10 percent of the average value of the three readings, or a final value of less than 10 nephelometric turbidity units (NTU).

Development water will be containerized for characterization and disposal in accordance with Section 6.3.5.

6.2.4 Groundwater Sampling

The following protocol will be used for low-flow groundwater sampling in general accordance with OEPA DERR FSOP 2.2.2, 2.2.4, 2.2.6, 2.2.8 and 2.2.10 (**Appendix A**) and the PADEP TGM (**Appendix C)**:

1. The groundwater level in each well from the reference point (i.e., top of casing) will be measured to the nearest 0.01 foot using an electric water level indicator.

2. The total depth of the monitoring well from the reference point (i.e., top of casing) will be measured to ±0.01 foot using a pre-cleaned, weighted, measuring tape, or by using an electric water level indicator (accounting for any vertical separation between the bottom of the weighted portion of the water level indicator tape and the electrical conductivity sensor used to identify immersion in water). The measured well depth will be compared to the constructed well depth to identify the presence of sediment that may have accumulated at the bottom of the well. The depth of well-bottom sediment will be considered when positioning the pump intake to avoid mobilizing the sediment while purging.

3. Purging will be conducted using a pre-cleaned stainless steel submersible pump or bladder pump. The preferred equipment for collecting samples is via a bladder pump, a submersible pump will be utilized in situations of bladder pump failure. The pumping rate will be designed to minimize drawdown and will not exceed 500 milliliters per minute (mL/min). The groundwater level will be measured and adjusted while purging to ensure that less than 0.3 feet of drawdown occurs. If the water level is lowered below the top of the screen during purging activities, volumetric sampling will be performed by purging three well volumes before collecting a sample. While purging, the pumping rate and groundwater level will be measured and recorded every 3 to 5 minutes. Purged water will be containerized for characterization and disposal in accordance with Section 6.3.5.

4. Stabilization of the purged groundwater is necessary prior to sampling to confirm that the samples obtained are representative of groundwater in the subsurface only and not influenced by stagnant groundwater stored in the well casing. The field parameters of pH, temperature, conductivity,

ORP, DO, and turbidity will be monitored while purging to evaluate the stabilization of the purged groundwater. Field parameters will be measured and recorded every 3 to 5 minutes during purging. Stabilization will be achieved when three consecutive recorded readings for each parameter are within the following limits:

pH	+/- 0.2 Standard Units (S.U.)
temperature	0.5 degrees Celsius
conductivity	+/- 3 percent
ORP	+/- 20 millivolts (mV)
DO	+/- 0.3 mg/L
Turbidity	+/- 10 percent of the average value of the three readings, or a final value of less than 10 NTU.

The field parameters pH, conductivity, temperature, ORP, DO, and turbidity will be monitored using a multi-parameter meter and a flow-through cell. At the start of purging, the purge water will be visually inspected for water clarity prior to connecting the flow-through cell. If the purge water appears extremely turbid, purging will continue until the purge water becomes visibly less turbid before connecting the flow-through cell.

In general, stabilization of the individual field parameters is expected to occur in the order listed above. Should stabilization not be achieved for field parameters, purging will continue for a maximum of two hours. If stabilization of the parameters is not achieved after that time, volumetric sampling will be conducted by purging three well volumes prior to sample collection while minimizing drawdown of the water level within the screen and not exceeding 500 milliliters per minute.

In the event that the groundwater recharge to the monitoring well is insufficient to conduct the minimal drawdown protocol, the well will be pumped dry and allowed to sufficiently recharge prior to sampling. Wells that are purged dry will not be subject to the above stabilization criteria. If the well cannot be purged dry and the water level stabilizes within the well screen, volumetric sampling protocols should be followed.

Following stabilization, groundwater samples will be collected as described below:

1. The flow-through cell will be disconnected prior to obtaining the sample.
2. The discharge line from the pump will be used to directly fill each sample bottle. Required preservatives will be added to the sample bottles in accordance with the laboratory SOP.
3. Each VOC sample vial will be inspected for the presence of bubbles. If bubbles are observed, the sampler will attempt to add sample volume to the vial to remove the bubbles. If bubbles continue to form, indicating effervescence, the sample will be discarded and recollected using an

unpreserved VOC sample vial. The laboratory will be notified that the samples are unpreserved, and the analyses will be completed within the appropriate hold time.

4. Quality control (QC) samples will be collected for chemical analysis as discussed in Section 6.7.
5. Sample containers will be placed in the sample cooler with packing material and bagged ice.
6. Single-use sampling equipment will be bagged for disposal, and reusable sampling equipment will be decontaminated using a detergent solution consisting of Alconox® or Liquinox® and triple-rinsed using purified water.

6.2.4.1 Co-located Sampling

Co-located sampling may be conducted when sampling is concurrent with OEPA, PADEP, or other agencies. Co-located sampling is when two sampling teams collect two individual sample sets from the same location, with the second sample set being collected after the first sample set is complete. This can result in a gap in sample time between the two sample sets.

6.2.5 Instantaneous Change in Head Testing (Slug Testing)

Slug tests will be performed within the screened interval of certain sentinel monitoring wells. The slug test data will be used to estimate hydraulic conductivity values using Bouwer and Rice or other and appropriate analysis methods for local hydrogeologic conditions and aquifer response during testing. Slug tests will be performed following development of the well. Slug tests will be performed in general accordance with Chapter 4 of the OEPA TGM (**Appendix B**). Generally, slug testing will consist of measuring temporal changes in water levels in response to a near instantaneous displacement of the water column (i.e., slug). The introduction and removal of the slug are referred to as “slug in” and “slug out” tests, respectively. Slug in tests will not be conducted for wells that bracket the water table. The groundwater level will be measured in the wells from top-of-casing prior to starting the test and after each test is completed.

Temporal changes in water level will be measured with a data logger and pressure transducer deployed within the sentinel monitoring well. The down-hole pressure transducer will be set in the well and positioned below the maximum depth of the slug. The pressure transducer will be connected to an electronic data logger that records the temporal water level changes. The water levels will then be recorded at logarithmic or regular intervals until reaching near static levels. A set of recorded time-displacement water level data will be produced for each test.

6.3 FIELD PROCEDURES

The sampling of sentinel wells will be completed in general accordance with OEPA DERR FSOP 2.2.2 in **Appendix A,** OEPA DERR TGM *Chapter 10* (**Appendix B**), and the PADEP TGM in **Appendix C**.

If PFAS sampling is requested by US EPA, water samples will be collected in accordance with the OEPA SOP For PFAS Sampling at Public Water Systems (March 3, 2020) (**Appendix D)** and the PFAS Field Sampling Protocol Checklist in **Appendix E**.

6.3.1 Field Equipment Description, Testing/Inspection, Calibration, and Maintenance

Field equipment will be inspected, tested, and calibrated daily (as applicable) prior to initiation of fieldwork by field sampling personnel. If equipment is not in proper working condition, then that piece of equipment will be repaired or taken out of service and replaced. Additional information regarding field equipment inspection and testing is included in the QAPP.

6.3.2 Field Documentation

Field documentation associated with the ground water sampling investigation activities will be recorded on either digital or paper field forms in general accordance with OEPA DERR FSOP 1.3 (**Appendix A**) and PADEP TGM (**Appendix C**). Field documentation associated with well installation activities will be recorded on either digital or paper field forms. Example field forms (Soil Boring, Well Development, Sample Purge Log) are provided as **Appendix F** to this Plan. Additional information regarding field documentation is provided below and included in the QAPP. In addition, during well installation field documentation will be maintained in a NSRC East Palestine Derailment dedicated field notebook or electronically.

Field logs generated under this project include boring logs and sentinel well installation logs, sentinel well development logs, daily calibration logs, and groundwater sampling logs. Field observations and measurements will be recorded and maintained to document field activities on days that samples are collected or well installation activities are occurring. General field notes will be recorded in a field notebook. Field observations and measurements will be recorded on the applicable forms (**Appendix F**). Deviations from the Plan will be documented in the field forms during field activities.

6.3.3 Preservation, Custody and Handling

Samples submitted for analysis at a Eurofins laboratory location or other approved laboratory will follow the procedures in this section and will be in general accordance with the laboratory SOPs (located on the Norfolk Southern SharePoint) for applicable methods, OEPA DERR FSOP 1.5 (**Appendix A**), and PADEP TGM (**Appendix C**) for sample preservation and handling. Once each sample container is filled, the lid will be secured. Each sample container will be checked to ensure that it is sealed, legibly labelled, and externally clean. No custody seals will be placed on individual sample bottles. Sample containers will be packaged in a manner as to prevent breakage during shipment.

If sample coolers are being shipped directly to the laboratory, coolers will be prepared for shipment by taping the cooler drain shut (if present) and lining the bottom of the cooler with packing material or bubble wrap and a large plastic liner. Sample containers will be placed in the cooler in an upright position. Small, uniformly sized, containers will be stacked in an upright configuration and packing material will be placed between the layers. Plastic containers will be placed between glass containers where possible. Ice will be placed around and among the sample containers to cool samples to 4 (±2) degrees Celsius (°C) during shipment. The cooler will be filled with additional packing material to secure the containers.

Samples will have CoC forms, shipping documents, and sample logs prepared and retained. Field Quality Control (QC) samples will be documented in both the field forms and on sample CoC forms. CoC forms will be reviewed daily for completeness. A QC check of samples in each cooler compared to groundwater sample IDs on sample bottles and the sample identification (IDs) on the corresponding CoC form will be completed.

The original CoC form will be placed in a resealable plastic bag taped to the inside lid of the cooler. A copy of the CoC form will be retained with the field notes in the project files. The total number of coolers required to ship the samples will be recorded on the CoC form. If multiple coolers are required to ship samples contained on a single CoC form, then the original copy will be placed in cooler one of "X" (marked as such) with copies placed in the additional coolers. Two signed and dated custody seals will be placed on the cooler lid. Packing tape (i.e., strapping tape) will be wrapped around the cooler to secure the sample shipment.

If the coolers are being picked up by the laboratory courier, the procedures above will be followed, with the exception of the custody seals on the cooler lid. Custody seals will not be placed on cooler when being picked up by a laboratory courier.

Upon receipt of the samples, the analytical laboratory will open the cooler and will sign "received by laboratory" on each CoC form. The laboratory will verify that the custody seals have not been previously broken. The laboratory will note the condition and temperature of the samples upon receipt and will identify discrepancies between the contents of the cooler and CoC form. If there are discrepancies, the laboratory project manager will immediately call the sampling team lead to resolve the issue and note the resolution on the laboratory check-in sheet.

6.3.4 Equipment Decontamination Procedures

Equipment decontamination will be performed for non-dedicated sampling equipment and instruments that come in contact with groundwater and soils to prevent cross-contamination in general accordance with OEPA DERR FSOP 1.6 (**Appendix A**) and PADEP TGM (**Appendix C**). Decontamination of drilling equipment will be conducted using a high-pressure washer/steam cleaner.

Decontamination activities will be performed away from sampling areas. Decontamination of non-disposable sampling equipment or instruments can be performed using deionized water and Alconox® or Liquinox® in 5-gallon buckets. Following decontamination, fluids will be containerized and disposed in accordance with Section 6.3.5.

Decontamination of sampling equipment and instruments (i.e., water quality cups/probes etc.) will be performed prior to use and between sampling locations. Decontamination activities will be documented in the field notes.

6.3.5 Waste Management

Investigation derived waste (IDW) generated during implementation of this Plan may include, but is not limited to:

- Soil cuttings;
- Well development water;
- Well purge water;
- Personal protective equipment;
- Calibration solutions;
- Decontamination fluids; and
- General trash.

IDW will be handled in accordance with the waste management plan, local, state, and federal regulations, and in general accordance with OEPA DERR FSOP 1.7 (**Appendix A**). Transportation and disposal of IDW will be coordinated with Incident Command Center personnel.

6.4 SAMPLE ANALYSIS

6.4.1 Groundwater

Samples are currently analyzed for the analytes listed on **Table 4** by the indicated analytical methods presented in the QAPP including the following: volatile organic compounds (VOCs) via US EPA Method 524.2, semi-volatile organic compounds (SVOCs)/pesticides via US EPA Method 525.2, select SVOCs via US EPA Method SW-846 8270, and glycols via US EPA Method SW-846-8015. The analytical methods and reporting limits are presented in the QAPP.

The analytical test methods presented in the February 2023 Potable Water Sampling Work Plan were developed using standard drinking water methods and are inclusive of hazardous materials identified from the railcars involved in the incident. After evaluating additional information, such as surface water results, a revised analyte list was developed. The analyte list for subsequent rounds of residential and PWS supply well sampling has been revised in coordination with US EPA, OEPA, ODH and CCHD. The revised analyte list uses standard drinking water test methods and omits analytes that have been determined not to be associated with the incident (e.g., pesticides). Additional compounds have been added that do not have drinking water standards but are associated with the incident (glycols and ethanol). The analyte list will continue to be evaluated and modified throughout the implementation of this plan, based on analytical results and in coordination with regulatory agencies.

Upon further evaluation, the analyte list presented in **Table 4** has been refined for sentinel well groundwater sampling events. This list has been refined during the development of this Plan and the Potable Water Work Plan in coordination with stakeholders to eliminate compounds that are not associated with the incident and/or do not have established screening criteria for comparison (e.g., ethanol). The analyte list presented in **Table 5** will be utilized going forward for all analyses associated with this Plan. **Table 5** may be refined further as additional information is evaluated as part of the overall program and as directed by the US EPA.

Analytes have been selected to be representative of chemicals released from the incident. Validation will be conducted in accordance with the QAPP.

If deemed necessary by US EPA and in consultation with OEPA and PADEP, laboratory analyses may be conducted for certain PFAS. US EPA Method 533 will be used for PFAS analysis, unless otherwise directed by US EPA. A summary of the suite of twenty-five PFAS analytes is presented in **Table 6**, along with applicable standards.

6.4.2 Soil

Select soil samples will be collected and analyzed for FOC by the modified Walkley-Black Method as outlined in the guidance presented in OEPA VA30007.14.022 (**Appendix A)**. FOC results will be used for groundwater modeling. Analytical methods, preservation requirements, container size, and holding times for each chemical parameter are presented in the QAPP.

6.5 QUALITY ASSURANCE/QUALITY CONTROL

As stated previously, the work will be conducted in accordance with the Sentinel Water Well Sampling QAPP. The QAPP addresses sampling and analysis activities associated with the sentinel well investigation activities under the UAO. The following sections provide details regarding quality assurance/quality control (QA/QC) requirements specific to sentinel well installation and monitoring activities.

6.6 QUALITY CONTROL SAMPLES

QA/QC samples will be collected during each sampling event and include equipment rinsate blanks, field duplicate samples, matrix spike/matrix spike duplicate (MS/MSD) samples, trip blanks (VOCs only) and field blanks. A sampling event for the sentinel program consists of sentinel well samples collected within one work week (e.g., samples collected between Monday through Sunday are considered one sampling event). Criteria for the number and type of QA/QC samples to be collected are specified below.

Field Duplicate Samples – One blind duplicate sample will be collected for every 10 samples or a minimum of one per matrix per sampling event. Duplicate samples will be prepared as blind duplicates and will be collected in two sets of identical, laboratory-prepared sample bottles. The primary and duplicate samples will be labelled as detailed in Section 6.6.1. Sample identifier information (i.e., sample times) will not be used to identify the duplicate samples. Actual sample identifiers for duplicate samples will be noted in the field notes. The duplicate sample will be analyzed for the same parameters as the primary sample.

Trip Blank – One trip blank will be included in each cooler with VOC samples. A trip blank is a blank solution that is put in the same type of bottle used for VOC sampling and is kept with the set of sample bottles both before and after sample collection.

MS/MSD Samples – A sufficient volume of sample will be collected for use as the MS/MSD. MS/MSD samples will be collected to allow matrix spike samples to be run to assess the effects of matrix on the accuracy and precision of the analyses. One MS/MSD sample will be analyzed for every 20 groundwater samples collected or a minimum of one per sampling event. The MS/MSD sample will be analyzed for the same analytes as the primary sample, except for parameters that are not amenable to MS/MSD. Laboratory duplicate analyses will be performed in lieu of MS/MSD for parameters not amenable to spiking.

Equipment Blanks (Rinsate Blanks) – One equipment (rinsate) blank will be collected a minimum of once per sampling event. The equipment blank will be collected by pouring organic-free deionized water into or over the decontaminated sampling equipment (e.g., a decontaminated water level meter or groundwater pump), then into the appropriate sample containers. The time and location of collecting the equipment blank sample will be noted in the Daily Field Activity Log. The sample will be analyzed for the same analytes as the sample collected from the location where the equipment blank is prepared. For PFAS sampling, PFAS free water will be used for equipment blanks.

Field Blank Samples - One field blank per day of sampling activity will be collected using organic-free water provided by the laboratory. Additionally, for PFAS sampling, PFAS free water will be provided by the laboratory for use. Field blanks are used to assess the potential for cross-contamination of aqueous samples during sampling activities due to ambient conditions. It is also used to validate the cleanliness of sample containers. Field blank collection is recommended if known or suspected sources of contamination are located within close proximity to the sampling activities. Laboratory supplied deionized water is utilized for field blank samples. **Table 7** summarizes the field quality control sample minimum frequencies.

Table 7 - Field Quality Control Sample Frequency

Field QC Sample	Acronym	Groundwater Frequency
Field Duplicate – (blind)	DUP	1 per 10 samples or a minimum of one per matrix per sampling event.
Trip Blank	TB	1 per cooler containing VOC samples
Matrix Spike/ Matrix Spike Duplicate	MS/MSD	1 per 20 samples or a minimum of one per matrix per sampling event.
Field Blank	FB	1 per day of sampling activity
Equipment Rinsate Blank	EB	1 per sampling event when using non-dedicated/non-disposable equipment

6.6.1 Sample Labels and Identification System

Sample identifications (IDs) will be recorded on sample container labels, custody records, and field documents. Each sample container will have a sample label affixed and secured with clear package tape as necessary to ensure the label is not removed. Information on sample labels will be recorded in waterproof, non-erasable ink. Matrix Spike/Matrix Spike duplicate samples will be indicated on the CoC in the comment column.

Groundwater samples collected for laboratory chemical analysis will be labelled as follows:

SMW-XX-YYYYMMDD

  - SMW for Sentinel Monitoring Well sampling
  - Two – digit sample location ID = XX (01 – XX)
  - Date as YYYYMMDD

Examples:

SMW-01-20230302– this is well SMW-01 that was sampled on March 2, 2023

SMW-DUP-001-20230301– this is a field Duplicate sample collected on March 1, 2023

SMW-DUP-002-20230301 – this is a second field duplicate sample collected on March 1, 2023

SMW-TB-001-20230301 – this is the first trip blank associated with the samples on March 1, 2023

7.0 DATA EVALUATION AND REPORTING

7.1 GROUNDWATER ANALYTICAL DATA

The results of the analysis will be reviewed following data validation and compared to screening Drinking Water Standards (DWSs) in units of micrograms per liter (ug/L). DWSs for comparison to groundwater sampled as part of this Plan have been established based on the following criteria:

1. Analytes not listed in (OAC 3745-81) and that do not have an MCL will be compared to US EPA Regional Screening Levels (RSLs) for Resident Tap Water (November 2022). For compounds with both carcinogenic and non-carcinogenic RSLs, the most protective value will be used. For non-carcinogens the RSLs used are based upon a Hazard Index of 1.0.
2. Analytes which do not have OAC 3745-81 criteria, MCLs, or RSLs will be compared to risk-based calculated criteria, where appropriate. This could include values provided by Agency for Toxic Substances and Disease Registry (ATSDR) and US EPA lifetime health advisory (LTHA).

A summary of the DWSs for COCs is presented in **Table 5** and **Table 6**. A report of sampling events will be provided to NSRC, US EPA, OEPA (PADEP if applicable), ODH and CCHD.

For the sentinel monitoring wells, validated data will be reviewed upon receipt. If detections of COCs are found at levels above the screening levels, stakeholders will be notified within 24 hours of receipt of the validated data and additional sampling efforts will be initiated, as specified in the QAPP.

Data generated under this Plan will be managed and reported in accordance with the UAO and Interim Data Management Plan (Project Navigator, Ltd, March 2023), and subsequent revisions.

7.1.1 Data Evaluation and Decision Criteria

Groundwater sampling is currently conducted weekly from the sentinel monitoring well network. The frequency may be increased or decreased upon US EPA approval. End points and decision criteria are presented in **Table 8**.

Table 8: Decision Criteria

Investigation Question	Action
What are the analytical results (Stantec or co-located, if provided) from sentinel wells compared to screening criteria	If the analytical results for the COCs (**Table 5**) are below the laboratory reporting limit and screening criteria, and the main line soil removal is complete, then sampling frequency will be reduced and comprehensive sampling will be conducted every 2 weeks (bi-weekly) until full delineation is achieved through the on-site monitoring

for analytes that are associated with the incident? Validated data and co-located data (if provided) will be reviewed. If results between validated and co-located samples (if provided) have an RPD that is significant (>40%), the validated data will take precedent. Validated data take precedent over non-validated data.	network under the Groundwater Characterization Work Plan. Once full delineation is achieved, sampling will be conducted approximately every 4 weeks until US EPA concurs with reduction (frequency, duration, and/or number of sampling points) or completion of sampling. If analytical results for the COCs (**Table 5**) exceed screening criteria, then the stakeholders will be immediately notified, and re-sampling will be initiated. Should additional sentinel monitoring wells be proposed, locations will be reviewed with Site stakeholders and approved by the EUL. If additional assessment indicates data gaps exist as determined by stakeholders, additional sentinel monitoring wells will be installed with approval of the EUL.
Has there been a detection above the reporting limit for validated data of a COC in groundwater?	If yes, then groundwater modeling will be conducted using the site-specific data, such as FOC and hydraulic conductivity, as well as the analytical models to estimate COC transport rates and potential travel distances. If site-specific values of input parameters are unavailable, then values from guidance documents, such as the OEPA TGM, PADEP TGM, or other literature will be used. If no, then modeling will not be conducted.
If the groundwater modeling is performed, does the fate and transport model indicate a COC could migrate to a receptor at concentrations above the screening criteria?	If yes, then evaluation of the existing sentinel well network in relation to potential receptors will be conducted. If the results of the sentinel well network evaluation show that potential receptors exist beyond the sentinel well network in a downgradient direction, then the installation of additional sentinel wells will be proposed. Requests for additional wells will be reviewed with the unified command and a determination will be made. If no, then no additional sentinel wells will be proposed. The monitoring program should continue.

7.2 REPORTING

7.2.1 Sentinel Well Groundwater Monitoring Summary Report

Following completion of each sampling event (weekly, bi-weekly, or monthly as outlined in **Table 8**) and receipt of the validated data, a sentinel well monitoring summary report will be prepared and submitted to the US EPA. The sentinel well monitoring report will outline the following:

- Sample location and methodology of sentinel monitoring well sampled during the event,
- Tabulation of groundwater elevation, geochemical parameters, and analytical results,
- A summary of the historical groundwater analytical results,
- Cross sections showing lithologies, groundwater elevations and other data collected during this investigation,
- Provide a Sentinel Well Location Map along with an updated potentiometric map to evaluate groundwater flow direction, and
- Provide a copy of the sentinel well low-flow purge logs, validated analytical report(s), and a copy of boring logs and well detail logs should additional sentinel monitoring wells be installed during the sampling period.

The sentinel well summary report is anticipated to be completed and uploaded to the Data Portal operated by NSRC within two weeks of receipt of the validated analytical results. A copy of the report will be available to other stakeholders upon request.

7.2.2 Groundwater Flow and Fate and Transport Modeling

If COCs are detected in groundwater, then site-specific data such as FOC and hydraulic conductivity results, will be used to develop groundwater flow and fate and transport modeling to estimate the rate and distance that COCs might advance via groundwater flow. The results of the modeling will be used to evaluate potential migration of COCs from the incident area. The modeling will be performed in general accordance with the applicable sections of Chapter 14 of the OEPA TGM (**Appendix B**) and the applicable portions of Section III of the PADEP TGM (**Appendix C**). Using the hydrogeologic conceptual site model, an analytical or numerical model will be constructed to simulate groundwater flow conditions and evaluate the importance of key assumptions. Prior to selection of a groundwater flow and transport model, NSRC will engage stakeholders for input on specific model selection. The model solutions are most applicable in aquifers exhibiting relatively uniform hydrogeologic conditions and impacted by a contaminant source that remains constant in time. However, this task will also include sensitivity analysis of transport model input parameters to assist in the assessment of the sensitivity to key assumptions and uncertainty related to the model predictions.

Once the model is completed, a summary document will be prepared to describe the components of the model. The document will include a summary of data used to construct the model, calibration, sensitivity analysis, predictive simulations, and interpretations made as a result of the model runs. Key decisions and assumptions to identify and address data gaps will be discussed and justified.

8.0 REFERENCES

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TABLES

Table 2
Summary of Sentinel Well Construction Information
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Well ID	Ohio DNR Well ID	Well Type	Date Constructed	Ground Surface Elevation	Top of Casing Elevation	Total Boring Depth (BGS)	Well Depth (BGS)	Screen Interval Depths (BGS)		Screen Interval Elevation (BGS)		Depth to Water (BTOC)*	Groundwater Elevation (BTOC)	Depth to Bedrock	Aquifer type / screen lithology
								top	bottom	top	bottom				
				(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	(ft)	
SMW-1	3006747	Sentinel	2/15/2023	973.26	973.13	40.00	39.50	29.50	39.50	943.76	933.76	3.84	969.29	NA	Gravel & Sand
SMW-2	3006754	Sentinel	2/15/2023	972.01	971.71	40.00	39.70	29.70	39.70	942.31	932.31	2.85	968.86	NA	Sand & Silt
SMW-3	3006758	Sentinel	2/16/2023	981.12	981.02	40.00	39.60	29.60	39.60	951.52	941.52	9.73	971.29	NA	Gravel & Sand
SMW-4	3006760	Sentinel	2/17/2023	978.42	978.35	40.00	39.60	29.60	39.60	948.82	938.82	8.06	970.29	NA	Gravel & Sand
SMW-5	3006763	Sentinel	2/19/2023	1038.04	1037.72	40.00	39.80	29.80	39.80	1008.24	998.24	23.86	1013.86	NA	Silt/Clay
SMW-6	3006811	Sentinel	3/13/2023	1038.13	1038.00	78.00	78.00	68.00	78.00	970.13	960.13	59.85	978.15	NA	Clay/Gravel/Sand
SMW-7	3006812	Sentinel	3/15/2023	1012.94	1012.87	42.90	38.00	28.00	38.00	984.94	974.94	20.62	992.25	NA	Clay/Gravel/Sand
SMW-8	3007035	Sentinel	3/21/2023	1014.20	1014.17	38.00	38.00	28.00	38.00	986.20	976.20	21.97	992.20	NA	Clay/Gravel/Sand
SMW-9	3006964	Sentinel	3/26/2023	1030.09	1029.85	68.00	68.30	58.30	68.30	971.79	961.79	57.21	972.64	NA	Clay/Sand/Gravel
SMW-10	3007037 / 3006966	Sentinel	3/23/2023	1031.96	1031.81	68.20	68.20	58.20	68.20	973.76	963.76	59.12	972.69	NA	Sand & Gravel
SMW-11	3007036	Sentinel	3/28/2023	1045.33	1045.02	89.10	89.10	79.10	89.10	966.23	956.23	71.69	973.33	NA	Clay/Sand/Gravel
SMW-13	NA	Sentinel	4/4/2023	1034.51	1034.44	76.20	76.20	66.00	76.00	968.51	958.51	60.06	974.38	NA	Sand/Silt/Clay/Gravel
SMW-14	NA	Sentinel	4/6/2023	1037.35	1037.20	82.00	82.00	72.00	82.00	965.35	955.35	58.22	978.98	NA	Sand/Silt/Clay/Gravel
SMW-15	NA	Sentinel	4/6/2023	1055.57	1055.69	102.00	102.00	92.00	102.00	963.57	953.57	81.64	974.05	NA	Sand/Silt/Clay/Gravel
MW-03**	3006906	Monitoring	3/6/2023	--	1031.54	72.00	72.00	62.00	72.00	--	--	58.13	973.41	NA	Clay/Sand/Gravel
MW-06**	3006904	Monitoring	3/2/2023	--	1039.22	72.00	72.00	62.00	72.00	--	--	64.51	974.71	NA	Clay/Sand/Gravel
MW-08**	3006905	Monitoring	3/4/2023	--	1041.72	72.00	72.00	62.00	72.00	--	--	64.18	977.54	NA	Clay/Sand/Gravel
MW-10**	3006901	Monitoring	2/27/2023	--	1020.80	62.00	62.00	52.00	62.00	--	--	47.71	973.09	NA	Clay/Sand/Gravel

Notes:
bgs = below ground surface
ft = feet
btoc - below top of casing
*Depth to water measurements collected on May 10, 2023
**Arcadis monitoring well
NA = not applicable
-- = data not available

Table 3
Summary of Potable Well Construction Information
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Well ID	Ohio DNR Well ID	Well Type	Associated Sentinel Well ID	Date Constructed	Top of Casing Elevation	Total Boring Depth (BGS)	Well Depth (BGS)	Screen Interval Depths (BGS)		Depth to Water (BTOC)	Depth to Bedrock	Aquifer type / screen lithology
								top	bottom			
					(ft)	(ft)	(ft)	(ft)	(ft)	(ft)		
PW-01	63124			10/20/1948	--	--	79.00	--	--	20.00	61.00	Shale
PW-03	780090	Domestic	SMW-11	5/24/1994	--	--	345.00	--	--	--	--	Cleanout
PW-06	504532	Industrial	SMW-15	3/1/1977	--	--	127.00	--	--	20.00	--	Sand & Gravel
PW-10	857357	Domestic	SMW-11	7/1/1997	--	--	240.00	--	--	105.00	134.00	Sandstone
PW-15	565653	Domestic	SMW-11	9/30/1980	--	--	300.00	--	--	33.00	--	Sandstone
PW-18	787877	Domestic	NA	4/11/1995	--	--	120.00	--	--	37.00	88.00	Shale
PW-19	611425	Domestic	NA	1/17/1984	--	--	65.00	--	--	15.00	40.00	Shale
PW-21	--	Tavern	SMW-06	--	--	--	--	--	--	--	--	--
PW-112	1007080	Domestic	SMW-11	7/10/2008	--	--	374.00	--	--	172.00	--	Siltstone
PW-300	--	Domestic	NA	--	--	--	80.00	--	--	--	--	--
PW-301	--	Domestic	NA	--	--	--	30.00	--	--	--	--	--
PW-303	--	Domestic	NA	--	--	--	200.00	--	--	--	--	--
PW-304	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-305	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-309	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-311	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-312	--	Domestic	SMW-11	1950	--	--	207.00	--	--	--	--	--
PW-330	--	Domestic	NA	--	--	--	25.00	--	--	--	--	--
PW-333	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-471	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-607	--	Domestic	NA	--	--	--	121.00	--	--	--	--	--
PW-611	--	Domestic	NA	--	--	--	75.00	--	--	--	--	--
PW-621	--	Domestic	NA	--	--	--	--	--	--	--	--	--
PW-1387	--	Domestic	SMW-06	--	--	--	--	--	--	--	--	No well - Spring Fed
PW-201	2075004	Municipal	SMW-03	5/28/2019	--	--	87.00	--	--	44.20	--	Gravel/Sand/Clay
PW-202	834001	Municipal	SMW-03	4/30/1996	--	--	75.00	--	--	38.72	--	Sand & Gravel
PW-203	534431	Municipal	SMW-03	9/22/1978	--	--	56.00	--	--	30.00	--	Sand & Gravel
PW-204	--	Municipal	SMW-03	--	--	--	--	--	--	--	--	--
PW-205	2057530	Municipal	SMW-03	6/14/2016	--	--	98.00	--	--	62.40	--	Sand & Gravel
--	2000913	Observation	SMW-03	10/13/2005	--	--	56.00	--	--	19.40	--	Sand & Gravel
--	9915205	Public / Semi-Public	SMW-04	--	--	--	787.00	--	--	--	137.00	Shale
--	594313	Public / Semi-Public	SMW-04	8/16/1982	--	--	46.00	--	--	12.00	--	Sand & Gravel
--	887148	Industrial	SMW-06	10/26/1999	--	--	123.00	--	--	14.00	108.00	Sandstone
--	920641	Domestic	SMW-06	10/30/2000	--	--	300.00	--	--	68.00	28.00	Siltstone
--	931400	Domestic	SMW-09	10/5/2001	--	--	145.00	--	--	--	--	Shale
--	594337	Municipal	SMW-10	1/24/1983	--	--	365.00	--	--	10.00	35.00	Sandstone
--	745935	Domestic	NA	3/6/1992	--	--	120.00	--	--	58.00	--	Shale
--	672757	Domestic	NA	10/13/1987	--	--	80.00	--	--	55.00	23.00	Shale
--	812794	Domestic	NA	8/25/1995	--	--	105.00	--	--	40.00	37.00	Shale
--	689354	Domestic	NA	5/1/1989	--	--	84.00	--	--	42.00	--	Sandstone

Notes:
bgs = below ground surface
ft = feet
btoc - below top of casing
NA = not applicable
-- = data not available

Table 4
Combined Analyte List with Selected Screening Criteria - Sentinel Well Sampling
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Analyte	CAS#	MDL	RL	Analytical Method^5	Units	Selected Screening Drinking Water Standard	Source of Criteria (see Notes)
4-Nitrophenol	100-02-7	2.1	9.6	8270C	µg/L	60	USEPA LTHA
ethylbenzene	100-41-4	0.2	0.5	524.2	ug/L	700	1,3
Styrene	100-42-5	0.2	0.5	524.2	µg/L	100	1,3
Benzyl chloride	100-44-7	0.4	0.5	524.2	µg/L	0.089	2
cis-1,3-Dichloropropene	10061-01-5	0.2	0.5	524.2	µg/L	--	
trans-1,3-Dichloropropene	10061-02-6	0.2	0.5	524.2	µg/L	--	
Deisopropylatrazine	1007-28-9	0.04	1	525.2	µg/L	--	
Heptachlor epoxide	1024-57-3	0.004	0.02	525.2	µg/L	0.2	1,3
Endosulfan sulfate	1031-07-8	0.02	0.1	525.2	µg/L	110	2
2-Ethylhexyl acrylate	103-11-7	0.5	0.5	524.2	µg/L	500	4
Di(2-ethylhexyl)adipate	103-23-1	0.02	0.6	525.2	µg/L	400	1,3
N-Propylbenzene	103-65-1	0.2	0.5	524.2	µg/L	660	2
n-Butylbenzene	104-51-8	0.2	0.5	524.2	µg/L	1000	2
4-Chlorotoluene (p-Chlorotoluene)	106-43-4	0.2	0.5	524.2	µg/L	250	2
1,4-Dichlorobenzene (p-Dichlorobenzene)	106-46-7	0.2	0.5	524.2	µg/L	75	1,3
Epichlorohydrin	106-89-8	0.8	1	524.2	µg/L	2.9	2
Ethylene Dibromide (1,2-Dibromoethane)	106-93-4	0.2	0.2	524.2	µg/L	0.05	1,3
1,3-Butadiene	106-99-0	0.5	5	524.2	µg/L	0.071	2
3-Chloro-1-propene (Allyl Chloride)	107-05-1	1.1	5	524.2	µg/L	0.73	2
1,2-Dichloroethane	107-06-2	0.2	0.5	524.2	µg/L	5	1,3
Propionitrile	107-12-0	1.3	5	524.2	µg/L	--	
Acrylonitrile	107-13-1	0.9	1	524.2	µg/L	0.052	2
Chloroacetonitrile	107-14-2	2	5	524.2	µg/L	--	
Vinyl acetate	108-05-4	2	5	524.2	µg/L	410	2
4-Methyl-2-pentanone (MIBK)	108-10-1	1.5	2	524.2	µg/L	6300	2
Isopropyl ether (Diisopropyl Ether)	108-20-3	0.5	0.5	524.2	µg/L	1500	2
1,3,5-Trimethylbenzene	108-67-8	0.2	0.5	524.2	µg/L	60	2
Bromobenzene	108-86-1	0.1	0.5	524.2	µg/L	62	2
Toluene	108-88-3	0.2	0.5	524.2	µg/L	1000	1,3
Chlorobenzene (Monochlorobenzene)	108-90-7	0.2	0.5	524.2	µg/L	100	1,3
Cyclohexanone	108-94-1	2	5	524.2	µg/L	1400	2
Phenol	108-95-2	0.12	0.96	8270C	µg/L	5800	2
1-Chlorobutane	109-69-3	0.7	5	524.2	µg/L	640	2
Tetrahydrofuran	109-99-9	1.4	5	524.2	µg/L	3400	2
trans-1,4-Dichloro-2-butene	110-57-6	1.4	5	524.2	µg/L	0.0013	2
Bis(2-chloroethyl)ether	111-44-4	0.8	2	524.2	µg/L	0.014	2
Diethylene Glycol	111-46-6	20	25	8015	µg/L	NE	
2-Butyloxyethanol	111-76-2	1.1	4	8270C	µg/L	2000	2
2-Butyloxyethyl acetate	112-07-2	0.099	0.099	524.2	µg/L	1200	4
Bis(2-ethylhexyl) phthalate	117-81-7	0.1	0.6	525.2	µg/L	6	1,3
Di-n-octyl phthalate	117-84-0	0.02	2	525.2	µg/L	200	2
Hexachlorobenzene	118-74-1	0.01	0.1	525.2	µg/L	1	1,3
Anthracene	120-12-7	0.01	0.1	525.2	µg/L	1800	2
1,2,4-Trichlorobenzene	120-82-1	0.2	0.5	524.2	µg/L	70	1,3
2,4-Dinitrotoluene	121-14-2	0.02	0.49	525.2/8270C	µg/L	0.24	2
Malathion	121-75-5	0.01	0.1	525.2	µg/L	390	2
Simazine	122-34-9	0.03	0.07	525.2	µg/L	4	1,3
1,4-Dioxane	123-91-1	0.6	5	524.2	µg/L	0.46	2
Chlorodibromomethane (Dibromochloromethane)	124-48-1	0.1	0.5	524.2	µg/L	80	2
Methacrylonitrile	126-98-7	1.7	5	524.2	µg/L	1.9	2
2-Chloro-1,3-butadiene	126-99-8	0.4	5	524.2	µg/L	0.019	2
Tetrachloroethene	127-18-4	0.2	0.5	524.2	µg/L	5	1,3
Pyrene	129-00-0	0.01	0.1	525.2	µg/L	120	2
xylenes, total	1330-20-7	0.5	0.5	524.2	µg/L	10000	1,3
sec-Butylbenzene	135-98-8	0.2	0.5	524.2	µg/L	2000	2
Ethyl acrylate	140-88-5	0.4	1	524.2	µg/L	140	2
n-Butyl acrylate	141-32-2	0.5	1	524.2	µg/L	560	4
1,3-Dichloropropane	142-28-9	0.1	0.5	524.2	µg/L	370	2
cis-1,2-Dichloroethene	156-59-2	0.2	0.5	524.2	µg/L	70	1,3
trans-1,2-Dichloroethene	156-60-5	0.2	0.5	524.2	µg/L	100	1,3
Trifluralin	1582-09-8	0.02	0.1	525.2	µg/L	2.6	2
Alachlor	15972-60-8	0.01	0.1	525.2	µg/L	2	1,3
Prometon	1610-18-0	0.05	0.1	525.2	µg/L	250	2
Methyl tert-butyl ether	1634-04-4	0.4	0.5	524.2	µg/L	14	2
m-Xylene & p-Xylene	179601-23-1	0.5	0.5	524.2	µg/L	--	
Chlorothalonil	1897-45-6	0.02	0.1	525.2	µg/L	4	2
Atrazine	1912-24-9	0.01	0.1	525.2	µg/L	3	1,3
Benzo[g,h,i]perylene	191-24-2	0.02	0.1	525.2	µg/L	0.12	4
Propachlor	1918-16-7	0.01	0.1	525.2	µg/L	250	2
Indeno[1,2,3-cd]pyrene	193-39-5	0.01	0.1	525.2	µg/L	0.25	2
Benzo[b]fluoranthene	205-99-2	0.01	0.1	525.2	µg/L	0.25	2
Fluoranthene	206-44-0	0.01	0.1	525.2	µg/L	800	2
Benzo[k]fluoranthene	207-08-9	0.01	0.1	525.2	µg/L	2.5	2
Acenaphthylene	208-96-8	0.01	0.1	525.2	µg/L	12	4
Metribuzin	21087-64-9	0.01	0.1	525.2	µg/L	490	2
Cyanizine	21725-46-2	0.02	0.1	525.2	µg/L	0.088	2
Chrysene	218-01-9	0.01	0.1	525.2	µg/L	25	2
Molinate	2212-67-1	0.02	0.1	525.2	µg/L	30	2
Butachlor	23184-66-9	0.02	0.1	525.2	µg/L	--	
Dipropylene Glycol	25265-71-8	20	25	8015	µg/L	NE	
Chloroneb	2675-77-6	0.02	0.1	525.2	µg/L	--	
Benthiocarb (Thiobencarb)	28249-77-6	0.01	0.1	525.2	µg/L	160	2
Chlorpyrifos	2921-88-2	0.01	0.05	525.2	µg/L	8.4	2
Aldrin	309-00-2	0.0081	0.1	525.2	µg/L	0.00092	2
Bromacil	314-40-9	0.02	0.1	525.2	µg/L	--	
alpha-BHC	319-84-6	0.01	0.1	525.2	µg/L	0.0072	2
beta-BHC	319-85-7	0.03	0.1	525.2	µg/L	0.025	2
delta-BHC	319-86-8	0.01	0.1	525.2	µg/L	--	
Endosulfan II	33213-65-9	0.02	0.1	525.2	µg/L	--	
Diazinon	333-41-5	0.03	0.1	525.2	µg/L	10	2
Acetochlor	34256-82-1	0.01	0.1	525.2	µg/L	350	2
trans-Nonachlor	39765-80-5	0.02	0.1	525.2	µg/L	--	
Pendimethalin	40487-42-1	0.01	0.1	525.2	µg/L	1400	2
4,4'-DDT	50-29-3	0.02	0.1	525.2	µg/L	0.23	2
Benzo[a]pyrene	50-32-8	0.012	0.02	525.2	µg/L	0.2	1,3
Chlorobenzilate	510-15-6	0.07	0.1	525.2	µg/L	0.31	2
cis-Chlordane (alpha-Chlordane)	5103-71-9	0.01	0.1	525.2	µg/L	3.6	2
Metolachlor	51218-45-2	0.01	0.1	525.2	µg/L	2700	2
Hexazinone	51235-04-2	0.02	0.1	525.2	µg/L	640	2
trans-Permethrin	51877-74-8	0.02	0.1	525.2	µg/L	--	
Permethrin	52645-53-1	0.01	0.2	525.2	µg/L	1000	2
1,2,3-Trimethylbenzene	526-73-8	0.2	0.5	524.2	µg/L	55	2

Table 4
Combined Analyte List with Selected Screening Criteria - Sentinel Well Sampling
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Dibenz(a,h)anthracene	53-70-3	0.01	0.1	525.2	µg/L	0.025	2
1,3-Dichlorobenzene	541-73-1	0.1	0.5	524.2	µg/L	--	
1,3-Dichloropropene, Total	542-75-6	0.2	0.5	524.2	µg/L	0.47	2
cis-Permethrin	54774-45-7	0.02	0.1	525.2	µg/L	--	
Carbon tetrachloride	56-23-5	0.1	0.5	524.2	µg/L	5	1,3
1,1-Dichloropropene	563-58-6	0.2	0.5	524.2	µg/L	0.47	4
Ethyl Parathion	56-38-2	0.09	0.5	525.2	µg/L	86	2
Benzo[a]anthracene	56-55-3	0.01	0.1	525.2	µg/L	0.03	2
Propylene Glycol	57-55-6	20	25	8015	µg/L	400000	2
Chlordane (n.o.s.)	57-74-9	0.05	0.05	525.2	µg/L	2	1,3
Caffeine	58-08-2	0.02	0.05	525.2	µg/L	--	
gamma-BHC (Lindane)	58-89-9	0.0084	0.02	525.2	µg/L	0.2	1,3
Terbacil	5902-51-2	0.02	0.1	525.2	µg/L	250	2
Terbuthylazine	5915-41-3	0.01	0.1	525.2	µg/L	--	
2-Hexanone	591-78-6	1.2	5	524.2	µg/L	38	2
Ethyl ether	60-29-7	0.3	2	524.2	µg/L	3900	2
Dimethoate	60-51-5	0.03	0.5	525.2	µg/L	44	2
Dieldrin	60-57-1	0.02	0.1	525.2	µg/L	0.0018	2
2,6-Dinitrotoluene	606-20-2	0.02	0.1	525.2	µg/L	0.049	2
3&4-Methylphenol(m&p Cresol)	615-62-3	0.18	1.9	8270C	µg/L	350	4
Desethylatrazine	6190-65-4	0.01	1	525.2	µg/L	--	
Dichlorvos	62-73-7	0.04	0.05	525.2	µg/L	0.26	2
1,1,1,2 Tetrachloroethane	630-20-6	0.3	0.5	524.2	µg/L	0.57	2
Tert-butyl ethyl ether	637-92-3	0.4	2	524.2	µg/L	70	2
Ethanol	64-17-55	5	10	524.2	µg/L	NE	ndard will be estab
Benzoic acid	65-85-0	12	48	8270C	µg/L	75000	2
Acetone	67-64-1	2	5	524.2	µg/L	18000	2
Chloroform	67-66-3	0.2	0.5	524.2	µg/L	80	80
Hexachloroethane	67-72-1	1.1	2	524.2	µg/L	0.33	2
Benzene	71-43-2	0.2	0.5	524.2	µg/L	5	1,3
1,1,1-Trichloroethane	71-55-6	0.2	0.5	524.2	µg/L	200	1,3
Endrin	72-20-8	0.0099	0.01	525.2	µg/L	2	1,3
Methoxychlor	72-43-5	0.01	0.1	525.2	µg/L	40	1,3
4,4'-DDD	72-54-8	0.02	0.1	525.2	µg/L	0.032	2
4,4'-DDE	72-55-9	0.01	0.1	525.2	µg/L	0.046	2
Prometryn	7287-19-6	0.02	0.1	525.2	µg/L	600	2
Endrin aldehyde	7421-93-4	0.03	0.1	525.2	µg/L	--	
Bromomethane	74-83-9	0.4	0.5	524.2	µg/L	7.5	2
Chloromethane	74-87-3	0.2	0.5	524.2	µg/L	190	2
Dibromomethane (Methylene Bromide)	74-95-3	0.2	0.5	524.2	µg/L	8.3	2
Ethyl bromide (bromoethane)	74-96-4	0.1	0.5	524.2	µg/L	--	
Chlorobromomethane	74-97-5	0.2	0.5	524.2	µg/L	83	2
Chloroethane (Ethyl Chloride)	75-00-3	0.2	0.5	524.2	µg/L	8300	2
Vinyl chloride	75-01-4	0.2	0.2	524.2	µg/L	2	1,3
Methylene Chloride (Dichloromethane)	75-09-2	0.4	0.5	524.2	µg/L	5	1,3
Carbon disulfide	75-15-0	0.2	0.5	524.2	µg/L	810	2
Bromoform	75-25-2	0.2	0.5	524.2	µg/L	80	2
Dichlorobromomethane (Bromodichloromethane)	75-27-4	0.1	0.5	524.2	µg/L	80	2
1,1-Dichloroethane	75-34-3	0.1	0.5	524.2	µg/L	2.8	2
1,1-Dichloroethene	75-35-4	0.2	0.5	524.2	µg/L	7	1,3
2-Methyl-2-propanol (tert-butyl alcohol)	75-65-0	0.6	2	524.2	ug/L	150	2
Trichlorofluoromethane	75-69-4	0.2	0.5	524.2	µg/L	5200	2
Dichlorodifluoromethane	75-71-8	0.3	0.5	524.2	µg/L	200	2
EPTC	759-94-4	0.01	0.1	525.2	µg/L	750	2
Pentachloroethane	76-01-7	1.1	2	524.2	µg/L	0.65	2
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.3	0.5	524.2	µg/L	10000	2
Heptachlor	76-44-8	0.0044	0.04	525.2	µg/L	0.4	1,3
Hexachlorocyclopentadiene	77-47-4	0.01	0.1	525.2	µg/L	50	1,3
Isophorone	78-59-1	0.01	0.1	525.2	µg/L	78	2
1,2-Dichloropropane	78-87-5	0.2	0.25	524.2	µg/L	5	1,3
2-Butanone (MEK)	78-93-3	2	5	524.2	µg/L	5600	2
1,1,2-Trichloroethane	79-00-5	0.2	0.5	524.2	µg/L	5	1,3
Trichloroethene	79-01-6	0.2	0.5	524.2	µg/L	5	1,3
1,1,2,2-Tetrachloroethane	79-34-5	0.2	0.5	524.2	µg/L	0.076	2
2-Nitropropane	79-46-9	0.9	2	524.2	µg/L	0.0097	2
Methyl methacrylate	80-62-6	1	1	524.2	µg/L	1400	2
Acenaphthene	83-32-9	0.01	0.1	525.2	µg/L	530	2
Diethyl phthalate	84-66-2	0.02	1	525.2	µg/L	15000	2
Di-n-butyl phthalate	84-74-2	0.07	2	525.2	µg/L	900	2
Phenanthrene	85-01-8	0.01	0.1	525.2	µg/L	50	4
Butyl benzyl phthalate	85-68-7	0.02	1	525.2	µg/L	16	2
fluorene	86-73-7	0.0099	0.099	525.2	ug/L	290	2
1,2,3-Trichlorobenzene	87-61-6	0.2	0.5	524.2	µg/L	7	2
Hexachlorobutadiene	87-68-3	0.2	0.25	524.2	µg/L	0.14	2
1-Methylnaphthalene	90-12-0	0.02	0.1	525.2	µg/L	1.1	2
Naphthalene	91-20-3	0.3	0.5	524.2	µg/L	0.12	2
Naphthalene	91-20-3	0.01	0.1	525.2	µg/L	0.12	2
2-Methylnaphthalene	91-57-6	0.01	0.1	525.2	µg/L	36	2
3,3'-Dichlorobenzidine	91-94-1	1.1	4.8	8270C	µg/L	0.13	2
o-Xylene	95-47-6	0.2	0.5	524.2	µg/L	190	2
2-Chlorotoluene (o-Chlorotoluene)	95-49-8	0.1	0.5	524.2	µg/L	240	2
1,2-Dichlorobenzene (o-Dichlorobenzene)	95-50-1	0.2	0.5	524.2	µg/L	600	1,3
1,2,4-Trimethylbenzene	95-63-6	0.2	0.5	524.2	µg/L	56	2
Endosulfan I	959-98-8	0.04	0.1	525.2	µg/L	--	
1,2-Dibromo-3-Chloropropane	96-12-8	0.2	0.2	524.2	µg/L	0.2	1,3
1,2,3-Trichloropropane	96-18-4	0.2	0.5	524.2	µg/L	0.00075	2
Methyl acrylate	96-33-3	0.8	1	524.2	µg/L	42	2
Ethyl methacrylate	97-63-2	1	1	524.2	µg/L	630	2
tert-Butylbenzene	98-06-6	0.2	0.5	524.2	µg/L	690	2
Isopropylbenzene (Cumene)	98-82-8	0.2	0.25	524.2	µg/L	450	2
Tert-amyl methyl ether	994-05-8	2	3	524.2	µg/L	--	
4-Isopropyltoluene	99-87-6	0.2	0.5	524.2	µg/L	--	
Total Trihalomethanes (TTHM)[6]	NA			524.2	µg/L	80	1,3

Notes:

CAS - Chemical abstract service

NE - no standard will be established

USEPA - United States Environmental Protection Agency

RSL - Regional screening level

TBD - to be determined

MCL - Maximum contaminant level

µg/L - Micrograms per liter

These compounds are targeted analytes and tentatively identified compounds (TICS) are not included

[1] Drinking Water Standards for Ohio Public Water Systems, September 2018 (Ohio Administrative Code Chapter 3745-81)

[2] USEPA RSLs Resident Tap Water (TR=1E-06/THQ=1.) - https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables

[3] MCLS - National Primary Drinking Water Regulations 40 CFR Part 141

[4] ATSDR - Agency for Toxic Substances and Disease Registry Calculated Criteria

[6] Includes the sum of detections for the following chemicals: chloroform, bromodichloromethane, dibromochloromethane, and bromoform

[5] Analtyical method or similar method will be utlized for analysis

Table 5
Analyte Summary with Selected Screening Criteria - Sentinel Well Sampling
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Analyte	CAS#	MDL	RL	Analytical Method[5]	Units	Screening Levels	
Ethylbenzene	100-41-4	0.2	0.5	524.2	ug/L	1.5	RSL
Benzaldehyde	100-52-7	0.759	2	8270E	µg/L	19	RSL
2-Ethylhexyl acrylate*	103-11-7	0.5	0.5	524.2	µg/L	500	ATSDR
Toluene	108-88-3	0.2	0.5	524.2	µg/L	1,100	RSL
Cyclohexane	110-82-7	0.48	1	8260D	µg/L	13,000	RSL
2-Butyloxyethanol (Ethylene Glycol Monobutyl Ether)*	111-76-2	1.1	4	8270C	µg/L	2,000	RSL
Anthracene	120-12-7	0.01	0.1	525.2	µg/L	1,800	RSL
Pyrene	129-00-0	0.01	0.1	525.2	µg/L	120	RSL
Dibenzofuran	132-64-9	0.268	1	8270E	µg/L	7.9	RSL
n-Butyl acrylate	141-32-2	0.5	1	524.2	µg/L	560	ATSDR
m-Xylene & p-Xylene	179601-23-1	0.5	0.5	524.2	µg/L	190	RSL
Benzo[g,h,i]perylene	191-24-2	0.02	0.1	525.2	µg/L	0.12	ATSDR
Indeno[1,2,3-cd]pyrene	193-39-5	0.01	0.1	525.2	µg/L	0.25	RSL
Benzo[b]fluoranthene	205-99-2	0.01	0.1	525.2	µg/L	0.25	RSL
Fluoranthene	206-44-0	0.01	0.1	525.2	µg/L	800	RSL
Benzo[k]fluoranthene	207-08-9	0.01	0.1	525.2	µg/L	2.5	RSL
Acenaphthylene	208-96-8	0.01	0.1	525.2	µg/L	12	ATSDR
Chrysene	218-01-9	0.01	0.1	525.2	µg/L	25	RSL
Benzo[a]pyrene	50-32-8	0.012	0.02	525.2	µg/L	0.03	RSL
Dibenz(a,h)anthracene	53-70-3	0.01	0.1	525.2	µg/L	0.03	RSL
Benzo[a]anthracene	56-55-3	0.01	0.1	525.2	µg/L	0.03	RSL
Benzene	71-43-2	0.2	0.5	524.2	µg/L	0.5	RSL
Vinyl chloride	75-01-4	0.2	0.2	524.2	µg/L	0.019	RSL
2-Butanone (MEK)	78-93-3	2	5	524.2	µg/L	5,600	RSL
Acenaphthene	83-32-9	0.01	0.1	525.2	µg/L	530	RSL
Phenanthrene	85-01-8	0.01	0.1	525.2	µg/L	50	ATSDR
Fluorene	86-73-7	0.0099	0.099	525.2	ug/L	290	RSL
Propylene Glycol	57-55-6	20	25	8015	ug/L	400,000	RSL
1-Methylnaphthalene	90-12-0	0.02	0.1	525.2	µg/L	1.1	RSL
Naphthalene	91-20-3	0.01	0.1	525.2	µg/L	0.12	RSL
2-Methylnaphthalene	91-57-6	0.01	0.1	525.2	µg/L	36	RSL
1,1-biphenyl	92-52-4	0.492	1	8270E	µg/L	0.8	RSL
o-Xylene	95-47-6	0.2	0.5	524.2	µg/L	190	RSL
1,2,4-Trimethylbenzene	95-63-6	0.2	0.5	524.2	µg/L	56	RSL
Methyl acrylate	96-33-3	0.8	1	524.2	µg/L	42	RSL
Isopropylbenzene (Cumene)	98-82-8	0.2	0.25	524.2	µg/L	450	RSL

Notes:

CAS - Chemical abstract service
MDL - Method Detection Limit
RL - Reporting Limit
USEPA - United States Environmental Protection Agency
RSL - Regional screening level
MCL - Maximum contaminant level
µg/L - Micrograms per liter

These compounds are targeted analytes and tentatively identified compounds (TICS) are not included

USEPA RSLs Resident Tap Water (TR=1E-06/THQ=1.) - https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables
ATSDR - Agency for Toxic Substances and Disease Registry Calculated Criteria

[5] Analtyical method or similar method will be utlized for analysis
*Analyzed by laboratory-modified method shown.

Table 6
Analyte Summary with Applicable Residential Standards for PFAS
Sentinel Monitoring Well Installation and Groundwater Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Analyte	Abbreviation	CAS #	Units	USEPA RSL
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	ppt	
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	ppt	
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	ppt	
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	ppt	60
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	ppt	
Perfluorobutanoic acid	PFBA	375-22-4	ppt	18,000
Perfluorobutanesulfonic acid	PFBS	375-73-5	ppt	6,000
1H, 1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	ppt	
Perfluorodecanoic acid	PFDA	335-76-2	ppt	
Perfluorododecanoic acid	PFDoA	307-55-1	ppt	
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	ppt	
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	ppt	
Perfluoroheptanoic acid	PFHpA	375-85-9	ppt	
1H, 1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	ppt	
Perfluorohexanesulfonic acid	PFHxS	355-46-4	ppt	390
Perfluorohexanoic acid	PFHXa	307-24-4	ppt	9,900
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	ppt	
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	ppt	
Perfluorononanoic acid	PFNA	375-95-1	ppt	59
1H, 1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	ppt	
Perfluorooctanesulfonic acid	PFOS	1763-23-1	ppt	40
Perfluorooctanoic acid	PFOA	335-67-1	ppt	60
Perfluoropentanoic acid	PFPeA	2706-90-3	ppt	
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	ppt	
Perfluoroundecanoic acid	PFUnA	2058-94-8	ppt	

Notes:

CAS - Chemical abstract service
USEPA - United States Environmental Protection Agency
RSL - Regional screening level
MCL - Maximum contaminant level
ppt - parts per trillion
USEPA RSLs Resident Tap Water (TR=1E-06/THQ=1.) - https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables

FIGURES

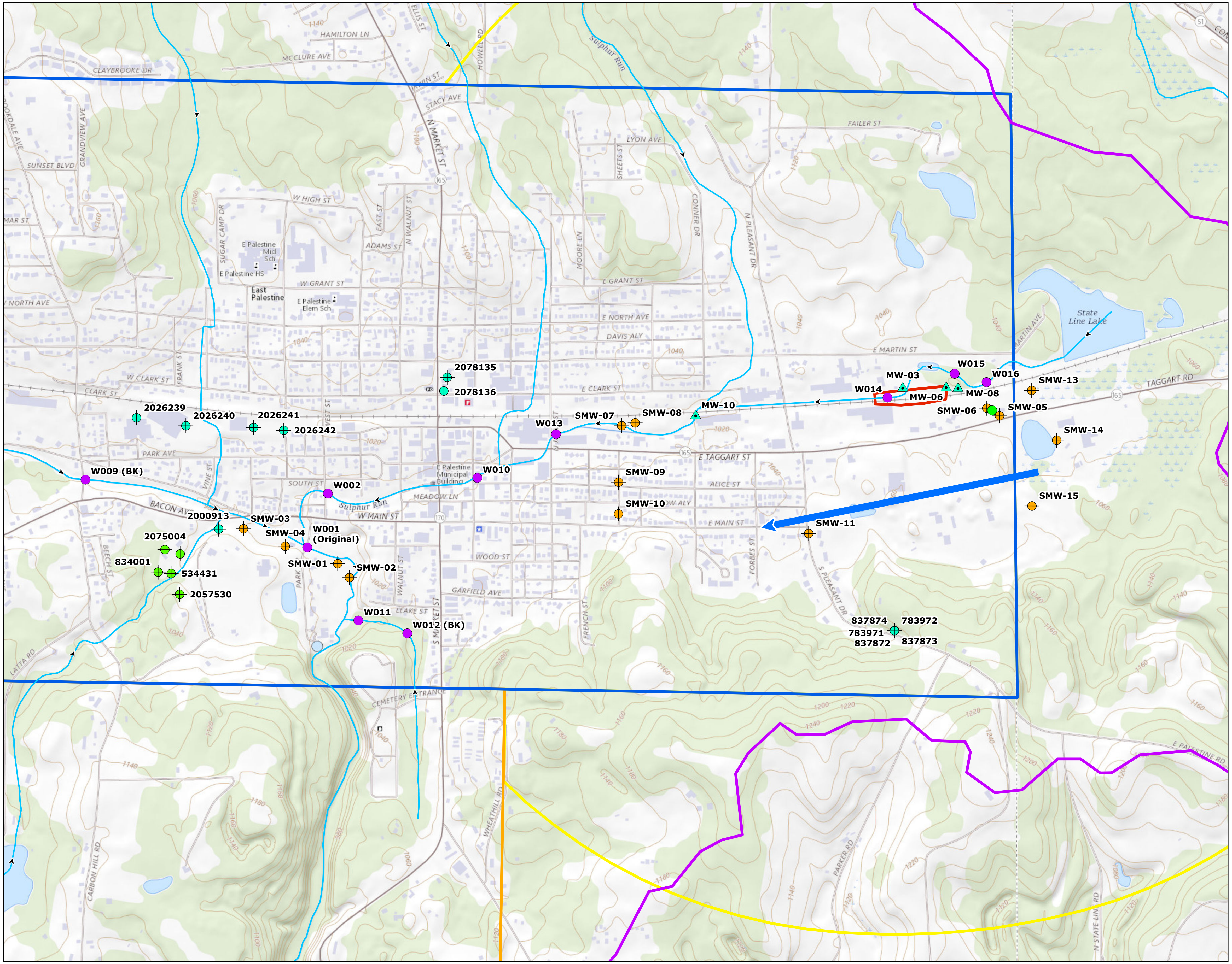


Figure No.
1

Title
Sentinel Monitoring Well Locations

Client/Project 172607922
Norfolk Southern

Project Location
East Palestine, Columbiana Co., OH
Prepared by KB on 2023-04-19

N

0 500 1,000
Feet
(At original document size of 11x17)
1:12,000

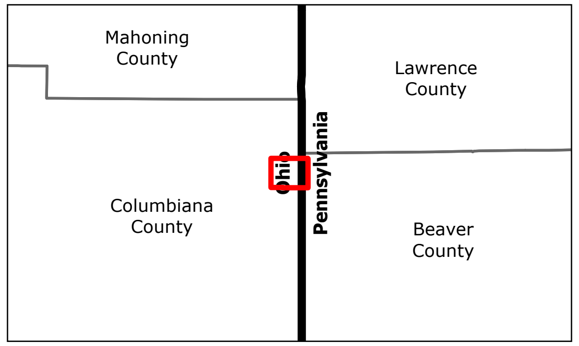
🟥 Incident Area

Priority Sampling Zones

- 🟦 Priority Zone 1
- 🟧 Priority Zone 2
- 🟨 Priority Zone 3
- ➡ Regional Inferred Groundwater Flow Direction
- ⊕ Sentinel Wells
- ▲ On-Site Monitoring Well
- ● Surface Water Samples
- ● Transient PWS Supply Well
- ⊕ Public Water Supply

OHDNR Wells

- ⊕ ODNR Classified Monitoring Well
- 🟪 Watershed Boundary
- → Streams



Notes
1. Coordinate System: NAD 1983 UTM Zone 17N
2. Data Sources: USGS, Ohio Department of Natural Resources
3. Background: USGS 7.5 Minute Quadrangle

Stantec

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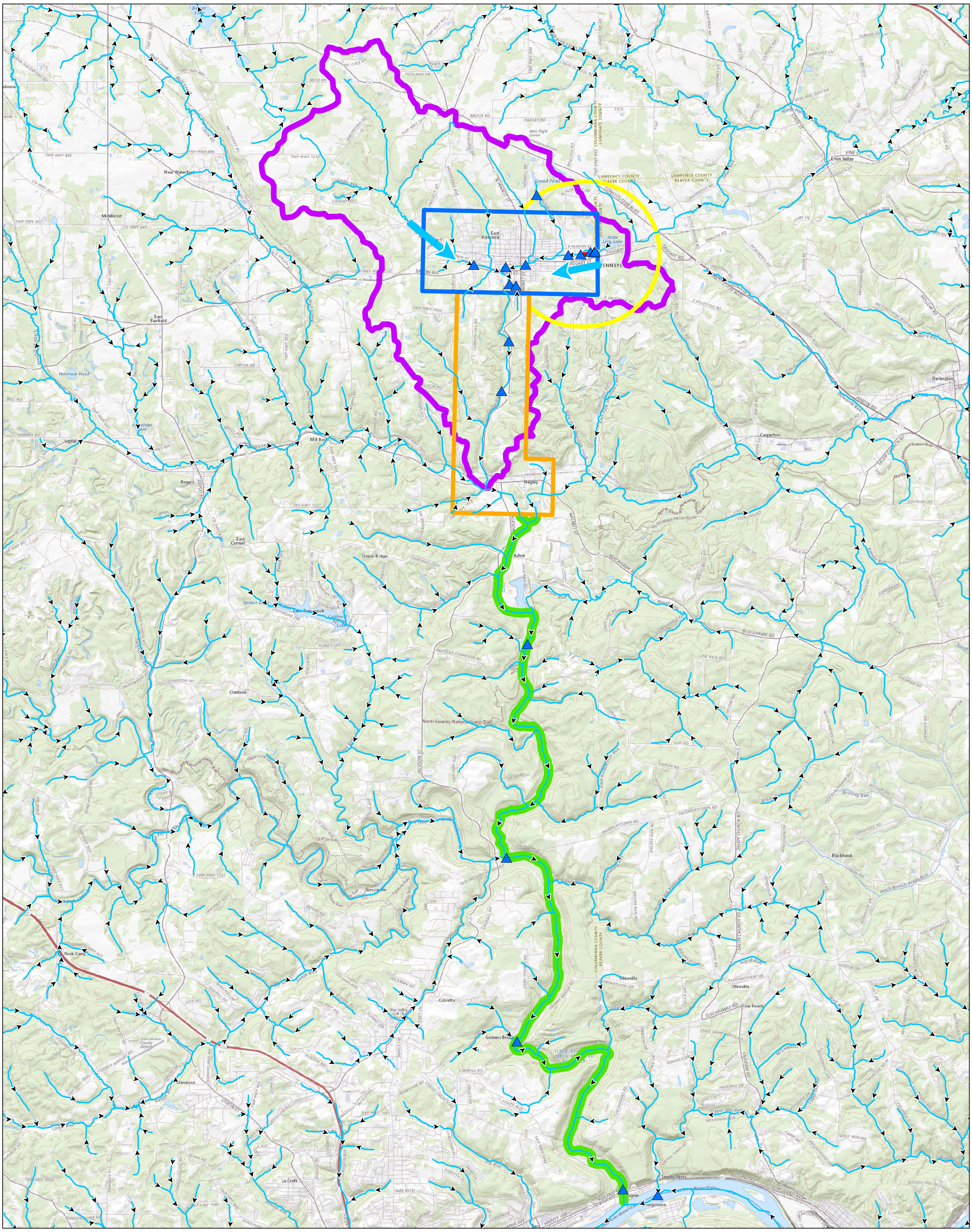

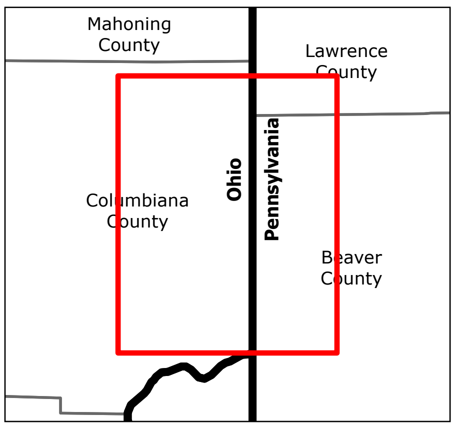

Notes
1. Coordinate System: WGS 1984 Web Mercator Auxiliary Sphere
2. Data Sources: USGS, Watershed boundary source was the USGS StreamStats Application. https://www.usgs.gov/streamstats
3. Background: USGS 7.5 Minute Quadrangle

Priority Sampling Zones

🟦	Priority Zone 1
🟧	Priority Zone 2
🟨	Priority Zone 3
🟩	Priority Zone 4
➜	Regional Inferred Groundwater Flow Direction
🟪	Watershed Boundary
→-	Streams
▨	Incident Area
▲	Approximate Surface Water Sample Location

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(At original document size of 11x17)
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Stantec

Project Location
East Palestine, Columbiana Co., OH

Prepared by KAB on 2023-04-19

Client/Project
Norfolk Southern

Figure No.
2

Title
Watershed Basin Map

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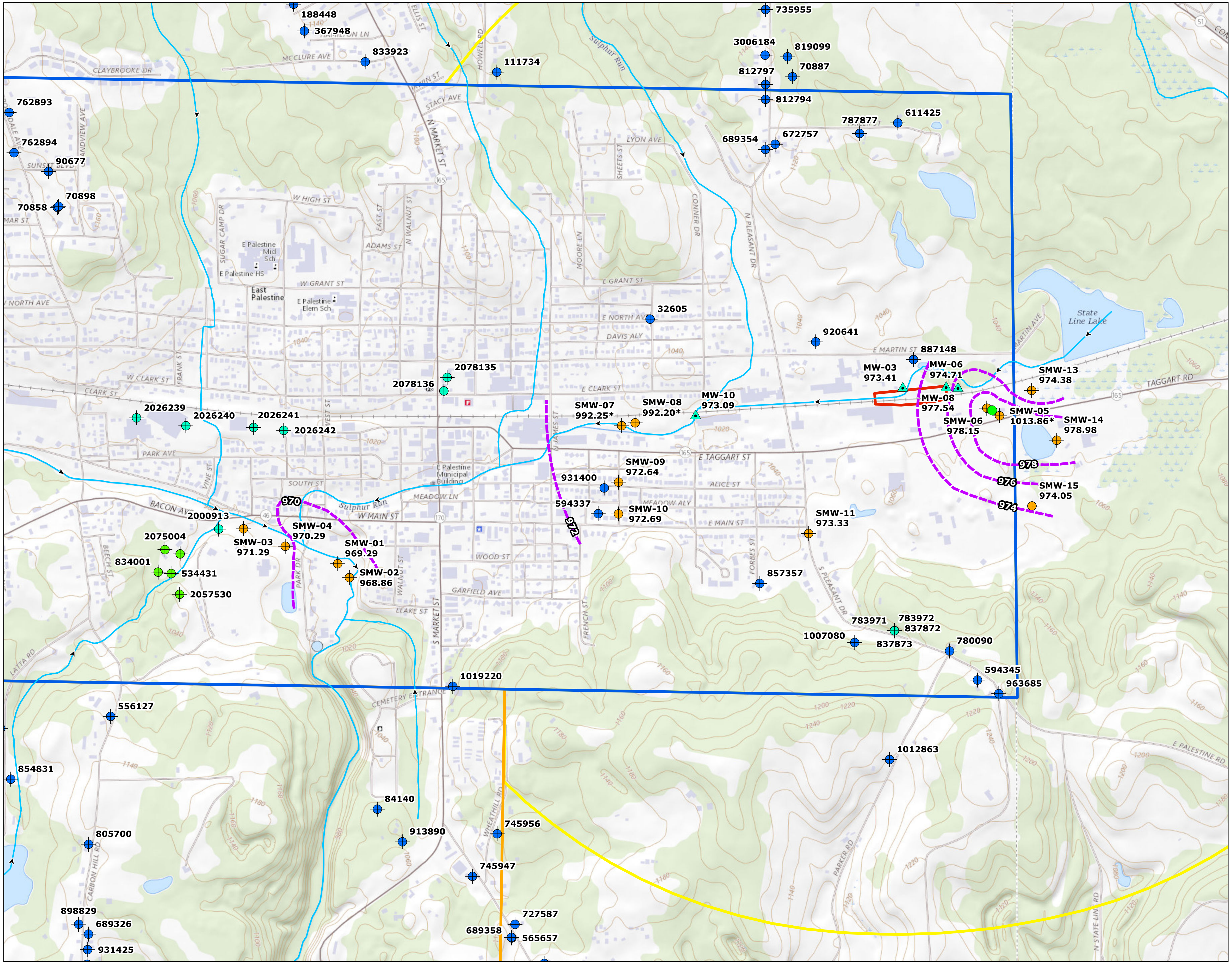

Figure No.
3

Title
Preliminary Potentiometric Surface Map - May 10, 2023

Client/Project
172607922
Norfolk Southern

Project Location
East Palestine, Columbiana Co., OH
Prepared by KB on 2023-05-16

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0 400 800
Feet
(At original document size of 11x17)
1:12,000

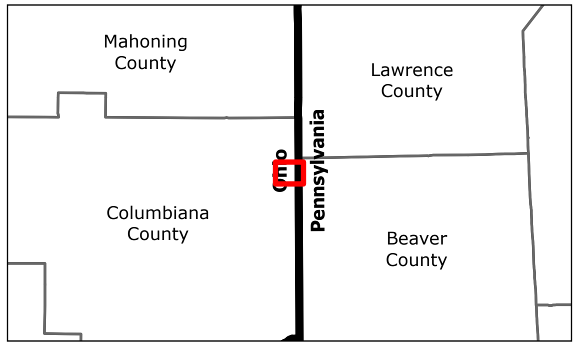
- 🟥 Incident Area

Priority Sampling Zones

- 🟦 Priority Zone 1
- 🟧 Priority Zone 2
- 🟨 Priority Zone 3
- ⊕ Sentinel Wells
- ▲ On-Site Monitoring Well
- ● Transient PWS Supply Well
- ⊕ Public Water Supply

ODNR Wells

- ⊕ ODNR Classified Monitoring Well
- ⊕ ODNR Classified Domestic Well
- ⇢ Streams
- ╌ Groundwater Contour (2ft Interval)



Notes
1. Coordinate System: NAD 1983 UTM Zone 17N
2. Data Sources: USGS, Ohio Department of Natural Resources
3. Background: USGS 7.5 Minute Quadrangle

*Groundwater elevation shown but not used for contouring

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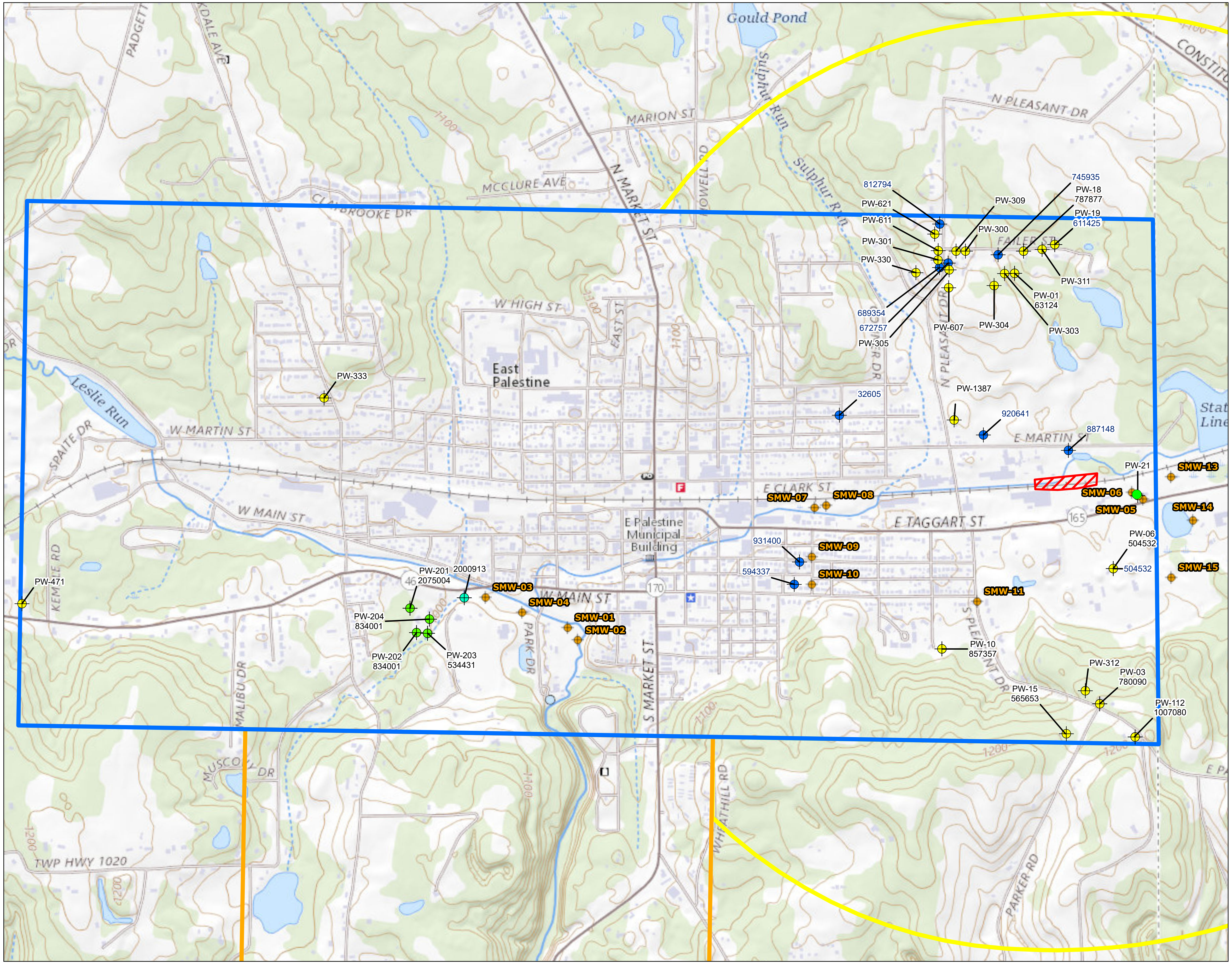

Figure No.
4

Title
Sentinel and Potable Well Locations

Client/Project 172607922
Norfolk Southern

Project Location Prepared by KB on 2023-06-01
East Palestine, Columbiana Co., OH

N

0 500 1,000 Feet
(At original document size of 11x17)
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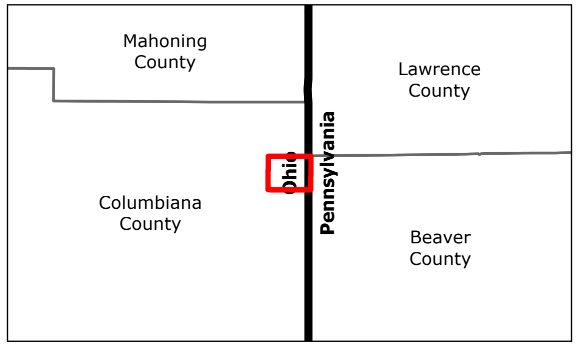
- ● Transient PWS Supply Well
- ⊕ ODNR Classified Monitoring Wells
- ⊕ Public Water Supply
- ⊕ Potable Wells in Zone 1
- ⊕ Sentinel Wells
- ⊕ ODNR Classified Domestic Wells
- ▨ Incident Area

Priority Sampling Zones

- ▭ Priority Zone 1
- ▭ Priority Zone 2
- ▭ Priority Zone 3



Notes
1. Coordinate System: NAD 1983 UTM Zone 17N
2. Data Sources: USGS, Ohio Department of Natural Resources
3. Background: USGS 7.5 Minute Quadrangle

Stantec

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APPENDIX A
OHIO EPA FIELD STANDARD OPERATING PROCEDURES (FSOPS) AND OEPA VAP TECHNICAL GUIDANCE COMPENDIUM VA30007.14.22

Field Standard Operating Procedures (FSOPs)

Table of Contents

FSOP 2.2.12 Field Filtering of GW Samples

FSOP 2.3.1 Surface Water Sample Collection

FSOP 2.3.2 Sediment Sample Collection

FSOP 2.4.1 Procedures for Active Soil Gas Sampling

FSOP 2.4.2 Install and Decom of Sub-Slab Vapor Ports

FSOP 2.4.3 Procedures for Collection of Indoor Air Samples

- FSOP 2.4.3 Attachment 1 Procedures for Collection of Indoor Air Samples_Indoor Air Bldg and Sampling Form
- FSOP 2.4.3 Attachment 2 Procedures for Collection of Indoor Air Samples_Instructions for Bldg Occupants Prior to IA Sampling
- FSOP 2.4.3 Attachment 3 Procedures for Collection of Indoor Air Samples_Vapor Sampling Data Sheet

FSOP 3.1.1 Photoionization Detector

FSOP 3.1.2 Multiple Gas Detection Meter

FSOP 3.1.3 Interface Meter

FSOP 3.1.4 Electronic Water Level Indicator

FSOP 3.1.5 Water Quality Meter

FSOP 3.1.6 Radiation Detection Meters

FSOP 3.1.7 X-Ray Fluorescence Analyzer

FSOP 4.1 Global Positioning Systems

FSOP 4.2 Down-Hole Well Cameras

FSOP 4.3 Magnetic Locating Instruments

FSOP 4.4 Electromagnetic Geophysical Sensor

Initial Site Entry
FSOP 1.1 (April 29, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

This field standard operating procedure (FSOP) helps ensure the safety of Division of Environmental Response and Revitalization (DERR) and other Ohio EPA personnel during initial entry into uncontrolled hazardous waste sites. While this FSOP is intended to address health and safety concerns generally associated with uncontrolled hazardous waste sites, it does not necessarily address every health and safety concern that may be encountered at a specific site and is not intended to serve as a substitute for a site-specific health and safety plan (HASP). Additional precautions, equipment, and procedures may be needed in addition to those prescribed in this procedure to provide a safe working environment. The FSOP assumes the following circumstances and conditions for initial entry onto suspected waste sites, including initial entry for site reconnaissance:

1.1. Ohio EPA has obtained permission to access the site from the owner and tenant (or operator) as applicable, following DERR's most recent Site Access Legal Protocol.

1.2. An ongoing emergency response situation is not occurring at the site.

1.3. Level D personal protective equipment (PPE) will provide adequate protection for Ohio EPA personnel entering the site, based on the review of available site data related to health and safety concerns (*i.e.,* conditions necessitating Level A, B, or C PPE cannot exist or be reasonably expected to occur during site entry).

1.4. During the initial site visit, Ohio EPA will not be performing any subsurface sampling (see FSOP 1.2 Utility Clearance). In some scenarios, limited sampling (*e.g.,* indoor air, surface water, etc.) may be appropriate.

1.5. If, based on historical knowledge of the site, radioactivity is expected to be present, the initial site entry team will consult with management prior to entry, and with ODH as appropriate. For initial site entry purposes, the team will utilize a radiation detection meter at the site (also see FSOP 3.1.6 Radiation Detection Meters).

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Reference Ohio EPA Standard Safety Operating Procedure Number SP11-19 (Working Alone) and OSHA 1910.120 and talk with management to determine if working alone for an initial site entry is appropriate given the site-specific circumstances and conditions.

3.2 **Never** enter an OSHA-defined confined space for any reason during an initial site entry or during any other field activity event. Contact management and the Agency Safety Coordinator to discuss the site and to identify appropriately trained staff to enter confined spaces for reconnaissance or sampling activities in accordance with Ohio EPA Standard Safety Operating Procedure Number SP14-4 (Confined Space Entry).

4.0 Procedure Cautions

Not applicable

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Field Communication / Field Documentation / Health and Safety References

6.1.1 Camera
6.1.2 Cell phone
6.1.3 Emergency contact information (hospital, police, fire department, etc.)
6.1.4 Field logbook or unbound log sheets
6.1.5 Site access agreement or documentation
6.1.6 Site background information (documenting the conditions expected)
6.1.7 Site contact information
6.1.8 Site Entry Atmospheric Action Levels (Table 1) and other reference guides (*e.g.,* National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards)
6.1.9 Site-specific HASP, if available

6.2 Level D PPE

6.2.1 Clothing appropriate for anticipated field conditions
6.2.2 Eye protection (to be worn when necessary)
6.2.3 First aid kits (including sunscreen, insect repellant, etc.)
6.2.4 Hard hat (to be worn when necessary)

6.2.5 Hearing protection (to be worn when necessary)
6.2.6 Protective gloves appropriate for expected field conditions or potential hazards
6.2.7 Safety boots

6.3 Atmospheric Monitoring Instruments (to evaluate site safety, as necessary, based on conditions anticipated or encountered)

6.3.1 Radiation survey meter
6.3.2 Lower explosive limit (LEL)/oxygen (O_2) meter
6.3.3 Photoionization detector (PID) or flame ionization detector (FID)
6.3.4 Other monitoring instruments appropriate for the expected site conditions, e.g., a carbon monoxide meter, colorimetric (chemical compound-specific) detector tubes, hydrogen sulfide meter, and/or a particulate meter.

7.0 Procedures

7.1 If a site-specific health and safety plan (HASP) has been prepared, review the HASP prior to the initial site entry to understand the hazards associated with the site.

7.2 If a site-specific HASP has not been prepared, review all available site information related to health and safety to evaluate the potential hazards that may be associated with the site.

7.3 If required, ensure that atmospheric monitoring instruments are calibrated and operating properly; refer to instrument-specific equipment manuals and/or FSOPs as necessary.

7.4 Unless otherwise directed (see Section 3.1), include at least two persons on the initial site entry team, preferably both Ohio EPA staff members.

7.5 Systematically search the site for potential physical, chemical, biological, and radiological hazards as necessary and use air monitoring equipment as needed to ensure that atmospheric conditions do not exceed Site Entry Atmospheric Action Levels (Table 1) or any action levels provided in the NIOSH Pocket Guide to Chemical Hazards.

7.6 If Level D PPE is adequate, perform additional tasks as necessary (*e.g.,* marking sampling locations, GPS surveying, photographing site features).

7.7 If the site conditions encountered require a greater degree of protection than that provided by Level D PPE:

7.7.1 Leave the site immediately.

7.7.2 Revise the site-specific HASP (or develop a site-specific HASP) before reentering the site. Only staff cleared to wear respiratory protection can enter or re-enter the site if respiratory protection is required.

7.8 If radioactive materials are encountered, leave the site immediately and contact management first, and ODH as appropriate, to discuss the site before reentry.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

Table 1, Site Entry Atmospheric Action Levels

11.0 References

DERR's Revised Site Access Legal Protocol

FSOP 1.2, Utility Clearance

FSOP 1.3, Field Documentation

Ohio Administrative Code 3701:1-38-13(A)(2)

Ohio EPA Standard Safety Operating Procedure Number SP11-19 (Working Alone)

Ohio EPA Standard Safety Operating Procedure Number SP14-4 (Confined Space Entry)

Ohio Revised Code 3781.25(H)

National Institute for Occupational Safety and Health Pocket Guide to Chemical Hazards (available online at http://www.cdc.gov/niosh/npg/)

TABLE 1, SITE ENTRY ATMOSPHERIC ACTION LEVELS

Atmospheric Hazard	Monitoring Equipment	Action Level	Response
Explosive Atmosphere	Lower Explosive Level (LEL) Meter (a.k.a. Combustible Gas Indicator, or CGI)	< 10% LEL	Continue monitoring.
		10%-25% LEL	If outdoors, continue monitoring with caution. If within a structure, explosion hazard. Exit structure.
		> 25% LEL	Explosion hazard, leave site.
O_2 Deficient Atmosphere	Oxygen (O_2) Meter	< 19.5% O_2	Leave site, LEL readings are not valid; toxic vapors or explosive gas may be displacing oxygen.
O_2 Enriched Atmosphere		> 23.5% O_2	Leave site, LEL readings are not valid.
Volatile Organic Compounds (e.g., benzene, methyl-ethyl ketone, vinyl chloride)	Photoionization Detector (PID) or Flame Ionization Detector (FID)	> 1 ppm background in breathing zone	Leave site. (Reenter with appropriate PPE if qualified.)
Hydrogen Sulfide (H_2S)	Hydrogen Sulfide (H_2S) Meter	> 10 ppm	Leave site.
Carbon Monoxide (CO)	Carbon Monoxide (CO) Meter	> 35 ppm	Leave site.
Other Inorganic & Organic Gasses & Vapors	Compound-specific monitoring equipment; consult the NIOSH Pocket Guide to Chemical Hazards for action levels and responses.		
Particulate Matter	Particulate Meter	Compound-specific monitoring equipment and site-specific circumstances; consult the NIOSH Pocket Guide to Chemical Hazards for action levels and responses.	
Radiation	Radiation Survey Meter or Dosimeter	< 2 millirem (mrem)/hr above background	Continue monitoring.
		> 2 millirem (mrem)/hr above background	Leave site and notify ODH.

Utility Clearance
FSOP 1.2 (April 29, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Underground utility clearance must be requested prior to conducting hand or mechanical excavation of soil or sediment per Ohio Revised Code (ORC) 3781.25(I).

1.2 The entity conducting the excavation/drilling work (*e.g.,* the excavator) must coordinate underground utility clearance. Utility clearance for work performed by Division of Environmental Response and Revitalization (DERR) staff may be coordinated by the DERR Site Investigation Field Unit (SIFU) staff or a DERR district office site coordinator or inspector. (See Section 4.1 regarding notification requirements for the Ohio Utilities Protection Service (OUPS) if a contractor is performing the work.)

1.3 SIFU or the DERR district office staff responsible for submitting the utility clearance request will be responsible for retaining documentation of the requests, in electronic format, per Ohio EPA record retention schedules.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Contact with underground or overhead utilities may result in injury or death to personnel or the public, damage to or destruction of equipment or facilities, and/or damage to the environment.

3.2 If the site does not appear to have been cleared (*e.g.,* no evidence of flags or paint markings or notification of clearance), contact the appropriate underground protection service, utility and/or facility as applicable before proceeding with work.

3.3 If a utility line is hit or damaged, walk away immediately and clear the area of personnel and the public. Contact OUPS and the appropriate local utility companies (see Section 4.1). As appropriate and safe, expeditiously notify the property owner and the local government of the situation. Call 9-1-1 if there is any injury or potential threat for injury or if a substance is being released to air, such as natural gas, or if there is a fire, explosion, or a threat of fire or explosion.

4.0 Procedure Cautions

4.1 Ohio currently requires that the excavator notify the OUPS prior to excavation, drilling or other underground activities (See Section 7.1.1). Note that if an LOE or other contractor is performing the work, then that contractor must notify OUPS.

4.2 Many manufacturing plants and other facilities have their own internal underground utilities and infrastructure that are not covered by OUPS (see Section 7.3). Knowledgeable facility staff, such as a plant engineer, maintenance supervisor, or health and safety personnel, should be contacted if possible, to locate and clear any facility-owned underground utilities or infrastructure.

4.3 OUPS member utilities may not mark lateral or service connections from main utility lines to residences and commercial or industrial buildings (see Section 7).

4.4 Do not excavate within the tolerance zone, or “approximate location” of the underground utility without the supervision of the owning utility. The “approximate location” as defined in ORC 3781.25(D), is *"the site of the underground utility facility including the width of the underground utility facility plus eighteen inches on each side of the facility."* Any excavation within the tolerance zone should be performed with hand tools in a careful and prudent manner until the marked utility is exposed.

4.5 Additional utility investigation procedures, such as those described in Section 7.2, may be appropriate as supplemental procedures but may never be used in place of contacting OUPS. In case of a dispute in utility locations between a supplemental procedure and OUPS, or member utilities, contact OUPS or appropriate member utility for verification of utility locations.

4.6 DERR staff members are not authorized to perform underground utility clearance. Do not attempt to use SIFU’s geophysical equipment or other DERR equipment to locate underground utilities (or to provide “supplemental” information) for utility clearance.

5.0 Personnel Qualifications

5.1 Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

5.2 It is strongly recommended that Ohio EPA personnel who request utility clearance for investigations attend safety training provided by OUPS so they have a solid understanding of utility clearance procedures.

6.0 Equipment and Supplies

Not applicable

7.0 Procedures

7.1 Contact the following underground protection services to clear utilities prior to excavation:

7.1.1 Contact OUPS at **8-1-1** or **(800) 362-2764** at least 48 hours [two (2) working days] but no more than 10 working days prior to digging. Working days do not include weekends or legal holidays. (As an alternative, OUPS may be contacted online using i-dig Newtin RTE. For more information on i-dig, see **www.oups.org**.)

7.1.1.1 Provide the necessary information as detailed on the attached OUPS Locate Work Order Form to OUPS to accurately locate site and/or work area. Let OUPS know if the sampling locations have been pre-marked (locations should be pre-marked with white paint and/or white flags). Also, let utility locator know if there is a distance around the marked location that should also be cleared (*e.g.,* 20 feet radius around marked location).

7.1.1.2 OUPS will provide notification to full membership utilities to mark or clear utilities.

7.1.1.3 OUPS will provide a ticket number for the location request. Make sure to record the ticket number in the site-specific work plan or other appropriate document accessible to personnel in the field. The entity that will be conducting the excavating/drilling activities may use OUPS Positive Response to check on the status of clearing or marking

7.1.1.4 If work does not begin within 10 working days of the request, another OUPS utility location request must be made.

7.1.1.5 Underground utility lines may be marked by utility companies or their locating services with flags or paint or both. Color codes for marking utilities are shown on the attached OUPS Utility Color Code Guide.

7.1.1.6 Work may continue until markings are no longer visible. If markings are no longer visible, OUPS must be contacted to remark utilities.

7.1.1.7 If the site is vacant, a sign with the street address may need to be posted so that OUPS can locate the site.

7.2 In addition to contacting OUPS, the use of a private utility locator service should be considered. This is especially applicable for large sites where OUPS does not locate facility-owned underground utilities, where site areas are located away from utility main lines, or at sites where the past land uses and industrial or commercial activities are not well known. This may also be applicable for sites involving residential properties.

7.3 If at a manufacturing plant or other facility, contact knowledgeable facility staff such as a plant engineer, maintenance supervisor, or health and safety personnel to locate any facility-owned underground utilities or infrastructure for utility clearance (please refer to paragraph 4.2).

8.0 Data and Records Management

Not applicable

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

Ohio Utility Protection Service Locate Work Order Form

Ohio Utility Protection Service Utility Color Code Guide

American Electric Power Ohio Public Safety Fact Sheet

11.0 References

Ohio Revised Code 3781.25(D) and 3781.25(I)

O.U.P.S. LOCATE WORK ORDER

CALL 48 HOURS BEFORE YOU DIG – 800-362-2764

COLOR CODES: Red = Electric Orange = Phone/Cable TV Yellow = Gas Blue = Water Green = sewer
White = Proposed Excavation

COMPLETING ENTIRE FORM HELPS TO ENSURE A MORE ACCURATE AND TIMELY LOCATE

Contact Phone # ________________________ Caller Name ___________________________

Company Name ____

Fax ____________________________ Email ____

County ______________________________ City/Township ____________________________

Address/Location of Work____

Extent of Work: Front/Sides/Rear ____________________Farthest Distance/Direction back off Road _____

Lot # __________ Subdivision ________________________________Builder Name _________________

Cross / Between Streets ____

Distance & Direction from Cross Street ____

Date of Excavation ________________________ Start Time of Excavation__________________________

Type of Work ____

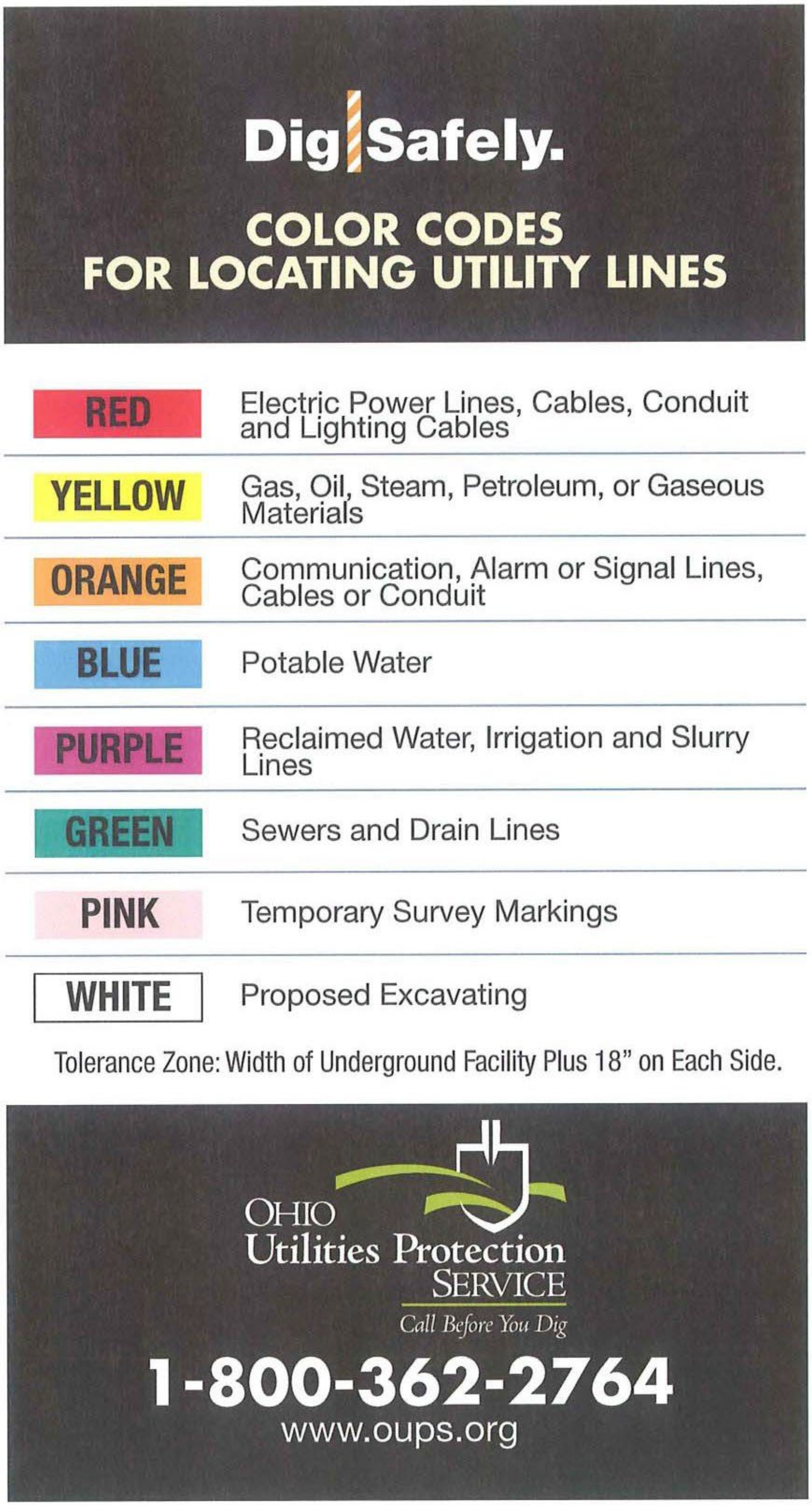
Working for Company __________________________Work Done By Company _____________________

_____________Means of Excavation ____ Blasting ____ Pre Markings ____ Meet

____ RR Right of Way ____Highway Mile Marker At/From ___________________________

Comments____

OUPS TICKET NUMBER _________________________________



Dig Safely.

COLOR CODES FOR LOCATING UTILITY LINES

RED	Electric Power Lines, Cables, Conduit and Lighting Cables
YELLOW	Gas, Oil, Steam, Petroleum, or Gaseous Materials
ORANGE	Communication, Alarm or Signal Lines, Cables or Conduit
BLUE	Potable Water
PURPLE	Reclaimed Water, Irrigation and Slurry Lines
GREEN	Sewers and Drain Lines
PINK	Temporary Survey Markings
WHITE	Proposed Excavating

Tolerance Zone: Width of Underground Facility Plus 18” on Each Side.

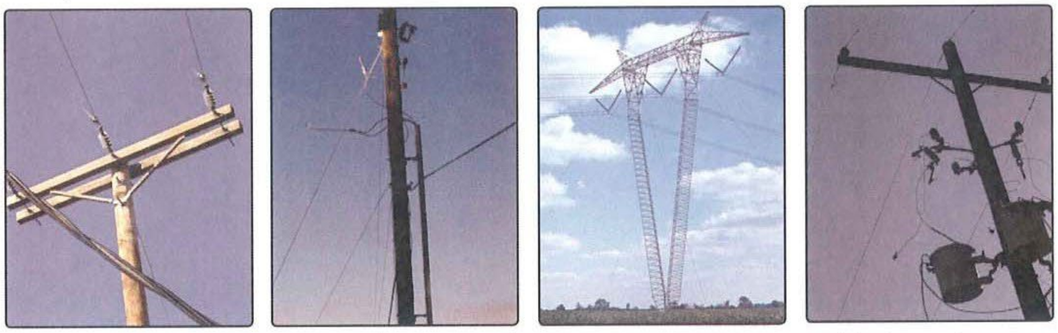
OHIO
Utilities Protection
SERVICE
Call Before You Dig

1-800-362-2764
www.oups.org

Public Safety

Look Up for Lines

Keep a Safe Distance from All Overhead Power Lines



Most contact with overhead power lines is accidental, but can result in severe injuries and even death. Fortunately, most, if not all, electrical accidents can be prevented. Before you begin any job, whether it's installing a TV antenna on your roof or constructing a new building, it's important to be aware of power line locations and the necessary safety precautions.

Working Around Electricity

Electricity always attempts to travel to the ground and will follow all paths to get there. If a conductor of electricity becomes available, the electricity will follow that path to ground. Tools and equipment you use, and even your own body, are excellent conductors.

What does this mean? Let's say you're using a ladder to do some work around your house. If that ladder accidentally touches an overhead power line, the ladder (and you) could become the path for the electricity, sending electricity through the ladder and your body, which can cause severe injuries or even death.

Minimum Clearances

Always look up first for overhead power lines. If you see some in the area, there is a MINIMUM clearance of 10 feet which should be maintained. The minimum clearance increases as the voltage increases. Minimum clearances also can be affected by weather conditions, the type of work being performed, the equipment being used and other factors. Additional minimum clearances for various voltages are shown in this chart.

Line Voltage	Minimum Clearances
Up to 50,000 volts	10 feet
50,000 to 200,000 volts	15 feet
200,000 to 350,000 volts	20 feet
350,000 to 500,000 volts	25 feet
500,000 to 750,000 volts	35 feet
750,000 to 1,000,000 volts	45 feet

Equipment and Overhead Lines

- Use a clean, dry wood or fiberglass ladder if electric lines are anywhere in the area. They are less likely to conduct electricity than a metal ladder.
- When installing an antenna, position it at least 1.5 times its total length away from power lines. If it starts to fall, let it go and stay clear.
- Be certain to maintain a safe clearance when the bed of a dump truck is raised.
- Know the minimum distance a crane can operate safely near a power line. Keep all parts of the crane and its load outside this area. If your crane does come in contact with an overhead line, don't leave the cab, call 9-1-1 and the power company immediately.
- Designate a worker responsible for signaling the crane operator when any part of the crane or its load approaches the minimum clearance limit. The worker should never touch the crane.
- Some jobs may require the line be de-energized to complete the task safely. The power company will work with you to determine if this is needed.
- Do not rely on proximity warning devices such as hook insulators or boom guards, because each has its limitations.
- Take time to plan any job and contact your local power company if you have any questions.

AEP OHIO®
A unit of American Electric Power

For more public safety information, visit: http://www.AEPOhio.com

Field Documentation
FSOP 1.3 (April 29, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Accurate and complete field documentation of sampling and other field activities is critical for ensuring the technical integrity and legal defensibility of environmental site assessments, remedial investigations/feasibility studies, remedial activity implementations, facility investigations, program field audits, and other field activities.

1.2 Field documentation may include, but is not limited to the following:

1.2.1 Field logbooks or field log sheets (including any LOE field logs)
1.2.2 Activity-specific field forms
1.2.3 Chain-of-Custody (COC) forms
1.2.4 Photographs
1.2.5 Electronic data (*e.g.,* Global Positioning System (GPS)) location coordinates, water level data

1.3 For Contract Laboratory Program (CLP) projects, additional field documentation requirements are applicable. Contact the DERR Site Investigation Field Unit (SIFU) for assistance with CLP project requirements before field activities are initiated.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

Not applicable

4.0 Procedure Cautions

Not applicable

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Appropriate activity-specific field forms (as needed)
6.2 COC forms, sample labels, custody seals (as needed)

6.3 Clipboard
6.4 Digital camera
6.5 Field logbook or field log sheets (waterproof, when necessary)
6.6 Field scale or ruler (as needed)
6.7 GPS and data logging equipment (as needed)
6.8 Maps or site plans for reference and documentation
6.9 Pens and markers (waterproof, when necessary)
6.10 Small dry-erase board with dry-erase markers (for photograph identification)

7.0 Procedures

7.1 Field logbook/field log sheet documentation:

7.1.1 Document the following types of information for site assessment activities in the field logbook or on log sheets, as appropriate for site-specific work plan activities:

7.1.1.1 Site or project name
7.1.1.2 Site location/address
7.1.1.3 People and affiliation present
7.1.1.4 Date(s) and time(s) of field activities
7.1.1.5 Weather conditions
7.1.1.6 Ohio EPA personnel and other persons on-site
7.1.1.7 Health and safety field monitoring data (*e.g.,* LEL/O2 meter or PID readings)
7.1.1.8 General field observations
7.1.1.9 Photograph log
7.1.1.10 Interview notes
7.1.1.11 Problems or unexpected conditions encountered

7.1.2 If activity-specific field forms are not available, use a field logbook to document sampling and other field activities. Record all form-required information, which may include, but is not necessarily limited to the following types of information (generally in the following order):

7.1.2.1 Sampler’s name(s)
7.1.2.2 Sample identification number (refer to FSOP 1.4, Sample Identification Nomenclature)
7.1.2.3 Sample collection date and approximate time
7.1.2.4 Sample location (narrative description as needed)
7.1.2.5 Sample matrix type (soil, sediment, groundwater, surface water, soil gas, etc.)
7.1.2.6 Depth intervals for soil samples
7.1.2.7 If required, the classification or description of soil samples
7.1.2.8 Sample type (grab, composite, duplicate, equipment blank, etc.)
7.1.2.9 Field screening data associated with the sample (*e.g.,* PID readings)

7.1.2.10 Laboratory parameters to be performed (*e.g.,* VOCs)

7.1.2.11 Sampling location photograph description/documentation

7.1.2.12 Any other relevant information needed to support the technical integrity or legal defensibility of the sampling process

7.2 The following activity-specific field forms should be used to document specific field activities:

7.2.1 Boring Log and Monitoring Well or Soil Gas Probe Construction Diagram
7.2.2 Ground Water Sampling
7.2.3 Monitoring Well Surveying
7.2.4 Monitoring Well Development
7.2.5 Vapor Intrusion Forms

7.3 Chain of Custody (COC) forms

7.3.1 Always complete a COC form when submitting samples to any laboratory for analyses.

7.3.2 If submitting samples to a DERR contract laboratory, contact the SIFU Laboratory Coordinator, a District Office Laboratory Coordinator, or the contract laboratory for specific instructions for completing COC forms.

7.3.3 If submitting samples to the Ohio EPA Division of Environmental Services (DES) laboratory, use DES COC forms. Contact DES for specific instructions on completing their COC forms.

7.3.4 For federal site assessment projects, use the required U.S. EPA Scribe sample management and reporting software program to create electronic COC forms for the U.S. EPA Contract Laboratory Program (CLP) sampling projects. DERR SIFU has access to the Scribe program.

7.3.5 For federal site assessment projects, vapor samples are to be sent to the U.S. EPA Analytical Services Branch (ASB) for analyses. ASB provides COC forms.

7.4 Photographic documentation

7.4.1 Take photographs to document site features and conditions that are relevant to the environmental site assessment process, including selected sampling locations and samples if necessary.

7.4.2 Log photographs as necessary for project documentation in the field logbook, log sheets, or on other suitable references (*e.g.,* maps or site plans) with respect location/orientation and subject matter.

7.4.3 Use digital cameras capable of embedding the locational, date and time data within the photograph file. It is strongly recommended not to take photographs with personal cell phones.

7.4.4 Site photographs are to be uploaded to the Ohio EPA photograph management system (*i.e.,* LYNX).

7.5 GPS data and other data logging documentation (*e.g.,* water-level or water chemistry dataloggers that may be used for aquifer testing and water quality evaluation). Site-specific file names are to be used for data files.

7.5.1 Create sample location identifications in accordance with FSOP 1.4, Sample Identification Nomenclature.

7.6 Retention of field documentation

7.6.1 Ensure that field documentation is properly filed for future reference. Always provide copies to the appropriate district office personnel.

7.6.2 Scan original copies of written field documentation so that electronic copies are readily available for transmission, review, and reference. Retain all original written field documentation and electronic copies at the appropriate district office.

8.0 Data and Records Management

Ensure that all field documentation records are managed in accordance with the Agency records retention policy. Also ensure that all field documentation records are maintained in compliance with Agency and DERR personally identifiable information (PII) policies.

9.0 Quality Assurance and Quality Control

The Superfund QAPP is to be referenced, primarily for federal site assessment activities.

10.0 Attachments

None

11.0 References

FSOP 1.4, Sample Identification Nomenclature

Sample Identification Nomenclature
FSOP 1.4 (April 29, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure provides a standard nomenclature convention for environmental sample identification. The use of a standard convention facilitates the progress of field sampling activities, reduces the potential for confusion regarding sample identification, and improves the ease of reviewing laboratory analytical results.

1.2 Alternative sample identification conventions may be used for the following circumstances:

1.2.1 When the regulatory program under which the sampling work is being performed requires an alternative sample identification convention

1.2.2 At sites where sampling already has been performed and where use of an existing sample identification convention would promote consistency and help avoid potential confusion

1.2.3 When soil or sediment samples are collected using incremental or other composite sampling methodologies

1.2.4 At sites where unique sampling situations are found to exist.

1.3 If collecting environmental samples from a site with multiple parcels or multiple areas of contamination (*e.g.,* a Voluntary Action Program (VAP) property with multiple identified areas), qualifiers that identify the sample location (*e.g.,* parcel or VAP identified area) may be added to the sample identification nomenclature. Due to the wide variety of sites and circumstances associated with environmental assessments, such nomenclature is best developed and applied on a site-specific basis.

1.4 Anticipated deviations from this procedure should be documented in the site-specific work plan with a brief explanation of the reason(s) for the deviation.

1.5 Ohio EPA's Quality Assurance Project Plan (QAPP) for Targeted Brownfield Assessments (TBAs) requires the use of this procedure.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

Not applicable

4.0 Procedure Cautions

4.1 The geographic location (latitude and longitude) of each sampling location will be determined using Global Positioning System (GPS). Accordingly, sample identification does not typically need to incorporate information regarding geographic direction, e.g., adding “N” to the identification of a soil sample collected from the north side of an excavation.

4.2 Given concerns regarding personally identifiable information (PII), the use of property owner names and addresses in sample nomenclature should be carefully evaluated, particularly for federal site assessment sites.

4.3 Certain regulatory programs (*e.g.,* the U.S. EPA Contract Laboratory Program or CLP) may require the use of sample identification conventions that differ from those prescribed by this procedure.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

Not applicable

7.0 Procedures

7.1 The sample identification consists of an abbreviation for the sample matrix type and a consecutive sample number separated by a hyphen, e.g., **SO-1** (soil sample number one) unless otherwise indicated. Environmental sample matrices and association abbreviations (**bold**) include the following:

7.1.1 Soil samples:

7.1.1.1 **SO** for soil samples collected using manual labor (*e.g.,* by scoop or hand auger) or from excavations; the **SO** abbreviation is followed by a consecutive sampling location number, a hyphen, and the approximate sample depth interval (expressed as tenths of feet) in parentheses, e.g., SO-1 (0.5-1.5ft)

7.1.1.2 **SB** for soil samples collected using drilling equipment; the **SB** abbreviation is followed by a consecutive boring location number, a hyphen, and the approximate sample depth interval (expressed as tenths of feet) in parentheses, e.g., SB-1 (0.5-1.5ft)

7.1.2 **SE** for sediment samples

7.1.3 **SW** for surface water samples

7.1.4 Ground water samples:

7.1.4.1 **MW** for monitoring well ground water samples

7.1.4.2 **GW** for ground water samples collected from an open borehole

7.1.4.3 If multiple samples are collected from a monitoring well or open borehole at different depths, add a designation at the end of the identification (*e.g.,* **MW-1(Shallow)**, **MW-1(Deep) or MW-1 (10.0-15.0ft)**, **MW-1 (20.0-25.0ft);** or **GW-1(Shallow)**, **GW-1(Deep)** or **GW-1 (10.0-15.0ft)**, **GW-1 (20.0-25.0ft)**

7.1.4.4 **RW** for ground water samples collected from residential water supply wells

7.1.4.5 **PW** for ground water samples collected from public water supply wells

7.1.4.6 For other types of wells (*e.g.,* remedial extraction wells, non-potable process water wells, irrigation wells) use a sample identification based on the well identification.

7.1.5 **LE** for leachate samples

7.1.6 **IA** for indoor air samples

7.1.7 **AA** for ambient air samples

7.1.8 **SS** for sub-slab vapor samples

7.1.9 **SG** for soil gas samples

7.1.10 **FP** for free product samples

7.1.11 **WA** for solid waste samples

7.1.12 Alternative sample nomenclature may be used for site-specific circumstances (*e.g.,* DRUM, TOTE, etc.).

7.2 Quality assurance/quality control (QA/QC) sample and blank identification consist of an abbreviation for the QA/QC sample or blank type and a consecutive sample/blank number separated by a hyphen, e.g., **FB-01** (field blank number one) unless otherwise noted. QA/QC samples/blanks and association abbreviations (**bold**) include the following:

7.2.1 Duplicate samples

7.2.1.1 **DUP** for duplicate samples, unless blind duplicates are required by the regulatory program (see 7.2.1.2). Duplicates may be numbered consecutively without reference to the sample from which the duplicate was split, e.g., **DUP-1** for a duplicate split from ground water sample MW-1, or identified by adding the suffix “DUP” to the identification of the sample from which the duplicate was split, e.g., **MW-1DUP** for a duplicate split from ground water sample MW-1.

7.2.1.2 Blind duplicates are duplicate samples, preferably split from the same container, which are numbered by the same convention as the other samples so that the laboratory does not know they are duplicates.

7.2.2 **FB** for field blanks

7.2.3 **EB** for equipment blanks

7.2.4 **TB** for trip blanks; if available, the date the trip blank was filled by the laboratory may be written in the “comments” section of the chain-of-custody form

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation

Sample Custody and Handling
FSOP 1.5 (May 6, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure describes standard practices used by the Division of Environmental Response and Revitalization (DERR) for custody and handling of environmental samples (generally water, soil, sediment, soil gas, or air) prior to receipt by a laboratory. See the U.S. EPA Sampler's Guide (October 2014) for additional information, particularly with regard to federal site assessment activities.

1.2 A chain of custody (COC) form documents the exchange of samples from sampling personnel to the laboratory and supports the integrity and legal defensibility of the sampling process. The COC form generally includes the following information:

1.2.1 Project name and location
1.2.2 Sampler's name and contact information
1.2.3 Laboratory name and contact information
1.2.4 Sample number/identification
1.2.5 Date and time of sample collection
1.2.6 Grab or composite designation
1.2.7 Number and types of containers comprising a sample
1.2.8 Analytical methods and preservatives
1.2.9 Requested analytical turnaround time
1.2.10 Notes concerning samples
1.2.11 Sampler's signature
1.2.12 Signatures of individuals involved in the sample transfer (except for commercial shipping personnel)
1.2.13 Air bill or shipping number

1.3 Agency personnel are responsible for the care and custody of samples from the time of collection to the time the samples are relinquished directly to the laboratory or to a commercial shipper for transportation to the laboratory. U.S. EPA Sampler's Guide (October 2014) considers a sample "under custody" under the following conditions:

1.3.1 The sample is in possession.

1.3.2 The sample was in possession and then secured or sealed to prevent tampering.

1.3.3 The sample was in possession when placed in a secured area.

1.4 Proper packaging and prompt shipment of samples is important for the following reasons:

1.4.1 Protecting samples from temperature increases that may cause changes in analyte composition or concentration.

1.4.2 Reducing sample degradation from exposure to ultraviolet rays.

1.4.3 Reducing the chance of leaking or breaking of sample containers and exposure of field sampling or laboratory personnel to toxic substances.

1.4.4 Ensuring compliance with shipping regulations.

1.4.5 Minimizing the potential for sample theft or tampering.

1.4.6 Ensuring that analytical holding times for samples are met.

1.5 This procedure is consistent with certain Contract Laboratory Program (CLP) requirements that are generally accepted practices for sample custody and handling for environmental investigations. However, it does not meet all CLP requirements. It is the responsibility of the DERR Site Investigation Field Unit (SIFU) to meet all CLP project requirements before and after field sampling activities.

1.6 This procedure does not apply to shipping samples that are defined as a hazardous material (also referred to as dangerous goods, see the Dangerous Goods List, Section 4.2 IATA). If shipping a suspected hazardous material always contact appropriate management for assistance. Shipping hazardous waste samples may be excluded from hazardous waste requirements under OAC 3745-51-14 (D).

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Large sample coolers filled with environmental samples and ice typically weigh between 40 and 60 pounds. Always use proper lifting techniques, and if needed request assistance to avoid injuries.

3.2 Glass containers may break during sample handling and packing. Always handle glass containers with care and be aware of the potential for broken glass when packing or rearranging. Broken glass may cause cuts or lacerations. Seek medical attention if needed and/or use first aid kit for cuts or lacerations.

3.3 Strong acids or bases, e.g., HCl, HNO_3, H_2SO_4, and NaOH, are often used to preserve water samples. Skin or eye contact with preservatives or preserved samples may result in injury. Wear appropriate personnel protective equipment (e.g., gloves and eye protection) to avoid chemical burns. Use potable water to flush exposed areas and seek medical attention if needed. (*If directly exposed to a concentrated acid or base, seek medical attention immediately.)*

4.0 Procedure Cautions

4.1 Most environmental samples must be preserved on ice at 4^oC (+/-2^oC) to prevent sample degradation. Temperature-sensitive samples should be shipped same-day or next-day delivery to the laboratory.

4.2 Do not use “blue ice” packs for temperature preservation of environmental samples. Natural ice is more reliable for maintaining a sample temperature of 4^oC (+/-2^oC). Additionally, “blue ice” typically contains ingredients (e.g., propylene glycol or styrene) that could contaminate volatile organic compound (VOC) or semi-volatile organic compound (SVOC) samples if the packs leak during transportation.

4.3 Never place loose ice in a sample cooler being prepared for commercial shipment. If the ice melts and water leaks from the cooler during transit, shipment to the laboratory may be delayed or terminated. Always contain ice in sealable plastic bags or within a sealed heavy-duty plastic bag used as a cooler liner.

4.4 In limited circumstances, special handling and shipping requirements will apply to environmental samples containing concentrated preservatives. Some chemical preservatives are regulated as hazardous materials by U.S. Department of Transportation (U.S. DOT). Reference the Hazardous Materials Transportation Act (49 CFR 170-179) which provides detailed guidelines for shipping hazardous materials.

4.5 Each sample cooler should contain a separate COC form documenting only the samples being transported within that cooler. This practice maintains the COC for all samples in case of a lost or misrouted shipment. In addition, this practice helps prevent potential confusion when the samples are received and logged at the laboratory.

4.6 If shipping samples on a Friday for next-day delivery, inform the laboratory that the samples will be arriving on Saturday. Confirm the receiving address for the Saturday delivery, which may be different than the receiving address for sample delivery during weekdays. Note that some commercial shippers may also require a special air bill for Saturday delivery or “Saturday Delivery” labels on the shipping cooler.

4.7 If shipping samples with expedited turnaround times or analytical holding times less than seven days, e.g., unpreserved water samples for VOC analysis, contact the laboratory on the day that the samples are shipped and remind or inform them of the expedited turnaround times. Also, be aware that the holding times for some analytical methods are so short that the samples must be delivered to the laboratory via Ohio EPA staff or courier on the same day. For example, SW- 846 Method 7196A for hexavalent chromium in ground water or surface water has a 24-hour holding time. If in doubt about sample holding time requirements, contact SIFU personnel for assistance.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 COC forms
6.2 Clear tape (for securing and protecting completed labels on sample containers)
6.3 Custody seals
6.4 Custody tape
6.5 Duct tape (for packaging sample containers)
6.6 Environmental samples (in appropriate jars/containers) to be shipped
6.7 Large heavy-duty plastic bags (for use as sample cooler liners)
6.8 Ice
6.9 Knife or scissors
6.10 Packing materials (*e.g.,* bubble wrap, foam molds, laboratory-supplied materials)
6.11 Pens and markers, preferably waterproof
6.12 Sealable plastic bags (pint to two-gallon size for sample containers, COC forms, and/or ice)
6.13 Shipping coolers
6.14 Shipping (mailing) forms for air or ground delivery (unless samples are being delivered directly to the laboratory by an Ohio EPA staff member or courier)
6.15 Shipping labels for package handling (including but not necessarily limited to “Fragile,” “This Side Up,” and “Do Not Drop”)
6.16 Shipping/Packaging tape (for sealing shipping coolers)
6.17 Temperature blanks (if required by the laboratory)
6.18 Trip blanks (if the shipping cooler includes samples for VOC analysis)

7.0 Procedures

7.1 Sample custody and COC forms

7.1.1 To maintain proper custody, keep samples in sight or in a secured location, e.g., a locked vehicle or room. If samples are to be stored overnight prior to shipment to the laboratory, if storage location is not secure then the sample cooler is to be sealed with custody tape/labels to prevent tampering.

7.1.2 District office personnel may leave samples at the Groveport Field Office in the custody of SIFU or other Ohio EPA field staff prior to delivery to a laboratory.

7.1.3 Use only blue or black ink to complete COC forms.

7.1.4 If samples are being shipped to a state contract laboratory, contact SIFU, a District Office Laboratory Coordinator, or the contract laboratory for specific instructions on completing the contract laboratory's COC form.

7.1.5 If submitting samples to the Ohio EPA Division of Environmental Services (DES) laboratory, use DES COC forms. Contact DES for specific instructions on completing their COC forms.

7.1.6 Prior to shipping a sample cooler, review the COC form for accuracy and ensure that each sample being shipped within that cooler is properly documented on the COC form. Never include samples being shipped in other coolers. If required, include the air bill or shipping tracking number on the COC form.

7.1.7 Sign and date each COC form.

7.2 Sample handling (packaging and shipping)

7.2.1 Inspect the sample containers to be shipped for loose or improper fitting lids, damaged lids, and incomplete or illegible sample labels. Document such problems as appropriate and correct if possible. If correction is not possible, inform the District Office Site Coordinator and the SIFU Sampling Team Leader or SIFU Laboratory Coordinator.

7.2.2 Use clear tape to cover and protect the labels on sample containers.

7.2.3 Wrap glass sample containers in bubble wrap and/or use other protective shipping materials such as foam molds to help prevent container breakage.

7.2.4 Place glass sample containers in sealable plastic bags to contain the contents and prevent potential cross contamination of other samples if broken in transit.

7.2.5 Seal any drainage holes in the shipping cooler. Use only clean, dry shipping coolers.

7.2.6 Place two large heavy-duty plastic bags in the shipping cooler as liners, one inside of the other.

7.2.7 Place sample containers upright inside the inner bag. Include a trip blank if samples are being submitted for VOC analysis and a temperature blank if required by the laboratory. Place larger, heavier containers on the bottom of the shipping cooler and smaller, lighter sample containers at the top. Use additional packing material between containers to help prevent breakage. Do not overfill the cooler with sample containers and packing material. Allow at least 25% of the cooler volume for ice.

7.2.8 Twist the inner bag (containing samples) closed while removing excess air volume. Seal the inner bag using duct tape.

7.2.9 Fill the available area between the inner bag and outer bag with fresh ice.

7.2.10 Twist the outer bag closed and seal it using duct tape.

7.2.11 As an alternative to Steps 7.2.6 through 7.2.10 for small-sized or medium-sized shipping coolers, place all sample containers in sealable plastic bags and make ice packs using one-gallon or two-gallon sealable plastic bags. The ice should be double bagged to help prevent leakage into the cooler.

7.2.12 If shipping by common carrier, place the completed COC form in a sealable plastic bag and either tape it to the top of the sample cooler or place it in the cooler on top of the bagged sample containers. Otherwise, give the COC to the laboratory courier or hand deliver it to the laboratory with the samples. (Remember to include the air bill or shipping tracking number on the COC form if required).

7.2.13 Check that the cooler lid closes properly. If it does not, remove some ice and/or reconfigure the sample containers (repeat Steps 7.2.6 through 7.2.11 as necessary).

7.2.14 Affix a signed and dated custody seal to the closed cooler. Protect the custody seal by covering it with clear tape.

7.2.15 Secure the lid by circling the cooler and lid several times with shipping/packing tape. For small to medium coolers, tape the left and right sides. For large coolers, tape the midsection of the cooler in addition to the right and left sides.

7.2.16 Affix “Do Not Drop,” “Fragile,” and “This Side Up” stickers, and any other needed shipping stickers to the sides or top of the cooler.

7.2.17 Complete the air bill and/or other shipping forms. If shipping overnight on a Friday, remember to check the “Saturday Delivery” box on the form. Never check “Shipper Release” or “Signature Release” boxes. Unless otherwise instructed by the SIFU Laboratory Coordinator, do not declare a value for the cooler and always bill the receiver (the laboratory).

7.2.18 If shipping by common carrier, attach the air bill and/or other shipping forms on the top of the cooler and ship same-day or next-day delivery.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Check the completed COC form for errors or omissions by comparing the sample cooler contents to the form prior to sealing the cooler for shipment.

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation

Hazardous Material Transportation Act, U.S. Code of Federal Regulations, 49 CFR 170-179

International Air Transportation Association, Dangerous Goods List, Section 4.2

Ohio Administrative Code OAC 3745-51-04(D)

U.S. EPA, 2014, Sampler’s Guide, Contract Laboratory Program Guidance for Field Samplers, OSWER 9200.2-147, EPA 540-R-014-013

Sampling Equipment Decontamination
FSOP 1.6 (May 12, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure describes standard practices used by the Division of Environmental Response and Revitalization (DERR) for the decontamination of sampling equipment. All equipment used to collect environmental samples should be decontaminated prior to use to avoid cross-contamination of samples, sampling personnel, or other environmental media.

1.2 When collecting soil samples, stainless steel pans and spoons should be used. Disposable pans and spoons should be used when heavy contamination is present. Non-disposable sampling equipment must be decontaminated either on site or preferably in a fixed-base facility such as the Ohio EPA Groveport Field Office. Use of a fixed-base facility is logistically easier, especially with regard to the containment and disposal of decontamination fluids.

1.3 Solvents and acids should not be used for equipment decontamination.

1.4 Equipment that cannot be effectively decontaminated using the procedures described in this FSOP must be disposed of properly in accordance with federal, state, and local requirements. Refer to FSOP 1.7, Investigation-Derived Wastes and Materials.

1.5 The procedures described herein are the minimum level of effort that should be expended for equipment decontamination.

1.6 This procedure applies to the decontamination of sampling equipment only. It does not apply to the decontamination of personnel, personal protective equipment (PPE), field monitoring instruments, or vehicles.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

Proper PPE should be worn when performing decontamination procedures to avoid exposure to contaminated media, or decontamination fluids. PPE typically includes but is not limited to protective gloves, safety glasses or goggles, and protective coveralls.

4.0 Procedure Cautions

4.1 Equipment decontamination generates one or more of the following materials:

- Residual soil or sediment
- Wash and rinse water
- Materials used during the decontamination process (*e.g.,* paper towels or plastic sheets)
- Personal protective equipment during the decontamination process (*e.g.,* gloves or coveralls)

Generally, these materials are not hazardous and may be disposed of as non-hazardous wastes; refer to FSOP 1.7, Investigation-Derived Wastes and Materials. However, if hazardous materials or highly elevated concentrations of hazardous substances are encountered during sampling activities, the associated decontamination wastes could be hazardous wastes. To ensure proper disposal, such decontamination wastes need to be characterized in accordance with Ohio Administrative Code (OAC) 3745-51-20 through -24 (Characteristic Hazardous Wastes) or (OAC) 3745-51-30 through -35 (Listed Hazardous Wastes) to determine whether they are hazardous.

4.2 If an equipment blank is needed to evaluate the effectiveness of decontamination procedures, the field team leader should request that the blank be collected at an undisclosed time. This practice helps avoid the introduction of bias into the decontamination procedures based on anticipation of the equipment blank.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Appropriate PPE
6.2 ASTM Type II, distilled, or reverse osmosis water
6.3 Detergent (non-phosphate detergent is recommended for field decontamination)
6.4 Clean cloths, paper towels, or disposable wipes
6.5 Brushes
6.6 Spray bottle
6.7 Buckets or pans
6.8 Plastic containers with resealable lids (to contain decontamination fluids in the field)
6.9 Plastic sheets (to cover the ground during field decontamination procedures)
6.10 Aluminum foil or sealable plastic bags (to contain decontaminated equipment)

7.0 Procedures

7.1 Decontamination procedures depend on anticipated field conditions and the nature of the investigation. Equipment may be decontaminated in the field or at a fixed-base facility (*e.g.,* Ohio EPA's Groveport Field Office). Decisions regarding the scope and location of equipment decontamination should be made during the preparation of the project work plan and in consultation with the Site Investigation Field Unit (SIFU).

7.2 Fixed-base facility decontamination procedures:

7.2.1 Remove excess soil or sediment contamination from the equipment while in the field. Remove as much residue as practically possible to minimize investigation derived waste and to keep the wash water as clean as possible.

7.2.2 Disassemble the equipment if necessary, for proper decontamination.

7.2.3 Wash the equipment with tap water and detergent.

7.2.4 Rinse the equipment with tap water.

7.2.5 Rinse the equipment a second time with ASTM Type II, distilled, or reverse osmosis water.

7.2.6 Allow the equipment to air dry or dry it with a clean cloth or paper towel.

7.2.7 If the equipment is not to be used immediately, wrap in aluminum foil or place in sealable plastic bags.

7.3 Field decontamination procedures:

7.3.1 Set up the decontamination area away from potential sources of dust, vapors, or other contaminants. Decontamination supplies should be placed on a clean sheet of plastic to prevent direct contact with the ground or other surfaces that may contain contaminants.

7.3.2 Remove excess soil or sediment contamination from the equipment.

7.3.3 Disassemble the equipment, if necessary, for proper decontamination.

7.3.4 Wash the equipment with ASTM Type II, distilled, or reverse osmosis water and detergent.

7.3.5 Rinse the equipment with ASTM Type II, distilled, or reverse osmosis water.

7.3.6 Dry the equipment with a clean cloth or paper towel.

7.3.7 If the equipment is not to be used immediately, wrap it in aluminum foil or place in a sealable plastic bag

7.4 All waste materials generated during equipment decontamination including rinse water (See Section 4.1) must be containerized and evaluated for proper disposal, regardless of whether the decontaminated equipment was used to sample media known to contain hazardous substances or hazardous wastes.

7.5 Waste materials generated during equipment decontamination are investigation derived waste and should be disposed of in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Decontamination.

9.0 Quality Assurance and Quality Control

An equipment blank may be required to evaluate the effectiveness of decontamination procedures.

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Decontamination

FSOP 1.7, Investigation Derived Wastes

Ohio Administrative Code 3745-51-20 through -24

Ohio Administrative Code 3745-51-30 through -35

Investigation Derived Waste
FSOP 1.7 (May 21, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Investigation derived waste (IDW) is a generic term used to describe a variety of waste materials generated during sampling and other site assessment activities. IDW typically includes environmental media such as soil boring cores or monitoring well purge water, used disposable sampling equipment, used personal protective equipment (PPE), decontamination fluids and used packaging materials. It may include a variety of waste materials regulated for disposal under federal, state or local regulations, including municipal solid waste (MSW), industrial and residual solid waste, infectious waste, construction and demolition debris, hazardous waste, petroleum waste, coal mine wastes, lime mining wastes, low-level radioactive wastes or wastes regulated by the Toxic Substances Control Act (TSCA) including polychlorinated biphenyls (PCBs) or asbestos-containing materials (ACM).

1.2 Management and disposal of IDW generated during DERR site assessments will be consistent with U.S. EPA guidance (see References below) and meet all applicable regulations. In the event that petroleum, hazardous, TSCA, infectious or low-level radioactive IDW is generated, DERR will comply with the regulations governing the management and disposal of these solid and/or liquid wastes. If IDW is non-petroleum, non-hazardous, non-TSCA, non-infectious and non-radioactive, DERR will manage and dispose of the solid materials as municipal solid waste regardless of whether or not the IDW is an MSW-regulated waste, e.g., unwanted soil cores or coal mine waste. DERR will manage and dispose of non-petroleum, non-hazardous, non-TSCA, non-infectious and non-radioactive fluids as sanitary wastewater.

1.3 When evaluating whether IDW may be petroleum, hazardous, TSCA, infectious or radioactive, DERR field personnel are expected to use the following resources, if available, before or during field work activities:

- Knowledge of site history, industrial processes, material handling and waste releases or disposal practices
- Field evidence (*e.g.,* visual appearance of contamination or waste materials; labeling, or type of discarded containers, etc.)
- Field screening instrument (*e.g.,* photoionization detector) results

These criteria represent the best information that is readily available to DERR management and staff for the evaluation of IDW regulatory status.
Therefore, use of these criteria constitutes both a good faith effort and due diligence on the part of DERR to properly manage (contain, handle, store and/or transport) and/or dispose of IDW.

1.4 This FSOP is applicable to site assessment activities conducted by DERR. It does not apply to the following situations:

- Management or disposal of remediation wastes (*e.g.,* removal of soil or ground water as a site cleanup remedy)
- Management or disposal of IDW generated from site assessment activities performed by Ohio EPA level-of-effort (LOE) contractors
- Management or disposal of IDW generated from emergency response activities
- Management or disposal of ACM - If IDW is known or suspected to include ACM, contact and defer to the Ohio EPA Division of Air Pollution Control for assistance with IDW management and disposal.
- Management or disposal of infectious wastes - If infectious wastes (e.g., medical waste containers with syringes, needles and blood-contaminated waste materials) are encountered during sampling or other site assessment activities, contact and defer to the Ohio EPA Division of Materials and Waste Management (DMWM) for assistance with IDW management and disposal. Attachment A includes a detailed description of the variety of materials that are defined as infectious waste.
- Management or disposal of low-level radioactive wastes - If low-level radioactive IDW is generated during site assessment activities, contact and defer to the Ohio Department of Health (ODH) for assistance with IDW management and disposal.

2.0 Definitions

2.1 For the purposes of the FSOP, **“non-hazardous waste”** means waste which consists of MSW, industrial or residual solid wastes, construction and demolition debris, mining wastes or other unwanted materials that are not defined as regulatory wastes such as soil or sediment, and is not petroleum, hazardous, TSCA-regulated, infectious or radioactive.

2.2 For the purposes of this FSOP, “**hazardous waste**” means any waste that contains or is otherwise contaminated with a listed hazardous waste at any concentration (including previously disposed or spilled hazardous waste) or that exhibits a characteristic of hazardous waste.

2.3 Soil is considered a regulated waste only when contaminated by hazardous waste, petroleum waste or other regulated wastes.

2.4 Refer to Attachment A for regulatory definitions of wastes and associated materials.

3.0 Health and Safety Considerations

3.1 IDW management (handling and storage) and disposal activities must be protective of human health, safety and the environment and must be performed in accordance with all applicable regulations.

3.2 Use appropriate PPE when handling IDW. Refer to the site-specific work plan (SSWP) and health and safety plan (HASP) for required PPE.

3.3 Conduct air monitoring as required when managing IDW. Refer to the SSWP for air monitoring applicability and to Table 1 of FSOP 1.1, Initial Site Entry for air monitoring action levels.

3.4 Exercise extra caution at landfills, construction and demolition debris facilities, or other waste disposal areas that may contain unique hazards such as sharps, medical wastes, chemical containers or ACM.

3.5 Always assume that infectious wastes encountered during site assessment activities are untreated, even within the disposal area of an MSW landfill facility.

4.0 Procedure Cautions

4.1 Every attempt should be made to seek a suitable location for disposal of decontamination water or ground water from monitoring wells. Local publicly owned treatment works (POTW) facilities often will accept purge water but may require analytical results before disposal can occur. On-site treatment facilities may often be a suitable option for disposing of water. If a small quantity (<15 gallons) of water is generated and no other options are available, water may occasionally be transported back to the Ohio EPA's Groveport Field Office or an Ohio EPA district office for disposal.

4.2 If ground water is known or assumed (with reasonable certainty) to be uncontaminated, then it may be suitable to dispose of the water on the ground.

4.3 Never dispose of monitoring well purge water or decontamination fluids on the ground if the contaminants or concentrations are unknown. Waste fluids must be containerized and transported to an appropriate disposal facility unless an alternative disposal option is available at the site or the facility being investigated, or the fluids must be stored on site until appropriate disposal can be arranged.

4.4 IDW containing soil and/or debris must be transported back to the Ohio EPA's Groveport Field Office or an Ohio EPA district office for disposal unless an alternative disposal option is available at the site or facility being investigated.

4.5 Samples may be excluded from hazardous waste regulations during transport to the laboratory and back to the sample collector, during storage in the laboratory before and after analysis, and during storage for evidence in enforcement cases. See OAC rule 3745-51-04

5.0 Equipment and Supplies

5.1 PPE
5.2 Heavy duty plastic bags
5.3 Sealable plastic buckets or other containers suitable for containing fluids
5.4 Department of Transportation (DOT) approved drums
5.5 Tools to open and close drums
5.6 Drum or container labels
5.7 Drum dolly or hoist
5.8 Duct tape
5.9 Plastic sheeting

6.0 Procedures

6.1 General Procedures for IDW Management and Disposal

6.1.1 Before performing field work, review the site history and available field screening, sampling, and analytical data or records of previous waste listing classification to evaluate the types of wastes and contamination likely to be encountered. Include this information in the SSWP, especially if the site is subject to the Resource Conservation and Recovery Act (RCRA) hazardous waste regulations. Use this information to anticipate the types of IDW likely to be generated during sampling and other site assessment activities. Evaluate management and disposal options based on the types and amounts of IDW likely to be generated.

6.1.2 Use sampling and other site assessment procedures that minimize the amount of IDW generated during sampling and investigation activities whenever possible. For example, using low-flow sampling techniques to collect ground water samples typically generates less monitoring well purge water than using bailers to collect ground water samples.

6.1.3 Evaluate if the IDW may be petroleum, hazardous, TSCA-regulated, infectious or radioactive based on the following site and field data:

- Knowledge of site history, industrial processes, material handling and waste releases or disposal practices
- Field evidence (*e.g.,* visual appearance of contamination or waste materials; labeling, or type of discarded containers, etc.)
- Field screening instrument results

These criteria represent the best information that is readily available to DERR management and staff for the evaluation of IDW regulatory status. Therefore, use of these criteria constitutes both a good faith effort and due diligence on the part of DERR to properly manage and/or dispose of IDW.

6.1.4 If IDW is suspected to be hazardous (based on good faith effort and due diligence), containerize, label, date, and retain the waste material until results of more definitive testing and evaluation are available to determine the appropriate disposal procedures.

6.1.5 If IDW is suspected to be hazardous due to mixture with or contamination from a listed hazardous waste, a site-specific contained-in decision may be appropriate for waste management. To make a contained-in decision, a project-specific tasking request will be submitted to the DERR Engineering & Risk Assessment Support Unit (ERAS) supervisor following the Contained-In Request Procedure (Attachment C) and consult with the DERR RCRA manager as necessary.

6.1.6 As a general work practice, manage and dispose of disposable sampling equipment and PPE in the same manner as IDW generated from the media being sampled or otherwise investigated.

6.1.7 If permissible and protective of human health and the environment, use facility equipment and procedures for containerizing and disposing non-hazardous IDW.

6.2 Management and Disposal of Non-Hazardous Wastes

6.2.1 Manage and dispose of IDW solids that are not regulated as petroleum, hazardous, TSCA, infectious, or radioactive waste as MSW. Such non-hazardous IDW may include, but is not limited to the following materials:

- Used PPE, used disposable sampling equipment and used packaging materials
- Soil (soil is not a regulated waste unless contaminated by hazardous waste, petroleum waste or other regulated wastes)
- Construction and demolition debris
- Sediment containing coal mining or lime mining wastes

6.2.2 Manage monitoring well purge water, decontamination fluids and other IDW liquids that are not regulated as petroleum, hazardous, TSCA-regulated, infectious, or radioactive waste as sanitary wastewater that can be disposed of in a POTW.

6.2.3 Containerize non-hazardous IDW solids in heavy duty plastic bags, buckets, other containers or drums.

6.2.4 Containerize non-hazardous IDW liquids in sealable buckets, other sealable containers or drums.

6.2.5 Dispose of non-hazardous IDW solids as MSW in a solid waste dumpster. Dispose of non-hazardous IDW liquids in the POTW as sanitary wastewater with permission from the POTW.

6.2.6 If permissible and protective of human health and the environment, solid or liquid non-hazardous IDW may be disposed of as MSW or sanitary wastewater at the site or facility being investigated.

6.2.7 Stabilize IDW consisting of semi-solid or sludge-like materials (*e.g.,* contaminated sediment) with granular bentonite or other inert absorbent material before disposing of it as solid waste. (Sludge-like materials should not be disposed of as solid waste unless it can pass the Paint Filter Liquids Test, SW-846 Method 9095).

6.3 Management and Disposal of Petroleum Contaminated IDW

6.3.1 If petroleum contaminated IDW solids are not visibly contaminated with free product, dispose of the IDW as MSW unless it is known or suspected to be a characteristic hazardous waste (if so, refer to Sections 6.3.2 and 6.4 below). U.S. EPA 2009 (Hazardous Waste Characteristics, A User-Friendly Reference Document) provides guidance on the RCRA hazardous waste characteristic regulations.

6.3.2 If petroleum contaminated IDW solids are visibly contaminated with free product, consult with the local MSW disposal facility regarding required pre-disposal testing. Required testing may include the Toxicity Characteristic Leaching Procedure (TCLP), SW-846 Method 1311 for benzene and other volatile petroleum constituents, Ignitability and Ignitability of Solids, SW-846 Methods 1010A, 1020B and 1030 or the Paint Filter Liquids Test, SW-846 Method 9095.

6.3.3 If IDW liquid consisting of free-phase petroleum product and water is generated during a site assessment (*e.g.,* monitoring well purge water containing free-phase gasoline), contact and defer to the Office of Emergency Response (OER) Level-of-Effort (LOE) Coordinator for assistance with IDW management and disposal. IDW liquids containing free-phase petroleum products may be characteristic hazardous wastes (refer to Section 6.4)

6.4 Management and Disposal of Hazardous IDW

6.4.1 If IDW is suspected to be hazardous based on the three criteria discussed in Section 6.1.3 or known to contain listed hazardous waste, contact and defer to the OER LOE Coordinator or the DERR RCRA manager for assistance with IDW management and disposal. Hazardous Waste Characteristics, A User-Friendly Reference Document (U.S. EPA 2009) provides guidance on the RCRA hazardous waste characteristic regulations.

6.4.2 When IDW is generated at a site that is not secured, or if potential spills or releases from the IDW containers exist, IDW solids or liquids suspected to be characteristic hazardous wastes based on toxicity, ignitability, or corrosivity may be temporarily stored in a secured location at the Groveport Field Office pending the results of testing (TCLP, SW-846 Method 1311; Ignitability SW-846 Methods 1010A, 1020B and (1030 the test results for this method cannot be used to directly classify a waste as a D001 ignitable hazardous waste); and appropriate corrosivity testing such as SW- 846 Method 9040C or 9041A). Wastes that are suspected or anticipated to exhibit the characteristic of reactivity may be too dangerous for DERR staff to handle, transport or store. Contact and defer to the OER LOE Coordinator for guidance on managing potentially reactive IDW.

6.4.3 If soil samples are managed and disposed as hazardous waste, then any grossly contaminated disposable sampling equipment and PPE used to collect and handle to soil cores will be managed and disposed as hazardous waste.

6.5 Management and Disposal of Toxic Substances Control Act IDW

6.5.1 Wastes regulated under the TSCA include polychlorinated biphenyls (PCBs) and asbestos-containing materials (ACM).

6.5.2 IDW consisting of PCB-containing soil, sediment, or soil-like wastes may be temporarily stored at the Groveport Field Office pending the results of PCB analysis. Contact and defer to the OER LOE Coordinator for assistance with IDW management and disposal.

7.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

8.0 Attachments

Attachment A, Regulatory Definitions for Wastes and Associated Materials

Attachment B, Contained-In Decision Request Procedure

Attachment C, Maximum Concentrations of Contaminants for the Toxicity Characteristic

9.0 References and Regulatory Contact Information

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

OAC 1301:7-9, BUSTR Regulations

OAC 1501:13-1, ODNR Coal Mining Regulations

OAC 1501:14-1, ODNR Lime Mining Regulations

OAC 3701:1-38, ODH General Radiation Protection Standards for Sources of Radiation

OAC 3745-20, Ohio EPA Asbestos Emission Control Regulations

OAC 3745-27, Ohio EPA Solid and Infectious Waste Regulations

OAC 3745-29, Ohio EPA Industrial Waste Regulations

OAC 3745-30, Ohio EPA Residual Waste Regulations

OAC 3745-50 through 52, Ohio EPA Hazardous Waste Management Standards

OAC 3745-400 Ohio EPA Construction and Demolition Debris Regulations

Ohio EPA Division of Air Pollution Control: (614) 644-2270, -2271 or -2272

Ohio EPA Division of Materials and Waste Management: (614) 644-2621

Ohio EPA Groveport Field Office: (614) 836-8800

OER LOE Coordinator: (614) 836-8761

DERR Site Field Investigation Unit: (614) 644-2305

Ohio Department of Health Bureau of Radiation Protection: (614) 644-2727 (main) or (614) 722- 7221 (for emergencies)

SW-846 Methods 1010A, 1020B and 1030, Ignitability of Solids

SW-846 Method 1311, Toxicity Characteristic Leaching Procedure

SW-846 9040C, pH Electrometric Measurement

SW-846 Method 9095, Paint Filter Liquids Test

U.S. EPA, 2009, Hazardous Waste Characteristics, A User-Friendly Reference Document: Materials Recovery and Waste Management Division, Office of Resource Conservation and Recovery

U.S. EPA, January 1992, Guide to Management of Investigation-Derived Wastes: Office of Solid Waste and Emergency Response, 9345.3-03FS

U.S. EPA, July 3, 2014, Management of Investigation-Derived Waste (SESD Operating Procedure): U.S. EPA Region 4, Science and Ecosystem Support Division. SESDPROC-202-R3

Toxic Substances Control Act, 15 U.S.C. §2601 et seq. (1976) (*refer to 40 CFR 761 U.S. EPA PCB Regulations*)

ATTACHMENT A

Regulatory Definitions for Wastes and Associated Materials

Asbestos-Containing Waste Materials [OAC 3745-20-01(B)(4)]

"Asbestos-containing waste materials" means mill tailings or any waste that contains commercial asbestos and is generated by a source subject to the provisions of this chapter. This term includes filters from control devices, friable asbestos-containing material, and bags or other similar packaging contaminated with commercial asbestos. As applied to demolition and renovation operations, this term also includes regulated asbestos-containing material waste and materials contaminated with asbestos including disposable equipment and clothing.

Clean Hard Fill [OAC 3745-400-01(E)]

"Clean hard fill" means construction and demolition debris which consists only of reinforced or nonreinforced concrete, asphalt concrete, brick, block, tile, and/or stone which can be reutilized as construction material. Brick in clean hard fill includes but is not limited to refractory brick and mortar. Clean hard fill does not include materials contaminated with hazardous wastes, solid wastes, or infectious wastes.

Coal Mine Waste [OAC 1501:13-1-02(W)]

“Coal mine waste” means coal processing waste and underground development waste.

Construction and Demolition Debris [OAC 3745-400-01(F)]

"Construction and demolition debris" or "debris" means those materials resulting from the alteration, construction, destruction, rehabilitation, or repair of any manmade physical structure, including, without limitation, houses, buildings, industrial or commercial facilities, or roadways. "Construction and demolition debris" does not include materials identified or listed as solid wastes, infectious wastes, or hazardous wastes pursuant to Chapter 3734 of the Revised Code and rules adopted under it; or materials from mining operations, nontoxic fly ash, spent nontoxic foundry sand, and slag; or reinforced or nonreinforced concrete, asphalt, building or paving brick, or building or paving stone that is stored for a period of less than two years for recycling into a usable construction material.

For the purpose of this definition, "materials resulting from the alteration, construction, destruction, rehabilitation, or repair of any manmade physical structure," are those structural and functional materials comprising the structure and surrounding site improvements, such as brick, concrete and other masonry materials, stone, glass, wall coverings, plaster, drywall, framing and finishing lumber, roofing materials, plumbing fixtures, heating equipment, electrical wiring and components containing no hazardous fluids or refrigerants, insulation, wall-to-wall carpeting, asphaltic substances, metals incidental to any of the above, and weathered railroad ties and utility poles.

"Materials resulting from the alteration, construction, destruction, rehabilitation, or repair" do not include materials whose removal has been required prior to demolition, and materials which are otherwise contained within or exist outside the structure such as solid wastes, yard wastes, furniture, and appliances. Also excluded in all cases are liquids including containerized or bulk liquids, fuel tanks, drums and other closed or filled containers, tires, and batteries.

Hazardous Waste [OAC 3745-50-10(A)(54)]

"Hazardous waste" means a hazardous waste as defined in rule 3745-51-03 of the Administrative Code. (*When attempting to determine whether or not a material is a hazardous waste, please request assistance from the Division of Environmental Response and Revitalization. The regulatory definition of hazardous waste is complex and includes numerous exclusions per OAC 3745-51-04. Accurate characterization of hazardous waste requires specialized knowledge of the hazardous waste rules.*)

Industrial Solid Waste [OAC 3745-29-01(A)]

"Industrial solid waste" or "industrial waste" means a type of solid waste generated by manufacturing or industrial operations and includes, but is not limited to, solid waste resulting from the following manufacturing processes: electric power generation; fertilizer/agricultural chemicals; food and food-related products/by-products; inorganic chemicals; iron and steel manufacturing; leather and leather products; nonferrous metals manufacturing; plastics and resins manufacturing; pulp and paper industry; rubber and miscellaneous plastic products; stone, glass, clay and concrete products; textile manufacturing; and transportation equipment. "Industrial solid waste" does not include solid wastes generated by commercial, agricultural, or community operations. Industrial solid wastes may be disposed in a licensed sanitary landfill facility, a licensed industrial waste landfill facility, or in a licensed residual waste landfill facility, provided that the class number for the residual waste landfill facility is not greater than the class number necessary for that residual waste as determined by the residual waste characterization and landfill classification in accordance with rules 3745-30-03 and 3745-30-04 of the Administrative Code.

Industrial Waste [ORC 6111.01(C)]

“Industrial waste” means any liquid, gaseous, or solid waste substance resulting from any process of industry, manufacture, trade, or business, or from the development, processing, or recovery of any natural resource, together with such sewage as is present.

Infectious Waste [OAC 3745-27-01(I)(6)]

"Infectious wastes" includes all of the following substances or categories of substances:

(a) Cultures and stocks of infectious agents and associated biologicals, including, without limitation, specimen cultures, cultures and stocks of infectious agents, wastes from production of biologicals, and discarded live and attenuated vaccines.

(b) Laboratory wastes that were, or are likely to have been, in contact with infectious agents that may present a substantial threat to public health if improperly managed.

(c) Pathological wastes, including, without limitation, human and animal tissues, organs, and body parts, and body fluids and excreta that are contaminated with or are likely to be contaminated with infectious agents, removed or obtained during surgery or autopsy or for diagnostic evaluation, provided that, with regard to pathological wastes from animals, the animals have or are likely to have been exposed to a zoonotic or infectious agent.

(d) Waste materials from the rooms of humans, or the enclosures of animals, that have been isolated because of diagnosed communicable disease that are likely to transmit infectious agents. Also included are waste materials from the rooms of patients who have been placed on blood and body fluid precautions under the universal precaution system established by the "Centers for Disease Control" in the public health service of the United States department of health and human services, if specific wastes generated under the universal precautions system have been identified as infectious wastes by rules referred to in paragraph (I)(6)(h) of this rule.

(e) Human and animal blood specimens and blood products that are being disposed of, provided that, with regard to blood specimens and blood products from animals, the animals were or are likely to have been exposed to a zoonotic or infectious agent. "Blood products" does not include patient care waste such as bandages or disposable gowns that are lightly soiled with blood or other body fluids, unless such wastes are soiled to the extent that the generator of the wastes determines that they should be managed as infectious waste.

(f) Contaminated carcasses, body parts, and bedding of animals that were intentionally exposed to infectious agents from zoonotic or human diseases during research, production of biologicals, or testing of pharmaceuticals, and carcasses and bedding of animals otherwise infected by zoonotic or infectious agents that may present a substantial threat to public health if improperly managed.

(g) Sharp wastes used in the treatment, diagnosis, or inoculation of human beings or animals or that have, or are likely to have, come in contact with infectious agents in medical, research, or industrial laboratories, including, without limitation, hypodermic needles and syringes, scalpel blades, and glass articles that have been broken. Such wastes are hereinafter in this chapter referred to as "sharp infectious waste" or "sharps."

(h) Any other waste materials generated in the diagnosis, treatment, or immunization of human beings or animals, in research pertaining thereto, or in the production of testing of biologicals, that the public health council created in section 3701.33 of the Revised Code, by rules adopted in accordance with Chapter 119. of the Revised Code, identifies as infectious wastes after determining that the wastes present a substantial threat to human health when improperly managed because they are contaminated with, or are likely to be contaminated with, infectious agents.

(i) Any other waste materials the generator designates as infectious waste.

Lime Mining Waste [OAC 1501:14-1-01(FF)]

“Lime Mining Wastes” means residual solid or semisolid materials generated from lime or limestone mining and processing operations, including, without limitation, lime kiln dust, scrubber sludge from kiln operations, lime or limestone materials not meeting product specification, lime hydrating materials, and other lime or limestone mining, processing, or calcining materials associated with lime or limestone mining or processing. “Lime Mining Wastes” does not include materials generated for the manufacture of cement.

Low-Level Radioactive Waste [OAC 3701:1-38-01(A)(175)]

"Waste" means those low-level radioactive wastes containing source, special nuclear, or byproduct material that are acceptable for disposal in a land disposal facility. For the purposes of this definition, low-level radioactive waste means radioactive waste not classified as high-level radioactive waste, transuranic waste, spent nuclear fuel, or byproduct material as defined in paragraphs (A)(26)(b), (A)(26)(c), and (A)(26)(d) of this rule.

Other Wastes [ORC 6111.01(D)]

“Other wastes” means garbage, refuse, decayed wood, sawdust, shavings, bark, and other wood debris, lime, sand, ashes, offal, night soil, oil, tar, coal dust, dredged or fill material, or silt, other substances that are not sewage, sludge, sludge materials, or industrial waste, and any other “pollutants” or “toxic pollutants” as defined in the Federal Water Pollution Control Act that are not sewage, sludge, sludge materials, or industrial waste.

Petroleum [OAC 1301:7-9-02(B)(44)]

“Petroleum” means petroleum, including crude oil or any fraction thereof that is a liquid at the temperature of sixty degrees Fahrenheit and the pressure of fourteen and seven-tenths pounds per square inch absolute. The term includes, without limitation, motor fuels, jet fuels, distillate fuel oils, residual fuel oils, lubricants, petroleum solvents, and used oils.

Petroleum Contaminated Soil [OAC 1301:7-9-16(B)(8)]

“Petroleum contaminated soil (PCS)” means soil that contains chemical(s) of concern in concentrations that exceed one or more of the re-use action levels in Table 1 found in paragraph (D)(1) of this rule and excludes soil defined as hazardous waste.

Residual Solid Waste [OAC 3745-30-01(B)]

"Residual solid waste" or "residual waste" is a type of solid waste and means:

(1) The following wastes generated by fuel burning operations which are regulated by rule 3745-17-10 of the Administrative Code and which burn as fuel primarily coal: air pollution control wastes, water pollution control wastes, and other wastes with similar characteristics which are approved by the director or his authorized representative.

(2) The following wastes generated from foundry operations: air pollution control dust, wastewater treatment plant sludge, unspent foundry sand, spent foundry sand, and other foundry wastes with similar characteristics which are approved by the director or his authorized representative.

(3) The following wastes generated from pulp and papermaking operations: wastewater treatment plant sludges, lime mud, lime grit, sawdust, wood chips, bark, hydropulper rejects, and other pulp and papermaking wastes with similar characteristics which are approved by the director or his authorized representative.

(4) The following wastes generated from steelmaking operations: air pollution control dust, wastewater treatment plant sludges, dust from steel processing and finishing operations, water softening sludge, flux material, and other steelmaking wastes with similar characteristics which are approved by the director or his authorized representative.

(5) The following wastes generated from gypsum processing plant operations: gypsum wallboard waste, paper surface preparation dust, wastewater treatment plant sludge, and other gypsum processing wastes with similar characteristics which are approved by the director or his authorized representative.

(6) The following wastes generated from lime processing operations: air pollution control dust and/or sludge, and other lime processing wastes with similar characteristics which are approved by the director or his authorized representative.

(7) The following wastes generated from Portland cement operations: air pollution control dust and other processing wastes with similar characteristics which are approved by the director or his authorized representative.

Other Wastes [ORC 6111.01(B)]

"Sewage" means any liquid waste containing sludge, sludge materials, or animal or vegetable matter in suspension or solution, and may include household wastes as commonly discharged from residences and from commercial, institutional, or similar facilities.

Other Wastes [ORC 6111.01(N)]

"Sludge" means sewage sludge and a solid, semi-solid, or liquid residue that is generated from an industrial wastewater treatment process and that is applied to land for agronomic benefit. "Sludge" does not include ash generated during the firing of sludge in a sludge incinerator, grit and screening generated during preliminary treatment of sewage in a treatment works, animal manure, residue generated during treatment of animal manure, or domestic septage.

Other Wastes [ORC 6111.01(O)]

"Sludge materials" means solid, semi-solid, or liquid materials derived from sludge and includes products from a treatment works that result from the treatment, blending, or composting of sludge.

Solid Waste [OAC 3745-27-01(S)(23)]

"Solid waste" means such unwanted residual solid or semisolid material, including but not limited to, garbage, scrap tires, combustible and noncombustible material, street dirt and debris, as results from industrial, commercial, agricultural, and community operations, excluding earth or material from construction, mining, or demolition operations, or other waste materials of the type that normally would be included in demolition debris, nontoxic fly ash and bottom ash, including at least ash that results from combustion of coal, biomass fuels, and ash that results from the combustion of coal in combination with scrap tires where scrap tires comprise not more than fifty percent of heat input in any month, spent nontoxic foundry sand, and slag and other substances that are not harmful or inimical to public health, and includes, but is not limited to, garbage, scrap tires, combustible and noncombustible material, street dirt, and debris. Solid waste does not include any material that is an infectious waste or a hazardous waste.

Toxic Waste [Toxic Substances Control Act, 15 U.S.C. §2601 et seq. (1976)]

The Toxic Substances Control Act (TSCA) addresses the production, importation, use, and disposal of specific chemicals including polychlorinated biphenyls (PCBs), asbestos, radon, and lead-based paint.

ATTACHMENT B

Maximum Concentrations of Contaminants for the Hazardous Waste Toxicity Characteristic (OAC 3745-51-24)

EPA Hazardous Waste Number	Contaminant	CAS[1] Number	Regulatory Level (mg/L)
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon Tetrachloride	56-23-5	0.5
D020	Chlordane	57-74-9	0.03
D021	Chlorobenzene	108-90-7	100.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D023	o-Cresol	95-48-7	200.0[3]
D024	m-Cresol	108-38-4	200.0[3]
D025	p-Cresol	106-44-5	200.0[3]
D026	Cresol	NA	200.0[3]
D016	2,4-D	94-75-7	10.0
D027	1,4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.13[2]
D012	Endrin	72-20-8	0.02
D031	Heptachlor (and its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	0.13[2]
D033	Hexachlorobutadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0

ATTACHMENT B

Maximum Concentrations of Contaminants for the Hazardous Waste Toxicity Characteristic (OAC 3745-51-24)			
EPA Hazardous Waste Number	**Contaminant**	**CAS[1] Number**	**Regulatory Level (mg/L)**
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	5.0[2]
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D040	Trichloroethylene	79-01-6	0.5
D041	2,4,5-Trichlorophenol	95-95-4	400.0
D042	2,4,6-Trichlorophenol	88-06-2	2.0
D017	2,4,5-TP (Silvex)	93-72-1	1.0
D043	Vinyl Chloride	75-01-4	0.2

Footnotes:

1. Chemical Abstracts Service number
2. Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.
3. If o-, m- and p-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200.0 mg/L.

ATTACHMENT C

Contained-In Decision Request Procedure

Background:

Listed hazardous waste and materials mixed with or contaminated by listed hazardous waste have special handling and management obligations that must be met by facilities, contractors and government officials, including Ohio EPA. A contained-in decision obtained through Ohio EPA's RCRA program allows media or debris contaminated by a listed hazardous waste to be managed as a non-hazardous waste if certain conditions are met. Contained-in decisions are made by using conservative risk assessment of the contaminated media or debris in a site-specific scenario to determine if the contaminated media or debris no longer requires management as a listed hazardous waste. If the contained-in decision is granted, the media or debris can be managed as non-hazardous waste following Ohio EPA's solid waste rules.

Contained-in decisions are primarily applicable to contaminated media, with media being defined as a naturally occurring material (e.g., soil, sediment, ground water and surface water). If media/contaminated media are mixed with other materials, generally Ohio EPA would describe this mixture as a contaminated media (as opposed to waste or debris) if it is made up of 50% or more of the naturally occurring media.

Hazardous debris includes items such as used personal protective equipment, used disposable sampling equipment, construction and demolition debris and other materials that are mixed or contaminated with listed hazardous waste. OAC rule 3745-270-45 essentially provides a contained-in decision for hazardous debris by allowing the hazardous waste generator to treat the debris using one of the treatment technologies provided in Table 1 of the rule (Alternative Treatment Standards for Hazardous Debris). Generally, the treatment technologies provide physical removal of any listed hazardous waste or media. Treated hazardous debris is no longer considered to be listed hazardous waste and is not required to be managed as hazardous waste unless the treatment was an immobilization technology. Be aware that any residue removed from the debris during treatment is still considered listed hazardous waste and needs to be handled accordingly.

Procedure:

Provide the following supporting information when requesting a contained-in decision for contaminated media. Please be as specific and detailed as possible.

1) Name
2) Division/district
3) Site name and location
4) Site history and information related to listed hazardous waste (listed hazardous waste codes, historical IDW management, etc.)
5) Current project and all potentially listed hazardous waste media or debris to be managed (expected volume of listed hazardous waste media or debris to be managed, planned management of media or debris, etc.)
6) Projected date of project
7) Expected concentrations in potentially listed hazardous waste media or debris to be managed

Forward the request and supporting information and submit the request to DERR ERAS and consult with the DERR RCRA manager as necessary to complete the request.

ODNR Well Construction Logs & Well Sealing Reports
FSOP 1.8 (May 14, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This FSOP is applicable to personnel who install or decommission monitoring wells, piezometers and borings used for ground water characterization. The Ohio Department of Natural Resources (ODNR), Division of Geological Survey requires that a well construction log be filed by anyone who constructs a well, and that a well sealing report be filed by anyone that seals a well.

1.2 Well construction logs ("well log and drilling report" forms) for each well must be completed and filed with the ODNR within 30 days after the installation of the well in accordance with Ohio Revised Code (ORC) 1521.05(B). ODNR well logs must be filed for all permanent or temporary monitoring wells and piezometers. Additionally, well logs must be filed for any boring used to collect a ground water sample when soil/geology is characterized for an aquifer or saturated zone.

1.3 Well casing materials do not have to be installed in the borehole to meet the definition of a well (*e.g.*, a boring used for the collection of a grab ground water sample from the open borehole is considered a well for purposes of filing a well construction log). Well construction logs, however, do not have to be filed for soil borings used solely to characterize soil or obtain soil samples or soil borings less than six feet deep. Refer to the ODNR, Division of Soil and Water Resources Fact Sheet 93-23, *When Does a Well Log Need to be Filed?* (attached).

1.4 Well sealing reports must be completed and filed with the ODNR within 30 days after the completion of the sealing of the well in accordance with ORC 1521.05(C). Well sealing reports must be filed for any well or boring that requires a well construction log to be filed. Refer to the ODNR, Division of Soil and Water Resources Fact Sheet 92-5, *State of Ohio Water Well Sealing Regulations* (attached).

2.0 Definitions

Sealing means to remove a well from service by pulling the pump and associated piping/wiring (if installed) and filling the well with a low-permeability grouting material, typically sodium bentonite granules, chips or slurry. The sealing method used depends on the well construction and the local geologic/hydrogeologic conditions. The well screen (if present) and casing may be removed. **Decommissioning** is sometimes used as a synonym for sealing. Refer to the State of Ohio *Regulations and Technical Guidance for Sealing Unused Water Wells and Boreholes* by the State Coordinating Committee on Ground Water (2015) for additional information.

3.0 Health and Safety Considerations

Not applicable

4.0 Procedure Cautions

Ohio EPA is registered with ODNR to file Well Construction Logs and Well Sealing Reports electronically. Ohio EPA's username and password can be obtained from SIFU or the DERR Ground Water Program. (Please do not create additional ODNR accounts under Ohio EPA's name.)

5.0 Personnel Qualifications

Not Applicable

6.0 Equipment and Supplies

6.1 Ohio EPA boring log (example attached)

6.2 ODNR Well Log and Drilling Report form (example attached; the official electronic version must be filed on-line)

6.3 ODNR Water Well Sealing Report form (example attached; the official electronic version must be filed on-line)

7.0 Procedure

7.1 Prior to the start of field activities, the DERR site coordinator will work with SIFU (and the LOE contractor, as necessary) to determine who is responsible for completing and filing ODNR Well Construction Logs and Well Sealing Reports.

7.2 Ohio EPA is registered with ODNR to file Well Construction Logs and Well Sealing Reports electronically. Ohio EPA's username and password can be obtained from SIFU and the DERR Ground Water Program. (Please do not create additional ODNR accounts under Ohio EPA's name.)

7.3 ODNR Well Construction Log Filing Procedures

7.3.1 Using the example Ohio EPA boring log, attached (or an equivalent form), document the boring and monitoring well installation. Refer to FSOP 2.1.5, Soil Description, Classification and Logging.

7.3.2 Within 30 days of completing the monitoring well or boring, file an electronic well log and drilling report form (example attached) with the ODNR using Ohio EPA's ID and password at the following website: http://apps.ohiodnr.gov/water/maptechs/submitlogs/driller_login.asp

7.3.3 Print out a copy of the completed ODNR well log and drilling report form for inclusion in the Ohio EPA project file.

7.4 ODNR Well Sealing Report Filing Procedures

7.4.1 Follow the procedures provided in FSOP 1.9, Boring and Monitoring Well Decommissioning. Record the relevant information on the ODNR well sealing report form (attached) or in a field log sheet or field book.

7.4.2 Within 30 days of completion of well sealing, file an electronic well sealing report form (example attached) with the ODNR using Ohio EPA's ID and password at the following website:

7.4.3 http://apps.ohiodnr.gov/water/maptechs/submitlogs/driller_login.asp

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

ODNR, Division of Soil and Water Resources Fact Sheet 93-23, *When Does a Well Log Need to be Filed?*

ODNR, Division of Soil and Water Resources Fact Sheet 92-5, *State of Ohio Water Well Sealing Regulations*

Ohio EPA Boring Log Form (example provided)

ODNR Well Log and Drilling Report Form

ODNR Water Well Sealing Report Form

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.9, Boring and Monitoring Well Decommissioning

FSOP 2.1.5, Soil Description, Classification and Logging

Ohio Revised Code (ORC) 1521.05(B) and 1521.05(C)

State of Ohio, Regulations and Technical Guidance for Sealing Unused Water Wells and Boreholes *(*State Coordinating Committee on Ground Water) 2015.

Boring and Monitoring Well Decommissioning
FSOP 1.9 (May 20, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

Borings that are drilled for sampling or subsurface exploratory purposes or monitoring wells that are no longer needed for site assessment purposes must be decommissioned [Ohio Administrative Code (OAC) 3701-28-07, 3745-9-03 and 3745-9-10]. Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring provides appropriate guidance for boring and monitoring well decommissioning (Chapter 9, Sealing Abandoned Monitoring Wells and Boreholes). Also refer to State of Ohio, Regulations and Technical Guidance for Sealing Unused Water Wells and Boreholes *(*State Coordinating Committee on Ground Water) 2015.

1.1 The process of decommissioning a boring or monitoring well includes the following:

- Verifying that the boring or monitoring well is no longer needed for site assessment or remediation purposes. Generally, soil borings not converted to monitoring wells are decommissioned upon completion of the boring.
- Permanently sealing the boring or well with a low-permeability material
- Documenting the decommissioning activities
- For monitoring wells or borings used to characterize or assess ground water, submitting a completed Ohio Division of Natural Resources (ODNR) Geologic Survey "Well Sealing Report" [Ohio Revised Code 1521.05(c), Form DNR 7810.12]. Refer to FSOP 1.8, ODNR Well Construction Log and Well Sealing Report Filing Requirements

1.2 Soil borings greater than six feet deep or that intersect the water table must be sealed with a low permeability sealing material upon completion. Bentonite granules or chips are typically used as a sealing material. Under some circumstances (*e.g.*, a boring that intersects multiple saturated zones), the boring may need to be sealed using positive displacement grouting, *i.e.*, installing bentonite grout slurry using a tremie pipe.

1.3 Soil borings 6 feet deep or less and that do not intersect the water table may be backfilled with the soil cuttings, topsoil, or other clean fill materials (*e.g.,* sand or gravel) rather than bentonite provided that:

- The DERR Site Coordinator or other Ohio EPA division representative approves of using a clean soil or fill material.
- The soil boring does not encounter any hazardous waste, solid waste, or construction and demolition debris (C&DD) materials.
- The soil cuttings or other materials used for backfill are not known to contain contaminants exceeding any federal or state regulatory concentration levels.
- The soil cuttings or other materials used for backfill do not contain any solid waste or C&DD.

1.4 Monitoring wells must be sealed when no longer needed and may be decommissioned by:

1.5.1 Physically removing the well materials (casing and screen) and sealing the boring with a low-permeability material using positive displacement grouting (*i.e.*, installing bentonite grout slurry, typically using a tremie pipe)

1.5.2 Decommissioning the monitoring well in-place by filling the screen and well casing with bentonite or filling the monitoring well with clean sand to approximately two feet above the top of the screen and filling the well casing with bentonite, removing the protective casing, removing the upper 1 to 3 feet of well casing if possible and filling the upper 1 to 3 feet of the borehole with soil or other clean fill materials

1.6 Under some circumstances, DERR's LOE contractor may be needed to decommission borings or monitoring wells. Such situations may include, but are not necessarily limited to, borings or monitoring wells that are greater than 2 inches in diameter, are installed in bedrock, or are installed within the paved area of a highway. These situations may require the use of drilling rigs and other equipment not available to Ohio EPA staff. Decommissioning procedures to be followed by the LOE contractor will vary with site conditions and will be approved through a site-specific work plan (SSWP).

1.7 Monitoring wells that are installed below the base of the uppermost saturated zone (*see Section 2.0, Definitions*) and intersect multiple saturated zones generally should be decommissioned by removing the screen and casing, which will require services of DERR's LOE contractor. Removing the screen and casing may not be possible due to the well location and work/equipment obstructions. Under such circumstances, abandoning the well in place may be acceptable.

2.0 Definitions

2.1 <u>Bentonite Chips (or Coarse Grade Bentonite)</u>: crushed sodium bentonite shale particles sized from $^3/_8$- to ¾-inch diameter that are intended to fall through a water column in a boring or well without bridging (also referred to as crushed or chip bentonite)

2.2 <u>Bridging</u>: the creation of a void within a decommissioned boring or monitoring well when bentonite chips, pellets or granules are either poured into the boring or well too quickly or prematurely hydrate and fail to form a continuous seal

2.3 <u>Granular Bentonite</u>: processed sodium bentonite with a particle size range of 2.4 to 0.8 mm (#8 to #20 mesh), typically used for bentonite grout slurries, but may also be used in dry form to seal borings under certain circumstances

2.4 <u>Neat Cement</u>: a mixture of Portland cement and fresh water (5 to 6 gallons of water per 94-pound sack of cement)

2.5 Tremie Grouting: pumping a grout slurry through a conductor pipe or tube that extends nearly to the bottom of a boring or monitoring well to positively displace (lift) ground water out of the boring or well as the denser grout is emplaced; this method prevents dilution of the grout, which could inhibit formation of a proper grout seal

2.6 Uppermost Saturated Zone: the first (shallowest) zone of saturation present at a given location. The uppermost saturated zone extends from the first ground water encountered to the base of the unit where saturated conditions are not present. For example, the uppermost saturated zone would be from 10 to 20 feet below ground surface (bgs) for a surficial 20-foot thick sand layer saturated from 10 to 20 feet bgs and underlain by low-permeability clay. A monitoring well installed anywhere within 10 to 20-foot bgs would be considered an uppermost saturated zone well. A well installed deeper than that, *i.e.*, below the confining clay layer in lower (second) saturated sand would not be considered an uppermost saturated zone well. Uppermost saturated zones may include perched ground water zones.

3.0 Health and Safety Considerations

3.1 Wear appropriate personal protective equipment (PPE) when working near a drilling rig or grout pump. At a minimum, PPE should include protective eyewear, footwear, and hearing protection.

3.2 Use hand protection to help prevent injuries when performing boring or monitoring well decommissioning activities that require the use of mechanical or manual equipment.

3.3 To avoid direct contact with chemical contaminants and prevent skin irritation, wear chemical-resistant or other protective gloves when handling grouting materials or soil from decommissioning activities. Wash your hands after completing boring or well decommissioning activities.

3.4 Well sealing materials, including but not limited to bentonite, cement and sand may present a silica dust hazard. Appropriate health and safety precautions should be implemented to present exposure to respirable silica, *e.g.*, engineering controls and/or respirators with the appropriate filter cartridges.

4.0 Procedure Cautions

4.1 When decommissioning a boring or monitoring well by pouring bentonite granules or chips into it, use a weighted tape or drilling rods to ensure that the bentonite does not bridge above the bottom of the boring.

4.2 Bring the bentonite to within approximately 1 to 3 feet of the ground surface and fill the remainder of the boring with appropriate clean fill materials (*e.g.*, topsoil in a residential lawn area, sand or gravel and asphalt mix in a paved area). If bentonite is brought nearer to the ground surface, it may expand out of the boring onto the ground. Decommissioned borings containing bentonite that has expanded to the ground surface are aesthetically unattractive and present a slip/fall hazard.

4.3 Ground water exhibiting elevated hardness (> 500 ppm) or chloride concentrations (> 1,500 ppm) can suppress the hydration of bentonite grouts. Ground water near solid waste landfill leachate plumes or salt piles may contain high concentrations of chlorides. Under such circumstances use of neat cement grout slurry or an alternative grouting material may be required.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Bentonite chips or granules
6.2 Topsoil, concrete mix, asphalt mix, sand and/or gravel
6.3 Potable water
6.4 Water level indicator
6.5 Weighted measuring tape or drilling rods
6.6 Shovel
6.7 Pry bar
6.8 Sledgehammer
6.9 PVC pipe cutter
6.10 Photoionization detector (PID)
6.11 PPE
6.12 Large heavy-duty trash bags
6.13 Decontamination equipment and supplies
6.14 Field book or decommissioning log form
6.15 Camera

7.0 Procedures

7.1 <u>Decommissioning soil borings 6 feet deep or less that do not intersect the water table:</u>

7.1.1 If the soil boring does not encounter any hazardous waste, solid wastes, or C&DD materials, then decommission the boring by backfilling it with soil cuttings, topsoil, or other clean fill materials (*e.g.*, sand or gravel). The soil cuttings or other materials used for backfilling must be known to not contain contaminants exceeding any federal or state regulatory concentration levels or any hazardous waste, solid waste or C&DD materials. If the soil boring is located within a paved area, complete the decommissioning in a manner that prevents pavement settling and fill the upper 4 to 6 inches (or pavement thickness) of boring space with concrete or asphalt mix, whichever is appropriate.

7.1.2 If the soil boring encounters hazardous waste, solid waste, or C&DD materials, then decommission the boring by backfilling it with bentonite chips or granules unless otherwise directed by the SSWP, DERR Site Coordinator or Ohio EPA client division. Use potable water to hydrate the granules or chips after installation.

7.2 Decommissioning soil borings deeper than 6 feet but less than the depth to the base of the uppermost saturated zone or any boring that intersects the water table:

7.2.1 Depending on the subsurface conditions encountered, decommission soil borings by backfilling with bentonite chips or granules.

7.2.2 Use a weighted tape or drilling rods to ensure that the bentonite does not bridge in the boring and form a void. The dry bentonite should be hydrated by adding potable water as needed.

7.3 Decommissioning monitoring wells installed in the uppermost saturated zone (in-place decommissioning technique)

7.3.1 Before decommissioning the monitoring well, record final static water level and total depth measurements.

7.3.2 Fill the monitoring well screen and casing with granular bentonite or chips. Use a weighted tape or drilling rods to ensure that the bentonite does not bridge in the boring and form a void. Clean sand may be substituted for bentonite from the bottom of the well to approximately two feet above the top of the screen.

7.3.3 The dry bentonite should be hydrated in lifts by adding potable water as needed.

7.3.4 Remove the protective surface casing and concrete seal and cut the well casing between one and three feet below the ground surface.

7.3.5 Fill the remaining void with topsoil or other clean fill materials appropriate for the use of the area in which the boring is located. For example, if the boring is in a lawn area, topsoil may be used. If the boring is in a paved area, use sand or gravel topped with a 4- to 6-inch thick layer of asphalt mix or concrete.

7.4 Decommissioning monitoring wells installed below the base of the uppermost saturated zone

7.4.1 Monitoring wells installed below the base of the uppermost saturated zone generally should not be decommissioned in place, *i.e.*, the casing and screen generally should be removed. However, removing the screen and casing may sometimes not be possible due to the well location and work/equipment obstructions. Under such circumstances, abandoning the well in place may be acceptable.

7.4.2 DERR’s LOE contractor should be mobilized to decommission monitoring wells installed below the base of the uppermost saturated zone if the casing and screen are to be removed.

8.0 Data and Records Management

8.1 Document soil boring and well decommissioning procedures, materials and observations on a field decommissioning log form or project field book. Refer to FSOP 1.3, Field Documentation.

8.2 For all wells and soil borings used to assess ground water quality or quantity, an ODNR water well sealing report must be filed. Refer to FSOP 1.8, ODNR Well Construction Log and Well Sealing Report Filing Requirements.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

Not applicable

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.8, ODNR Well Construction Log and Well Sealing Report Filing Requirements

Ohio EPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (February 2009): Chapter 9, Sealing Abandoned Monitoring Wells and Boreholes

Ohio Administrative Code (OAC) 3701-28-07, 3745-9-03 and 3745-9-10 Ohio Revised Code (ORC) 1521.05(c)

State of Ohio, Regulations and Technical Guidance for Sealing Unused Water Wells and Boreholes *(*State Coordinating Committee on Ground Water) 2015.

Discrete Soil Sampling
FSOP 2.1.1 (May 26, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 While there are multiple mechanical drilling methods (*e.g.,* direct-push, hollow stem auger, rotosonic) for sample collection, unless otherwise approved by Division of Environmental Response and Revitalization (DERR) management, the direct-push method will be used on DERR projects.

1.2 Discrete soil sampling is the process of collecting a single soil sample from a specific location and depth interval. Discrete soil sample locations and depths are typically selected based on existing knowledge about site conditions, including:

- Site history and land use
- Type of contaminant and the nature of release
- Visual evidence of releases or source areas, e.g., staining, stressed vegetation, leachate seeps
- Site soil types, geology and hydrogeology
- Field survey data, e.g., geophysical surveys
- Field screening results, e.g., PID or mobile laboratory data
- Analytical results from previous investigations

1.3 The number of discrete soil sample locations needed to characterize site conditions is primarily based on professional judgment, which incorporates knowledge of site information, project goals and data quality objectives (DQOs). Discrete sampling is often used to evaluate the spatial distribution of contaminants or other constituent concentrations within a soil unit (see ITRC reference below). Examples include but not limited to:

- Sampling to define the extent of soil contamination from a surface spill
- Sampling to identify and define the extent of soil contamination associated with a leaking Underground Storage Tank (UST) system
- Sampling to verify that the extent of a contaminated soil excavation meets remedial objectives
- Sampling to determine background concentrations or provide concentration data for geochemical modeling or risk assessment based on statistical evaluation, e.g., calculation of a 95% upper confidence limit on the mean

1.4 The relatively small size of a single discrete sample is generally inadequate to definitively characterize the large volume of un-sampled soil surrounding it, and analytical results should not be extrapolated beyond the immediate vicinity of the sampling location (see ITRC reference below). Discrete sampling may <u>not</u> be preferred when:

- Sampling to determine the average concentrations of constituents in soil underlying a specified area
- Sampling to determine background concentrations or provide concentration data for geochemical modeling or risk assessment based on statistical evaluation when statistical data analysis is not required

For these situations either composite or incremental sampling may be appropriate.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Please refer to FSOP 1.2, Utility Clearance. Underground utility clearance must be requested prior to conducting hand or mechanical excavation of soil or sediment per Ohio Revised Code (ORC) 3781.25(I).

3.2 Wear appropriate personal protective equipment (PPE) when working in the vicinity of drilling or other types of mechanical soil sampling equipment. At a minimum, PPE should include sample gloves, protective eyewear, and protective footwear (OSHA 1910.136). Hearing protection is required in noisy environments. A hard hat (ANSI 289.1-2003 Type II Class E, protection from top and side impact) is required if overhead hazards are present or if required by the facility where work is being performed. Canvas coveralls (or similar protective clothing) are also recommended.

3.3 Use heavy protective gloves to help prevent hand injuries when using hand augers or other manual sampling equipment or handling and opening core barrels, split spoons or core liners.

3.4 Wear chemical-resistant gloves when handling soil samples to avoid direct contact with chemical contaminants. Always thoroughly wash your hands after completing soil sampling activities.

3.5 If free product or splash hazards are a concern during drilling and sampling, use of a chemically resistant suit (*e.g.,* Saranex or coated Tyvek) is recommended.

3.6 If dusty conditions are present, respiratory protection may be necessary to provide protection from dust-inhalation hazards. Work must be stopped to assess site conditions. Work requiring respiratory protection may only be performed by staff certified to wear respiratory protection. Depending on site-specific conditions and chemicals of concern, monitoring with a particulate meter or other air monitoring instruments may be appropriate. To review action levels, refer to the NIOSH Pocket Guide to Chemical Hazards.

3.7 Conduct air monitoring in accordance with the site-specific health and safety plan. For action levels, refer to Table 1 of FSOP 1.1, Initial Site Entry.

3.8 Dress appropriately for anticipated weather conditions, and always have ample drinking water available when working in hot weather. Insect repellant may be needed for protection from ticks, mosquitoes, and other biting insects in heavily wooded areas.

4.0 Procedure Cautions

4.1 Review the site-specific work plan (SSWP) before performing field work to ensure that the discrete sampling method is appropriate for project objectives and the associated DQOs.

4.2 Evaluate access to all borings/soil sampling locations before mobilization of drilling or other sampling equipment to the site

4.3 Hand augers (bucket augers) or triers (probes) may be difficult to advance in dense clayey soils or gravelly soils.

4.4 Loose sandy soils may fall out of hand augers or triers as these samplers are extracted from the subsurface.

4.5 Triers are limited to a relatively small sample volume (*e.g.,* a 5/8-inch by 12-inch soil core) that may not be adequate for analysis of multiple constituents (*e.g.,* semi-volatile organics (SVOCs), pesticide, polychlorinated biphenyls (PCBs), and metals) without collecting multiple co-located samples.

4.6 Complete all activities associated with soil sampling (*e.g.,* soil boring logging or field screening). These activities will be described in the SSWP.

4.7 Use insect repellants and other chemicals in a manner that minimizes the potential for soil sample cross contamination, e.g., apply insect repellent in the morning before drilling and sampling activities begin.

4.8 Avoid excessive handling or manipulation of soil samples collected for laboratory analysis. Portions of a soil sample used for logging or screening purposes should not be used for laboratory analysis. Soil samples collected for laboratory analysis should be placed in laboratory containers and appropriately preserved as soon as possible.

4.9 Soil samples collected for VOC analysis require special sampling and handling techniques. Refer to FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods, or FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Soil sampling equipment, including but not limited to spoons, trowels, triers (probes), hand augers (bucket augers), shovels and/or drilling equipment
6.2 Soil screening equipment (*e.g.,* PID) and supplies, as needed
6.3 PPE
6.4 Stainless steel pans, disposable aluminum pans, stainless steel spoons and/or stainless-steel spatulas for splitting, homogenizing, or otherwise manipulating soil samples
6.5 Plastic sheeting
6.6 Tools for clearing vegetation and surface debris from soil sampling locations (*e.g.,* shovels, brush axes, etc.)
6.7 Laboratory containers and labels
6.8 Sample cooler(s) with ice (if needed)
6.9 Field documentation supplies and equipment, including pens, markers, field log/data sheets, field logbook, chain-of-custody forms, camera
6.10 Decontamination equipment and supplies
6.11 SSWP and HASP

7.0 Procedures

7.1 Before performing soil sampling activities, review the SSWP. The SSWP will provide locations and approximate depths for discrete soil samples, information regarding anticipated subsurface conditions at the site (*e.g.,* soil types, nature of contamination, depth to ground water, etc.), and any required field screening or soil logging activities.

7.2 Refer to FSOP 1.4, Sample Identification Nomenclature, for sample labeling and identification.

7.3 Discrete Soil Sample Collection Using Manual Equipment

7.3.1 Use manual sampling equipment capable of extracting soil samples that will meet both project goals and DQOs.

7.3.2 Place sampling equipment and supplies on a clean plastic sheet adjacent to each sampling location to prevent cross-contamination by direct contact with the ground surface.

7.3.3 Remove surface debris such as vegetation, gravel or other materials or debris prior to sampling.

7.3.4 Wear a new pair of clean sampling gloves when collecting each discrete soil sample.

7.3.5 If required, perform soil field screening or logging activities using a representative portion of the soil sample that is not needed for laboratory analysis. Screening and logging may be performed on a separate split or subsample before or after laboratory containers have been filled. Refer to FSOP 2.1.4, Sample Headspace Screening, and FSOP 2.1.5, Soil Description, Classification and Logging.

7.3.6 Soil samples for VOC analysis should be collected first in accordance with the following FSOPs, depending on project objectives and DQOs identified in the SSWP:

- FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods
- FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A

7.3.7 For non-VOC soil samples, use a disposable aluminum pan or a stainless-steel pan or bowl to contain and homogenize the soil sample prior to filling laboratory container (if applicable).

7.3.8 For non-VOC constituents, fill the laboratory containers with a representative portion of the soil increment sampled in the order of decreasing sensitivity to volatilization (*e.g.,* SVOCs, pesticides, PCBs, metals).

7.3.9 If required for analytical sample preservation, immediately place the labeled and filled laboratory containers in a cooler on ice.

7.3.10 Complete the chain-of-custody form and applicable boring logs, field forms, logbook or log sheets in accordance with FSOP 1.3, Field Documentation.

7.3.11 Decontaminate non-disposable sampling equipment between sampling locations unless the SSWP requires more frequent decontamination (*e.g.,* between depth intervals at each location). Refer to FSOP 1.6, Sampling Equipment Decontamination.

7.4 Soil Sample Collection Using Direct-Push Drilling Equipment

7.4.1 Two types of direct push samplers are typically used for the collection of discrete soil samples:

- The Macro-Core^{TM} Soil Sampling System is used to collect continuous soil cores from an uncased boring (the sampler and rods are removed from the boring after each soil sample is collected and then reinserted to collect the next sample).

- The Dual Tube Soil Sampling System is used to collect continuous as well as discrete depth soil cores from within a sealed casing (the boring remains open while soil samples are collected and extracted). Soil cores are approximately one inch in diameter by 48 inches long.

Disposable acetate core liners are used with both sampler types.
The sampler type(s) selected should produce soil samples that meet both project goals and DQOs. For example, if a large volume of soil sample will be needed for multiple constituents (*e.g.,* SVOCs, pesticides/PCBs and metals) the Macro-Core^{TM} sampling system is likely the best choice.

However, if samples need to be collected below a zone of soil contamination, the Dual Tube sampling system will minimize potential cross contamination between contaminated and uncontaminated soils.

7.4.2 Wear a new pair of clean chemical resistant sampling gloves when collecting each discrete soil sample.

7.4.3 If any of the soil in the sampler appears to be caved or sloughed material from the open boring overlying the sampled interval, remove it from the sampler. Do not submit it for laboratory analysis or log it as part of the sampled interval. If in doubt based on sample appearance, consult with the driller regarding the stability of the borehole (*i.e.,* is it collapsing or heaving between sample intervals?) Treat this material as investigation-derived waste per FSOP 1.7, Investigation Derived Waste.

7.4.4 Record the depth interval and recovery of each soil sample to the nearest one-tenth (0.1) foot. Do not record a recovery that is greater than the length of the soil core. For example, if a core sampler pushed from 8.0 to 10.0 feet recovers only 1.5 ft of soil core, record the recovery as 1.5 ft (or 8.0 to 9.5 ft), not 2.0 ft (or 8.0-10.0 ft).

7.4.5 If required, perform soil field screening or logging activities (*e.g.,* PID screening, soil type identification and description) using a representative portion of the soil sample that is not needed for fixed-base laboratory analysis. Screening and logging activities may be performed before or after laboratory containers have been filled. Refer to FSOP 2.1.4, Sample Headspace Screening, and FSOP 2.1.5, Soil Description, Classification and Logging.

7.4.6 Soil samples for VOC analysis should be collected first in accordance with the following FSOPs depending on project objectives and DQOs identified in the SSWP:

- FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods
- FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A

7.4.7 For non-VOC constituents, fill the laboratory containers with a representative portion of the soil increment sampled in the order of decreasing sensitivity to volatilization (*e.g.,* SVOCs, pesticides/PCBs, metals).

7.4.8 If required for analytical sample preservation, immediately place the labeled and filled laboratory containers in a cooler on ice.

7.4.9 Complete the chain-of-custody form and applicable boring logs, field forms, logbook or log sheets in accordance with FSOP 1.3, Field Documentation.

7.4.10 Direct-push (*e.g.,* Geoprobe^{TM}) sampling equipment does not need to be decontaminated between sampling locations because soil cores are collected in disposable acetate liners. However, if gross contamination (*e.g.,* non-aqueous phase liquids) is encountered or if the potential for cross-contamination is a concern, the direct-push Geoprobe^{TM} sampling equipment should be decontaminated in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.5 Prepare samples for delivery to the laboratory in accordance with FSOP 1.5, Sample Custody and Handling.

7.6 Dispose of unused soil samples, disposable sampling equipment and used supplies in accordance with FSOP 1.7, Investigation Derived Waste.

7.7 After sampling activities are completed, decommission the boring or shallow excavation in accordance with FSOP 1.9, Boring and Monitoring Well Decommissioning

7.8 After sampling activities are completed, file ODNR well logs as necessary in accordance with the requirements of FSOP 1.8, ODNR Well Construction Logs & Well Sealing Reports.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

9.0 Quality Assurance and Quality Control

Quality assurance/quality control (QA/QC) samples may include equipment blanks, field blanks and/or trip blanks depending on the site-specific chemicals of concern and conditions. Duplicate soil samples are to be collected at a minimum of 1 per 10 soil samples collected. Duplicate samples are required for U.S. EPA Contract Laboratory Program sampling events conducted at Federal CERCLA sites. Duplicate soil samples should not be collected at sites under other regulatory programs unless otherwise directed by DERR management.

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.2, Utility Clearance

FSOP 1.3, Field Documentation

FSOP 1.4, Sample Identification Nomenclature

FSOP 1.5, Sample Custody and Handling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Waste

FSOP 1.8, ODNR Well Construction Logs & Well Sealing Reports

FSOP 1.9, Boring and Monitoring Well Decommissioning

FSOP 2.1.4, Sample Headspace Screening

FSOP 2.1.5, Soil Description, Classification and Logging

FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods

FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A

ITRC (Interstate Technology & Regulatory Council), 2012, Incremental Sampling Methodology (ISM-1): Interstate Technology & Regulatory Council, Incremental Sampling Methodology Team, Washington, D.C., www.itrcweb.org. [Note: ISM-2 is scheduled for release in Fall 2020.]

Ohio Revised Code 3781.25(I)

OSHA 1910.136, Personal Protective Equipment (Foot Protection)

<u>Composite Soil Sampling</u>
FSOP 2.1.2 (June 3, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Composite sampling is the process of physically combining and homogenizing several discrete soil increments to form a single sample. Composite sampling is most commonly used for the following:

- Estimating the average concentration of a constituent of concern to meet regulatory sampling requirements (*e.g.,* sampling to characterize the concentrations of inorganics in a predetermined target area)
- Providing a laboratory-defined sample volume for analysis when discrete sample volumes are inadequate
- Reducing the number of discrete analyses as a cost-saving measure

1.2 Composite sampling involves a three-step process:

- Collecting sample increments using a specific sampling design within a defined area or volume of contaminated media (the sampling unit or SU)
- Homogenizing the sample increments
- Collecting subsamples from the homogenized composite for laboratory analysis

The collection of increments for a composite sample may be based on judgmental, simple random, stratified, systematic/grid or other sampling designs (see U.S. EPA 2002 guidance listed below). Homogenization of sample increments should be performed in a laboratory or similar controlled environment. Homogenization and collection of analytical subsamples from the homogenized composite are the most critical steps of the process with respect to obtaining a representative sample.

1.3 This FSOP is applicable to the collection of composite soil samples as well as composite samples from sediment and certain industrial wastes (*e.g.,* fly ash, foundry sand, and cement kiln dust).

1.4 Composite samples differ from discrete samples in that composite samples are used to characterize average contaminant concentrations in a defined area or volume of contaminated media, and are collected in accordance with appropriate sampling design, homogenization and subsampling protocols based on project and data quality objectives (DQOs). Discrete samples are used to characterize the concentration variation and spatial distribution of contaminants at a contaminated site. Therefore, unlike composite sampling, discrete sampling relies more heavily on field observations and professional judgment that incorporate knowledge of site information as well as project objectives and DQOs. Examples of discrete sampling scenarios include:

- Sampling to define the extent of soil contamination from a surface spill of an organic solvent

- Sampling to determine the maximum contaminant concentration present in sediment contained with an industrial wastewater lagoon
- Sampling to verify that the extent of a contaminated soil excavation meets remedial objectives

For projects where variability or spatial distribution or variability of soil or sediment contaminant concentrations is needed, perform soil sampling in accordance with FSOP 2.1.1, Discrete Soil Sampling or sediment sampling in accordance with FSOP 2.3.2, Sediment Sample Collection.

1.5 Composite samples differ from multi-incremental samples in that composite samples are used to estimate average contaminant concentrations based on a defined SU, whereas multi-incremental samples are used to determine representative concentrations in a decision unit (DU).

Multi-incremental samples typically require a higher number of discrete sample increments (at least 30 to 50 increments) than composite samples (typically much less than 30 increments). The higher number of increments provide a greater degree of statistical certainty with respect to average contaminant concentrations within the DU, which in turn provides support for the associate decision. Examples of multi-incremental sampling include:

- Sampling to determine representative (*i.e.,* average) concentrations of inorganic or organic constituents in soil underlying a vacant two-acre parcel located in a former industrial park to determine if the property can be developed as a city park
- Sampling to determine naturally occurring background concentrations of metals in an uncontaminated portion of a soil unit
- Sampling to provide contaminant concentration data for geochemical modeling or risk assessment

If data are needed for project decisions based on a DU, perform incremental soil sampling in accordance with FSOP 2.1.3, Incremental Sampling for Soil and Sediments. Otherwise, use a composite sampling technique in accordance with this FSOP (assuming discrete sampling is not appropriate to meet project objectives).

1.6 Composite sampling may not be an acceptable technique for quantitative assessment of site contamination (*i.e.,* determining representative concentration and extent) due to the limitations identified in section 4.6.

1.7 Composite sampling is not recommended for collecting data to support environmental risk assessments; instead, discrete or multi-incremental sampling techniques should be used. Any site-specific work plans (SSWPs) that include sampling to specifically support risk assessment should be reviewed by Division of Environmental Response and Revitalization’s Engineering & Risk Assessment Support (ERAS) unit.

1.8 Composite sampling is not an acceptable technique for determining background concentrations in soil or sediment. Discrete or multi-incremental sampling techniques should be used to collect background samples.

1.9 Sampling designs for composite sampling may be based on regulatory program requirements (*e.g.,* collecting a composite sample from an underground storage tank excavation soil stockpile for benzene analysis under the Ohio Bureau of Underground Storage Tank Regulations) or technical guidance. Recommended technical guidance includes U.S. EPA (January 2013, December 2002 and August 1995), Patil (2002), Splitstone (2001) and Gilbert (1987).

1.10 Composite samples cannot be used to evaluate RCRA land disposal restrictions (LDRs). The LDR rules require grab (discrete) samples.

1.11 SSWPs that include composite sampling should be reviewed by DERR ERAS staff and/or lead technical staff prior to sample collection to ensure that the composite sampling design and appropriate procedures meet project DQOs.

2.0 Definitions

Decision Unit (DU): the smallest area or volume of soil where a decision is needed regarding the evaluation and/or remediation of contaminated media with respect to the potential environmental hazards posed by existing or anticipated future land use based on Incremental Sampling Methodology (ISM).**Hot Spot**: soil or sediment area/volume with relatively high contaminant concentration(s) that may be present at a site, but whose location and dimensions cannot be anticipated prior to sampling based on existing site information and sampling data

Sampling Unit (SU): an area/volume of soil or sediment from which increments are collected to determine an estimate of the mean concentration for that volume

Source Area: waste disposal units, spills, releases, and areas/volumes of soil or sediment shown by previous sampling to have significant contaminant concentrations relative to the surrounding soil/sediment

3.0 Health and Safety Considerations

3.1 Refer to the site health and safety plan (HASP) for site-specific safety issues.

3.2 Follow all applicable health and safety considerations provided in FSOP 2.1.1, Discrete Soil Sampling and/or FSOP 2.3.2, Sediment Sample Collection.

4.0 Procedure Cautions

4.1 Carefully review the SSWP before performing field work to fully understand the composite sampling procedures that need to be implemented. Composite sampling procedures, including collecting sample increments according to a specific sampling design, homogenizing the sample and sub-sampling the homogenized composite for laboratory analysis, are highly variable site- and project-specific activities. A complete consideration of the scope of composite sampling scenarios is beyond the scope of this FSOP, which is intended to provide general procedures. A detailed discussion of site- and project-specific procedures should be provided in the SSWP. If not, contact DERR-Site Investigation Field Unit staff and/or DERR site coordinator for assistance.

4.2 Integrity of the SU is critical for composite sampling (*i.e.,* the SU should not incorporate different soil, sediment or waste types and should not incorporate both contaminated and uncontaminated media).

4.3 Follow all applicable procedure cautions provided in FSOP 2.1.1, Discrete Soil Sampling and/or FSOP 2.3.2, Sediment Sample Collection.

4.4 Each discrete subsample should contribute an equal amount of material to the composite sample.

4.5 Discrete subsamples must be collected from the same material (*e.g.,* the same soil or fill type).

4.6 Composite sampling for volatile organic compound (VOC) analysis is not recommended (U.S. EPA January 2013). The manipulation of the sample during the compositing/homogenization process raises concerns with potential loss of VOCs. However, if the SSWP requires analysis of a composite sample for VOCs, FSOP 2.1.3 Incremental Sampling for Soils and Sediments should be used.

4.7 To ensure adequate homogenization, the composite subsamples should be homogenized at the Groveport Field Office or by the analytical laboratory. This is because it is more difficult to produce a representative composite sample via field homogenization. If appropriate based on the SSWP and associated DQOs, the sample homogenization procedures in FSOP 2.1.3 Incremental Sampling for Soils and Sediments may be used.

4.8 Subsampling of the homogenized composite sample for laboratory analysis is the most critical part of the composite sampling process. The SSWP should provide detailed procedures for subsampling or reference the subsampling procedures provided in SOP 2.1.3, Incremental Sampling for Soils and Sediments. If clarification is needed regarding the subsampling procedures, contact DERR-SIFU staff and/or the DERR site coordinator.

4.9 Soils or sediments with high clay content may be difficult to composite and require drying and grinding of the sample for adequate homogenization.

4.10 Sample homogenization procedures must not adversely impact the integrity of the target analytes.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

Depending on the SSWP requirements, refer to FSOP 2.1.1, Discrete Soil Sampling, FSOP 2.3.2, Sediment Sample Collection and/or FSOP 2.1.3, Incremental Sampling for Soils and Sediments as applicable for sample collection and homogenization equipment and supplies.

7.0 Procedures

7.1 Before performing sampling activities carefully review the SSWP, which should provide detailed project-specific composite sampling procedures (sampling design and increment collection, sample homogenization, collecting and submitting subsamples for laboratory analysis). If clarification is needed regarding the SSWP procedures, contact the DERR-SIFU staff and/or the DERR site coordinator.

7.2 For the collection of composite sample increments, follow the procedures in the SSWP and/or FSOP 2.1.1, Discrete Soil Sampling, FSOP 2.3.2, Sediment Sample Collection and/or FSOP 2.1.3, Incremental Sampling for Soils and Sediments as applicable based on the SSWP.

7.3 Triplicate samples (one sample and two replicates) should be collected at a rate of 10% of the total number of composite samples. The triplicate increments should be collected in the same manner as the sample increments (same sampling design/grid, depth interval, sampling tool, etc.) but should not be collected from the same exact locations as the sample increments (or other triplicate increments). Efforts should be taken to ensure that all increments for each triplicate sample are collected in different locations to ensure the ability to evaluate sample and SU variability. Triplicate sample results can be used to calculate a 95% upper confidence interval for the mean concentration that helps quantify the uncertainty in the estimate of the mean contaminant concentration(s) for the composite SU.

7.4 For sample homogenization and the selection of subsamples for laboratory analysis, follow the procedures in the SSWP and/or FSOP 2.1.3, Incremental Sampling for Soils and Sediments as applicable based on the SSWP.

7.5 Excess soil or sediment volume left over after homogenization and compositing (*e.g.,* excess sample volume not needed for laboratory sample submission) must be disposed of in accordance with FSOP 1.7, Investigation Derived Waste after the sample results are received and reviewed.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

9.1 A clear record of the discrete sample increments that comprise each composite sample must be maintained.

9.2 Quality assurance/quality control (QA/QC) samples may include equipment blanks, field blank, and/or trip blanks depending on the site-specific chemicals of concern, site conditions and SSWP requirements.

9.3 Triplicate samples should be collected as described in paragraph 7.3 to statistically evaluate the uncertainty in the estimate of the mean contaminant concentration(s) for the composite SU.

10.0 Attachments

Not applicable

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.7, Investigation Derived Waste

FSOP 2.1.1, Discrete Soil Sampling

FSOP 2.1.3, Incremental Sampling for Soils and Sediments

FSOP 2.3.2, Sediment Sample Collection

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U.S. EPA, January 2013, *Waste Analysis at Facilities that Generate, Treat, Store, and Dispose of Hazardous Wastes – Draft 2*: Solid Waste and Emergency Response, EPA 530-R-12-001

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Incremental Sampling for Soils
FSOP 2.1.3 (June 9, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Incremental sampling methodology (ISM) is a structured composite sampling and processing protocol that reduces data variability and increases sample representativeness for a specified area/volume of soil. ISM is a two-part process (sample collection and subsequent laboratory processing with subsampling) that is designed to obtain a single analytical sample having all constituents in the same proportion as an explicitly defined area/volume of soil called the decision unit (DU). A DU is site-specific and represents the smallest volume of soil about which a decision is to be made (ITRC February 2012; update due in 2020). ISM improves the accuracy and precision of COC concentrations for bulk volumes of soil. COCs may include metals, semivolatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), or pesticides. Generally, VOC sampling is not recommended using ISM. The Interstate Technology & Regulatory Council (ITRC) Incremental Sampling Technology (February 2012; update due in 2020) provides detailed ISM guidance and is Ohio EPA's primary reference for ISM. The procedures described in this FSOP are consistent with the ITRC guidance. Example applications of ISM include:

- Determining representative concentrations of inorganic or organic constituents in soil underlying a vacant parcel located in a former industrial park
- Determining representative background concentrations of metals
- Providing representative constituent concentration data to be used for geochemical modeling or risk assessment when statistical evaluation of discrete samples is not required or desired

1.2 ISM procedures are designed to minimize the sources of sampling error associated with soil sampling (Table 1). Discrete soil sampling methodology (*e.g.,* FSOP 2.1.1, Discrete Soil Sampling) typically does not account for these errors, which artificially increase the variability of analytical results. The most significant are fundamental error (FE) caused by variations in particle size and/or composition and grouping and segregation error (SE) caused by variations in particle type distributions. ISM reduces these errors by increasing the mass of the field sample (combining multiple sample increments), reducing particle size (grinding) and homogenizing the field sample, and using unbiased subsampling techniques to select a representative analytical sample.

1.3 A site-specific work plan (SSWP) with incremental sampling should include:

- A description of the nature and extent of contamination
- Site-specific data quality objectives (DQOs)
- DUs based on a conceptual site model (CSM)
- One or more ISM sampling designs
- Volumes and number of ISM sample increments

- Laboratory requirements for sample volumes and subsampling techniques

ISM sampling designs include those typically used for composite sampling, which include simple random, stratified random and systematic random sampling designs. ITRC (February 2012, update due in 2020), U.S. EPA (August 2002), U.S. EPA (December 1995) and Gilbert (1987) provide detailed information on composite sampling designs that are appropriate for ISM. DUs should be selected based on input from the entire project team (*e.g.*, SIFU personnel, site coordinators, risk assessors, engineers, management, and laboratory personnel as needed). Appendix A of this SOP provides guidance for selecting DUs.

1.4 Generally, due to feasibility and cost considerations, ISM is often limited to the evaluation of surface soils (less than two feet deep) that can be collected manually. This FSOP assumes that manual sampling equipment (*e.g.*, soil probes, hand augers, sampling spoons) will be used to collect ISM samples from surface soils. Related FSOPs include:

- FSOP 2.1.1, Discrete Soil Sampling
- FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A

In the event that samples are collected using direct push or other mechanical sampling equipment, please consult applicable FSOPs, equipment user manuals, and/or the SSWP and health and safety plan (HASP) for health and safety considerations, procedure cautions, and sample collection procedures. ITRC describes field procedures appropriate for performing ISM on subsurface soil cores (refer to Chapter 5, *Field Implementation, Sample Collection, and Processing*). Figure 1 shows an ISM field sampling implementation flowchart (ITRC, February 2012, update due in 2020).

1.5 DUs normally should not exceed one-quarter acre (approximately 11,000 square feet), unless justified by special sampling scenarios or site-specific circumstances. See Appendix A, Guidance on Determining Decision Units

2.0 Definitions

Decision Unit (DU): the smallest area/volume of soil (or sediment) where a decision is needed regarding the extent and magnitude of contaminants with respect to the potential environmental hazards posed by existing or anticipated future exposures; the smallest volume of soil for which a decision will be made based on ISM sampling

Hot Spot: soil volume with relatively high contaminant concentration(s) that may be present at a site, but whose location and dimensions cannot be anticipated prior to sampling based on existing site information and sampling data

Sampling Unit (SU): a volume of soil from which increments are collected to determine an estimate of the mean concentration for that volume

Source Area: waste disposal units, spills, releases, and volumes of soil shown by previous sampling to have significant contaminant concentrations relative to the surrounding soil

3.0 Health and Safety Considerations

3.1 Prior to conducting hand (or mechanical) excavation of soil, underground utilities must be cleared. Please refer to FSOP 1.2, Utility Clearance.

3.2 Use heavy protective gloves to help prevent hand injuries when using hand augers or other manual sampling equipment, or handling and opening core barrels, split spoons or core liners.

3.3 Wear chemical-resistant gloves when handling soil samples to avoid direct contact with chemical contaminants. Always thoroughly wash your hands after completing soil sampling activities.

3.4 Dress appropriately for anticipated weather conditions, and always have ample drinking water available when working in hot weather. Insect repellant may be needed for protection from ticks, mosquitoes, and other biting insects.

3.5 Refer to the site HASP for site-specific safety issues.

4.0 Procedure Cautions

4.1 The DQO’s in the SSWP should document the need for use of the ISM to meet project objectives, provide a detailed description of the DUs, and explain the site-specific sample collection and homogenization procedures.

4.2 Be aware that ISM data may not be acceptable for some regulatory programs.

4.3 ISM sampling equipment should be selected to minimize increment delimitation error (DE) and increment extraction error (EE) (Table 1). In general, sampling tools should have minimum diameter of 16 mm and should equally retain all particles in the sample(s) over the entire depth of interest. Sampling tools that obtain cylindrical or core-shaped increments over a constant depth are preferred over other types of tools (*e.g.,* spoons). For non-cohesive soils, scoops or trowels may be used, but care should be taken to collect a “core-shaped” increment over the entire depth interval of interest.

4.4 Unless required by the SSWP, avoid collecting ISM samples greater than 1 kg, because larger samples require more time and effort to process (sieve, grind and homogenize). The targeted ISM sample size should be specified in the SSWP and should be based in part on the analytical laboratory’s requirements.

4.5 In general, ISM samples composed of at least 30 to 50 increments are adequate for most DUs. However, for DUs that are large or are expected to contain heterogeneous soils, 50 to 100 increments may be needed. Alternatively, larger areas or areas with physical, chemical or site screening variability may need to be separated into different DUs. The number of DUs and their spatial configuration and the targeted number of increments per ISM sample should be specified in the SSWP. Note that the number of increments will depend on the total sample mass, contaminant variability, selected sampling design (*e.g.,* gridding), and the volume of each increment. Refer to the ISM guidance on the ITRC website (February 2012, update due in 2020) for information on calculating incremental soil mass.

4.6 ISM sample increments need to be approximately equal in weight/volume. Therefore, calibrating field sampling equipment may be necessary to achieve a constant increment size or volume (*e.g.,* adjusting or marking a soil probe to collect a three-inch core).

4.7 The SSWP should clearly identify whether SIFU or Ohio EPA's contract laboratory will be processing (sieving, grinding, homogenizing and subsampling) ISM samples. Sample processing should occur in a controlled environment (*e.g*., Groveport Field Office or Ohio EPA's contract laboratory) to control sampling error. In addition, the SSWP should briefly describe the processing procedures to be used for each analyte group (*e.g.,* metals, semi-volatiles, pesticides/herbicides, PCBs or volatiles).

4.8 If soil samples collected for mercury, SVOCs, PCBs or pesticides need to be dried before ISM processing, do not heat the sample in an oven or with any other device. Allow the samples to air dry for a period of one to three days. Heating a sample (even at a relatively low temperature) may result in COC loss. If the samples are being analyzed for metals only (excluding mercury), then oven-drying is acceptable.

4.9 Samples collected for COCs that may be easily lost through volatilization (*e.g.,* VOCs, certain SVOCs and mercury) should not be processed by sieving or grinding prior to submission to the laboratory.

4.10 Refer to FSOP 2.1.1, Discrete Soil Sampling, for additional procedure cautions associated with discrete soil sampling.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

- 6.1 SSWP copy for field reference
- 6.2 Field logbook, chain-of-custody and other field forms
- 6.3 GPS unit for locating/delineating DUs
- 6.4 Field screening and soil logging equipment and supplies, if needed
- 6.5 Disposable and/or decontaminated soil sampling equipment, including but not limited to spoons, scoops, trowels, probes (triers), hand augers (bucket augers), shovels (Note: generally, a 7/8-inch diameter soil probe is preferred for soils)
- 6.6 Tool(s) to extract soil from sampling device (*e.g.,* a flathead screwdriver for removing clayey soil from a probe)
- 6.7 Stainless steel pans, disposable aluminum pans, stainless steel spoons and/or spatulas
- 6.8 Field sampling containers (jars or bags)
- 6.9 Tape measure
- 6.10 Marking flags or stakes
- 6.11 Personal protective equipment
- 6.12 Decontamination equipment and supplies
- 6.13 Sample processing supplies and equipment (when performed at GFO)
  - 6.13.1 Large rectangular pans for drying soil samples and post-size reduction/homogenization subsampling
  - 6.13.2 #4 (4.75 mm) and/or #10 (2 mm) sieves
  - 6.13.3 Stainless steel grinders
  - 6.13.4 Small rectangular scoops (stainless steel or plastic)
- 6.14 Laboratory containers, preservatives (methanol for VOCs) and labels
- 6.15 Sample cooler(s) with ice

7.0 Procedures

7.1 <u>Decision Unit Designation</u>

Carefully review the SSWP for DU locations and descriptions, field sampling design and ISM sampling protocol before planning field sampling activities. The targeted sample weight/volume, number of increments, and the sampling depth interval should be specified in the SSWP. If additional information is needed to implement ISM sampling as described in this FSOP, then consult with the DERR District Office Site Coordinator or SIFU Sampling Team Leader. Obtain additional input from a DERR risk assessor/lead technical worker or DERR management as needed. The extent of contamination should be understood prior to selecting DUs.

7.2 <u>ISM Sample Collection for Non-Volatile COC Soil Samples (including metals, SVOCs, PCBs or pesticides)</u>

7.2.1 Locate/delineate each DU using GPS (or manually with a tape measure from site structures/features if necessary).

7.2.2 Using tape measures and marking flags or stakes, set up the sampling design (typically with a grid) in accordance with the SSWP. Document any deviations from the SSWP that may be necessary due to site conditions.

7.2.3 Based on the sample weight/volume and number of soil increments specified in the SSWP, calibrate the sampling tool to collect an appropriate increment weight/volume. For example, if the total sample volume needed is 1 L and 30 increments are specified, a 1-inch diameter soil probe should be marked or adjusted to collect a 2.5-inch soil core at each incremental sampling location (30 – 2.5-inch x 1-inch diameter soil cores fill a volume of approximately 1 L).

7.2.4 Collect the required soil increments as described in the SSWP. Typically, a 1-inch stainless-steel step probe is used to collect each increment. Depths can range up to two feet below ground surface and may vary depending on the SSWP and associated DQOs.

7.2.5 If field screening or logging activities are required, collect a co-located screening/logging sample at each increment sampling point.

7.2.6 Combine all increments into an appropriate sample container. Use two or more containers if necessary and be sure to label each container with the same sample label information.

7.2.7 ITRC (February 2012, update due in 2020) recommends that triplicate samples (one sample and two replicates) be collected. The triplicate increments should be collected in the same manner as the sample increments (*i.e.,* same sampling design/grid, depth interval, sampling tool) but should not be collected from the same locations as the other sample increments. The triplicate samples should be independent sampling events with new locations selected for each set of aliquots based on the sample design. Triplicate sample results are used to calculate a 95% upper confidence interval for the mean concentration that helps quantify the uncertainty in the estimate of the mean for the DU. Variability of the contamination and constancy of the sampling team and laboratory subsampling can also be evaluated based on the results of the triplicate samples.

7.2.8 Decontaminate soil sampling equipment between DUs in accordance with FSOP 1.6, Sampling Equipment Decontamination. Decontaminating sampling equipment between soil increments within the same DU is not necessary.

7.3 ISM Sample Processing for Non-Volatile COC Soil (or Moist/Wet) Samples (including metals, SVOCs, PCBs or pesticides)

7.3.1 The SSWP should indicate whether the sample (and replicates) should be sent directly to the contract laboratory for processing and analysis or processed by SIFU and then submitted to the laboratory for analysis. If SIFU performs the processing, use the following procedures (refer to the

February 2012 ITRC ISM guidance for more detail).

7.3.1.1 Allow the sample (or replicate) to air dry for one to three days if necessary. Refer to paragraph 4.8 for the applicability of drying procedures based on COCs and/or sample matrix.

7.3.1.2 Unless otherwise directed by the SSWP, pass the sample through a #4 (4.75 mm) or #10 (2 mm) sieve to remove gravel and other large particles such as twigs, roots, incidental waste materials, etc.

7.3.1.3 Unless otherwise directed by the SSWP, grind and homogenize the entire sample using a stainless-steel grinder.

7.3.1.4 Spread the sample out on a clean, flat surface to form a layer approximately 0.5 to 1 inch thick. Collect the required increments using a rectangular scoop using a random, stratified random or systematic random sampling design. Place these increments in the analytical container to be submitted to the laboratory. Repeat this step as necessary for multiple COCs (*e.g.,* metals, SVOCs). Sample volume should be only that required by the lab for analysis.

7.3.1.5 Ship the sample to the laboratory for analysis in a cooler preserved with ice (4^o to 6^o C).

7.4 <u>ISM Sample Collection and Processing for VOC Soil Samples</u>

While the ITRC ISM guidance includes procedures for sample collection and processing for VOC soil samples, Ohio EPA DERR does not typically utilize this method. However, procedures are provided below in the event use of the method is desired. Management approval would be required.

7.4.1 Soil samples collected for VOC analyses should be collected and preserved with methanol or collected using zero-headspace vapor tight sampling devices (*e.g.,* EnCore samplers). Ohio EPA's contract laboratory will prepare methanol-preserved sample containers. If zero-headspace sampling devices are used, one device will be needed for each increment (*e.g.,* 30 increments would require 30 EnCore samplers).

7.4.2 Follow the procedures described above in paragraphs 7.2.1 through 7.2.5 as applicable.

7.4.3 To avoid collecting soil than may have lost VOCs due to volatilization, samples should be collected from a depth of at least 6 inches below grade or at least 6 inches within an excavator/backhoe soil scoop. The 6-inch depth limit can be adjusted based on site conditions.

7.4.4 If preserving the sample with methanol, immediately place each sample increment in the laboratory-provided container. Containers should be pre-preserved prior to sampling and should have a volume of methanol equal to the volume of all of the increments to be collected (*e.g.,* 30 sample increments require 30 “units” of methanol, with each unit of methanol being approximately equal in weight to the sample increment weight). Be careful not to spill any methanol preservative while filling the sample container. The container should be closed between the addition of each increment.

7.4.5 If using zero-headspace sampling devices, follow the manufacturer’s instructions to collect each soil increment. Immediately place each filled sampling device in a sample cooler preserved with ice (4^o to 6^o C).

7.4.6 Follow the procedures described above in paragraphs 7.2.7 through 7.2.8 as applicable.

7.4.7 Ship the sample to the laboratory for analysis in a cooler preserved with ice (4^o to 6^o C).

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

9.1 Quality assurance/quality control (QA/QC) samples may include equipment blanks, field blank, and/or trip blanks depending on the site-specific chemicals of concern, site conditions and SSWP requirements.

9.2 Triplicate samples should be collected as described in paragraph 7.2.7 to statistically evaluate the uncertainty in the estimate of the mean contaminant concentration(s) for the incremental sampling DU.

10.0 Attachments

Not applicable

11.0 References

FSOP 1.2, Utility Clearance

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 2.1.1, Discrete Soil Sampling

FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW 846 Methods 5035 and 5035A

FSOP 2.3.2, Sediment Sample Collection

Gilbert, R.O., 1987, *Statistical Methods for Environmental Pollution Monitoring*: Van Nostrand Reinhold, New York (ISBN 0-442-23050-8)

The Interstate Technology & Regulatory Council (ITRC), February 2012, *Incremental Sampling Methodology*: Incremental Sampling Methodology Team, ISM-1, Washington, D.C., www.itrcweb.org [update due in 2020]

Ohio Revised Code 3781.25(I)

U.S. EPA, August 2000, *RCRA Waste Sampling Draft Technical Guidance: Planning Implementation and Assessment*: EPA530-D-02-002, Office of Solid Waste, Washington, D.C.

U.S. EPA, December 1995, *Superfund Program Representative Sampling Guidance, Volume 1: Soil (Interim Final)*: EPA 540/R-95/141, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, Washington, D.C.

Table 1
Summary of Soil Sampling Errors and Control Measures[1]

Sampling Error	Cause	Description	Control
Fundamental Error (FE)	Compositional heterogeneity	Error caused by particle size and compositional distribution	Increase sample mass and reduce the size of the largest particles sampled
Grouping and Segregation Error (GE)	Distributional heterogeneity	Error caused by heterogeneous particle distribution	Increase sample mass or number of samples, properly homogenize the sample before selecting a subsample for analysis
Long-Range Heterogeneity Fluctuation Error (CE_2)	Large-scale heterogeneity	Error generated by changes in concentration across space or time	Reduce the spatial interval between samples
Periodic Heterogeneity Fluctuation Error (CE_3)	Periodic heterogeneity	Error generated by periodic changes in concentration over time	Change the spatial or temporal intervals between samples
Increment Delimitation Error (DE)	Sample increment geometry	Error resulting from the shape of the sample increment	Select a sampling plan design and equipment that samples a representative portion of the soil unit of interest
Increment Extraction Error (EE) (ME)?	Sampling device shape	Error resulting from the size and shape of the sampling device	Select sampling equipment that does not exclude certain soil particles based on size or shape, use proper sampling protocols
Preparation Error (PE)	Sample handing	Loss or gain of constituents during sample handling and analytical preparation	Use appropriate sample handling, preservation, transport and preparation protocols

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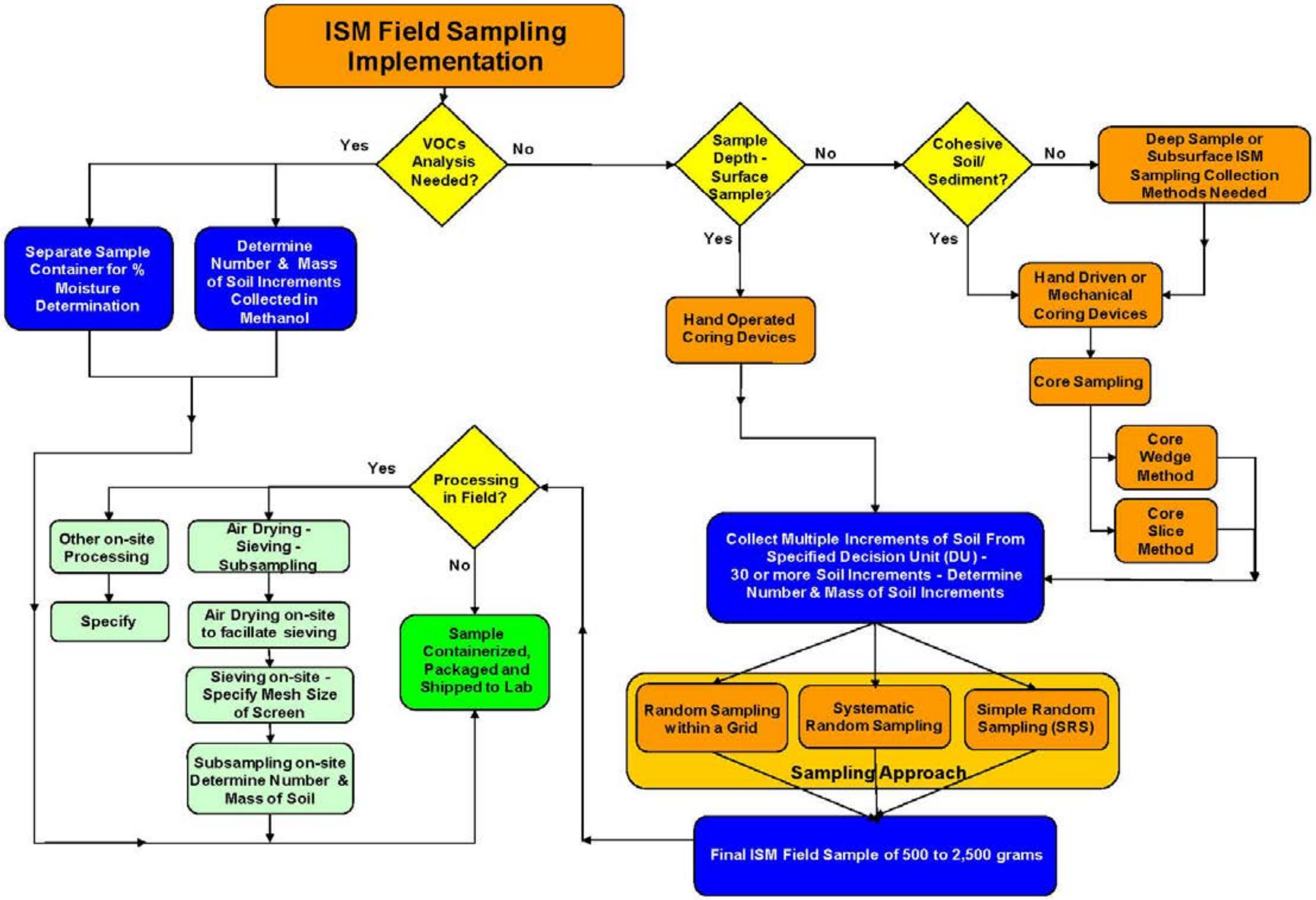
[1] Adapted from the February 2012 ITRC *Incremental Sampling Methodology*, Table 2-2, p. 28

Figure 1
ISM Field Sampling Implementation Flowchart[2]



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[2] From the February 2012 ITRC *Incremental Sampling Methodology*, Figure 5-1, p. 96

APPENDIX A

Guidance on Determining Decision Units

Decision units (DUs) are carefully selected during the development of the site-specific work plan (SSWP), with input from the SIFU sampling team, DERR site coordinator, DERR risk assessor (or other lead technical staff) and DERR management. This guidance is to assist the team in the selection of appropriate DUs.

ISM requires the designation of a DU from which the sample is collected. A DU is the smallest area/volume of soil where a decision is needed regarding the extent and magnitude of contaminants with respect to the potential environmental hazards posed by existing or anticipated future exposures. DUs should be based on a conceptual site model (CSM) and site-specific data quality objectives (DQOs). Considerations in selecting DUs include:

- COCs and their associated environmental hazards
- Present and future exposure scenarios
- Knowledge of spills, extent of contamination, releases or disposal practices and/or other historical site information
- Site geology and physical characteristics that could influence COC distribution and migration
- Evaluation of existing sampling or field screening data

DUs normally should not exceed one-quarter acre (approximately 11,000 square feet), unless justified by special sampling scenarios or site-specific circumstances. Such circumstances may include:

- Metal contaminants from incinerator or smelting plant emissions that were deposited uniformly in surface soil over an extensive area
- Agricultural pesticide contamination from aircraft application over a large farm field

When used over relatively large areas (greater than one-quarter acre), ISM typically captures the broad effects (*i.e.,* proportional representation and thus higher average concentrations) of hot spots due to the improved spatial coverage within the DU, but it does not provide information on the spatial location of smaller volumes of soil containing hot spots of contaminants within the DU, nor does it indicate the magnitude of these areas of elevated concentration if they exist. To detect and delineate potential hot spots using ISM, DUs must be scaled down to be consistent with the area and depth (or volume) of soil of potential concern for hot spots. In other words, to detect a hot spot of a given size, the spatial dimensions of the DUs have to be that size or smaller. Additionally, the hot-spot DUs need to contiguously cover the area suspected of containing hot spots. While smaller DUs may provide better spatial resolution, as discussed above with discrete sampling approaches, there are practical limits on the number of DUs that can be designated, sampled, and analyzed. Therefore, using ISM to detect relatively small hot spots may also be infeasible in many situations (ITRC, February 2012).

Sample Headspace Screening
FSOP 2.1.4 (June 16, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Headspace is the air space above a sample in a partially filled and sealed sample container. Field headspace screening of soil or other solid or liquid samples with a portable vapor/gas detector such as a photoionization detector (PID), flame ionization detector (FID), or other field screening instrument may be used to determine the relative concentrations of certain gasses or vapors in sample headspace.

1.2 Headspace screening can provide a basis for laboratory sample selection. By comparing relative concentrations of volatile contaminants among sample locations and depths, headspace screening is the preferred screening method for the selection of soil samples for volatile organic compound (VOC) analysis. Depending on project data quality objectives, one or more sample screening methods may be appropriate.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Hazardous vapor or gas may be present in concentrations requiring use of personal protective equipment such as respiratory protection (refer to Table 1, FSOP 1.1, Initial Site Entry). Ambient (breathing zone) air conditions need to be monitored.

3.2 Consult the instrument manual to determine if the instrument is intrinsically safe prior to use in potentially flammable or combustible atmospheres.

4.0 Procedural Cautions

4.1 The user should be familiar with the operation of the instrument being used. Consult the instrument manual for operating and calibration instructions specific to the instrument prior to use. FSOP 3.1.1, Photoionization Detector, provides general instructions for proper use of a PID for environmental site assessment activities.

4.2 PIDs and FIDs do not identify specific compounds and the instrument's response is not a one to one response, i.e., ppm to ppm. The response on the instrument can vary from one compound to another. In cases when the compound detected is known with certainty, the response will likely require a correction factor to estimate the concentration. These instruments are calibrated using a relatively non-toxic gas such as isobutylene and zeroed to background air or a clean air source. Since other compounds have different ionization potentials, the instruments response will be either higher or lower than the response to isobutylene.

4.3 PIDs only detect molecules that can be ionized by the type of lamp installed. PIDs are equipped with ultraviolet lamps of different ionization energies (IE), typically 9.8 electron volt (eV), 10.2 eV, 10.6 eV, and 11.7 eV. The IE of the lamp must be higher than the ionization potential (IP) of the compound(s) being screened.

4.4 PID performance may be adversely affected by temperature fluctuations. PID readings can be significantly affected by high humidity environments due to condensation on the ultraviolet lamp. Methane and other compounds, such as constituents in air, nitrogen, oxygen, and carbon dioxide, have ionization potentials greater than 12 eV and will not be detected by the PID. An FID is generally is preferred in situations where large temperature fluctuations, very moist or humid conditions, or methane is a target compound.

4.5 Excessively dusty environments may overwhelm a PID inlet filter and reduce performance by fouling the ionization chamber or lamp. Regularly inspect and change filters during PID use in excessively dusty environments.

4.6 Never allow the instrument probe to draw in liquid or solid material from the sample container, which may damage the instrument.

4.7 Always use a new clean plastic bag or other container (*e.g.,* glass jar) for each headspace screening sample. Do not submit the portion of sample used for headspace screening to the laboratory for volatile organic compound analysis or any analysis that may be compromised due to cross contamination from the screening container. For example, plastic bags can be a source of phthalate cross contamination.

4.8 When performing U.S. EPA Method SW-846 5035/5035A sampling for soils using EnCore® or similar headspace-free sampling devices (FSOP 2.1.7, Soil Sample Collection for VOC Analysis 5035/5035A), the core may be screened directly to determine the best location for sample collection. However, after collecting the sample, a portion of soil core adjacent to the sample location can be placed in a bag or jar for headspace screening. The headspace screening results (and not the core-screening results) should be used for laboratory sample selection.

4.9 Soil and solid samples for laboratory analysis must be collected immediately from the sampling collection device, placed in the laboratory-supplied container, and preserved on ice. Do not perform headspace screening or sample logging activities or otherwise handle or manipulate soil or other solid materials intended for laboratory analysis prior to placing the sample in a laboratory-supplied container. Delaying sample collection or handling the sample excessively prior to collection will likely result in a significant loss of VOCs and compromise sample integrity. To avoid this problem, soil core samples should be split into a screening subsample and a laboratory subsample when collecting bulk (jar) samples per FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Calibration gasses (*e.g.,* isobutylene for PID)
6.2 Clean containers such as sealable plastic bags or jars with foil or film covers
6.3 Hydrogen cylinder (for FID)
6.4 Log book, log sheets, or appropriate field form
6.5 Monitoring instrument with operation manual
6.6 Pens and markers
6.7 Personal protective equipment appropriate for site-specific work activities

7.0 Procedures

7.1 Calibrate the instrument before screening samples, and ensure that the instrument is zeroed, or record background readings before screening.

7.2 Fill the sealable sample container approximately half-full, with the sample to be screened. Disaggregate (*e.g.,* break up) soil or solid samples to the extent possible when placing the sample in the container.

7.3 Seal the container and shake for several seconds.

7.4 Place the container out of direct sunlight and in an area of at least room temperature (65°-70° F) for at least ten minutes. In cold weather, the sample container may need to be taken indoors or placed inside a vehicle to warm to approximately room temperature.

7.5 Immediately prior to screening, shake the container for several seconds again. Open the seal slightly or pierce the foil/film cover with a small hole and insert the instrument probe into the headspace. Take care to not allow soil, water or other materials to enter the tip of the probe.

7.6 Observe and record the maximum instrument reading after placing the instrument probe into the container. This usually occurs within a few seconds of placing the probe into the container. All headspace screening data collected to evaluate the presence of VOC analyses must be recorded on a boring log or field logbook.

7.7 After withdrawing the probe, allow sufficient time for the instrument reading to return to zero or background level before screening the next sample.

7.8 In addition to the procedures described above, the instrument may be used to field screen the borehole atmosphere to evaluate the bulk concentration of VOCs (PID or FID) or gases (other meters, refer to FSOP 3.1.2, Multiple Gas Detection

Meters). This field screening data may be used to monitor health and safety concerns, evaluate the potential for soil VOC contamination before opening soil sample liners, or used as real-time screening information to help evaluate the need for additional sampling or other site assessment activities while in the field. However, under no circumstances are borehole atmosphere screening data to be used for the selection of soil samples for VOC or other chemical analysis. Instead, use the procedures described in paragraphs 7.1 through 7.7 to perform soil sample headspace screening as the basis for selecting soil samples for chemical analysis.

7.9 After headspace screening is completed, dispose of the sample material as investigation derived waste (IDW) in accordance with FSOP 1.7, Investigation Derived Waste.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.7, Investigation Derived Waste

FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods

FSOP 2.1.7, Soil Sample Collection for VOC Analysis (5035/5035A)

FSOP 3.1.1, Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meters

Soil Description, Classification and Logging
FSOP 2.1.5 (June 30, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure describes standard practices and recommendations used by the Division of Environmental Response and Revitalization (DERR) for field soil description, classification and logging.

1.2 This FSOP is not intended to replace the education or experience of Ohio EPA staff members who have degrees in geology, hydrogeology, soil science, geotechnical engineering, or similar fields. This FSOP should be used in conjunction with professional judgment.

1.3 For the purposes of this FSOP, “soil” includes natural deposits or natural fill materials consisting primarily of granular or cohesive mineral particles derived from sedimentary deposition or the weathering of bedrock. In addition, soil may contain minor amounts of natural organic debris or minor amounts of inorganic or organic waste materials. Soil may be unconsolidated or consolidated but is never cemented or lithified.

1.4 As discussed in this FSOP, soil description is a method of documenting the observed physical properties of soil for scientific or engineering purposes. Soil properties that are important for evaluating the behavior and fate of contaminants at waste sites include, but are not necessarily limited to the following:

- texture (also referred to as grain-size or particle size distribution)
- plasticity characteristics
- color
- moisture content
- sedimentary structures
- anthropogenic influence: the presence of fill materials, waste materials, hazardous substances, or petroleum

The soil properties and soil property criteria described in the FSOP are based on ASTM D2488-09a, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure). ASTM D2488 is also recommended by the Ohio EPA Division of Drinking and Ground Water (DDAGW) Technical Guidance Manual for Ground Water Investigations (TGM), Chapter 3, Characterization of Site Hydrogeology, for soil description and classification for hydrogeologic investigations.

1.5 Soil classification is a method of systematically categorizing soil into groups with similar physical properties based on field description or laboratory testing. For environmental site assessment and engineering purposes, a soil classification system provides a uniform description of the physical properties of soil. U.S. EPA

(April 1999) recommends the use of the following soil classification systems for environmental investigations at hazardous waste sites:

1.5.1 The Unified Soil Classification System (USCS) as described by ASTM D2488-09a, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)

1.5.2 The United States Department of Agriculture (USDA) Soil Textural Triangle, USDA Natural Resources Conservation Service Soil Survey Manual, Chapter 3, Examination and Description of Soils (Figure 3-16)

Project data quality objectives (DQOs) should determine whether the USCS or USDA systems (or both) are used.

1.6 Soil description and classification should be performed: 1) during the collection of soil samples for laboratory analysis; 2) during the installation of borings, monitoring wells or soil gas/vapor probes; or 3) whenever characterization of subsurface geologic conditions is needed to meet site assessment project or data quality objectives.

Describing and classifying soil samples in an accurate and consistent manner:

- is critical for understanding site geology and hydrogeology
- helps to ensure proper location and construction of monitoring wells and soil gas probes
- facilitates the selection of samples for laboratory analysis and the subsequent evaluation of contaminant distribution and migration
- may provide an understanding of contaminant migration pathways
- determines the thickness of cover materials or depth of wastes or contaminated soil layers
- provides a means of correlating soil types with geophysical surveys

1.7 Logging the description and classification of soil samples includes the continuous recording of drilling and sampling, field monitoring, and well or probe construction data. A field logging form (example attached) is recommended for logging soils collected with direct-push or rotary drilling rigs or excavating equipment. The form may also be designed to record ground water data and serve as a monitoring well or soil gas probe construction diagram.

2.0 Definitions

Refer to the attached list (Soil Descriptive Terminology).

3.0 Health and Safety Considerations

3.1 Wear appropriate personal protective equipment (PPE) when working in the vicinity of drilling rigs or other types of mechanical equipment used for soil sampling, in accordance with the site-specific health and safety plan. At a minimum, PPE should include protective eyewear, footwear, and hearing protection. In addition, a hard hat is required when working in the vicinity of drilling rigs and the use of canvas coveralls or similar protective clothing is recommended.

3.2 Use heavy protective gloves to help prevent hand injuries when opening and handling split-spoon samplers, core barrels, or plastic soil core liners.

3.3 Wear chemical-resistant gloves when handling soil samples to avoid direct contact with chemical contaminants. Always thoroughly wash your hands after completing soil logging activities.

3.4 If free product or splash hazards are a concern during drilling or sampling, use of a chemically resistant suit (e.g., Saranex® or coated Tyvek®) is recommended.

3.5 If drilling and soil sampling activities cause dusty conditions, respiratory protection may be necessary to provide protection from dust-inhalation hazards. Work should be stopped to assess site conditions. Work requiring respiratory protection may only be performed by staff certified to wear respiratory protection. Depending on site-specific conditions and chemicals of concern, monitoring with a particulate meter and/or other air monitoring instruments as appropriate. For action levels, refer to Table 1 of FSOP 1.1, Initial Site Entry.

3.6 Conduct air monitoring in accordance with the site-specific health and safety plan. For action levels, refer to Table 1 of FSOP 1.1, Initial Site Entry.

3.7 Dress appropriately for anticipated weather conditions, and always have ample drinking water available when working in hot weather. Insect repellant may be needed for protection from ticks, mosquitoes, and other biting insects in heavily wooded areas.

4.0 Procedure Cautions

4.1 For logging soil borings or excavations greater than six feet deep, a field logging form (example attached) is preferred. Logging soil borings using a field logbook or log sheets may be difficult due to the volume of information that typically needs to be recorded.

4.2 Use a level of detail for soil descriptions that is consistent with the site-specific work plan and project DQOs.

4.3 If the driller is collecting soil samples so quickly that logging is difficult, direct the driller to slow down or stop. Soil cores should be processed (*i.e.,* logged, screened, and sampled) as soon as possible after being retrieved from the ground.

4.4 When recording soil descriptions, use a consistent format such as that recommended in paragraph 7.9. Doing so makes logging easier, improves the readability of the field log, and facilitates subsequent data entry in the office.

4.5 Do not indiscriminately apply soil classification systems. Project DQOs will determine whether the USCS, USDA classification system, or both systems should be used for a project. Additionally, DQOs may indicate how soil classification should be applied at a site with respect to boring locations and depth of investigation.

4.6 An accurate location of each boring should be included on the logging form (or field notebook). The location could include a narrative description of the boring location with reference to site features, a schematic and/or GPS coordinates.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard. In addition, personnel who log soil borings should have a background in geology, hydrogeology, soil science or geotechnical engineering, or should have received training in soil classification, description and logging from a qualified individual.

6.0 Equipment and Supplies

6.1 Field logging form (example attached)
6.2 Field logbook or log sheets (*recommended for use as an alternative to a logging form only if soil logging activities are limited to borings or excavations less than six feet deep*).
6.3 Engineering ruler or measuring tape with 0.1 foot increments for measuring soil cores
6.4 Stainless steel spatula or knife for examining and sampling soil core
6.5 Field guide for soil classification/description or soil texturing, a geotechnical (sand) gauge, and/or Munsell Soil Color chart (optional)
6.6 Hand lens (optional, helps identify waste materials)
6.7 Magnet (optional, helps identify waste materials)

7.0 Procedures

7.1 Before drilling begins record project information, boring identification and location, the date, and drilling and sampling method(s) on the soil logging field form.

7.2 Be sure that the driller identifies the top of each core sample.

7.3 If any of the soil in the sampler appears to be caved or sloughed material from the open boring overlying the sampled interval, remove it from the sampler. Do not log it as part of the sampled interval or submit it for laboratory analysis. If in doubt based on sample appearance, consult with the driller regarding the stability of the borehole, i.e., is it collapsing or heaving between sample intervals?

7.4 Using the ruler or tape, measure the length of the soil core recovered from each sampled interval (excluding any caved/sloughed material if present). Record the sampler type and the sampled interval recovery to the nearest 0.1 foot on the soil logging field form. Do not record a recovery that is greater than the length of soil core actually recovered. For example, if a core sampler pushed from 8.0 to 10.0 ft recovers only 1.5 ft of soil core, record the recovery as 1.5 ft (or 8.0 to 9.5 ft) and not 2.0 ft (or 8.0-10.0 ft).

7.5 Discuss possible reasons for core loss with the driller, as well as the driller’s insight on likely soil or fill materials encountered based on the behavior of the drilling and sampling equipment.

7.6 Split or scrape any soil core consisting of cohesive soils (silts or clays) using a stainless steel knife or spatula.

7.7 Quickly examine the soil core and evaluate the following properties (preliminary evaluation) to select samples for field screening and/or analytical sampling:

- Soil texture (*i.e.,* is it mostly gravel, sand, silt, or clay?) and changes in texture within the core sample
- Moisture content
- The presence of waste materials, potentially hazardous substances, or petroleum (*the hand lens and/or magnet may be helpful*)

7.8 As required, collect soil samples for field screening and laboratory analysis based on project DQOs and preliminary core examination (paragraph 7.5). Assign each screening or laboratory sample an identification number). Record the sample identification and depth interval to the nearest 0.1 foot on the soil logging form.

7.9 Record a description of the soil core. The soil properties included in the description will depend on project DQOs; however, a soil description should generally include the following information:

7.9.1 **Soil color:** the following colors (with Munsell Soil Color Chart numbers for reference only) are recommended for soil description:

Brown Shades	**Munsell #**	**Gray Shades**	**Munsell #**
Brownish yellow	10YR 6/6	Grayish brown	2.5Y 5/2
Light brown	10YR 7/4	Light gray	2.5Y 7/1
Reddish brown	5YR 5/4	Gray	2.5Y 5/1
Brown	10YR 4/3	Greenish gray	GLEY1 5/1
Dark yellowish brown	10YR 4/6	Olive gray	5Y 4/2
Dark brown	10YR 3/3	Dark gray	2.5Y 4/1

If the soil exhibits a primary color and one or more secondary colors, describe the soil color as “mottled” or “with mottling”, e.g., “gray with brownish yellow mottling” or “mottled light brown, dark yellowish brown, and light gray”.

7.9.2 **Soil classification:** follow the attached Unified Soil Classification System Field Guidance to classify soils according to the USCS or the attached Estimating Soil Texture By Feel (Presley and Thien, September 2008) to classify soils according to the USDA System.

7.9.3 **Moisture content:** ASTM D2488-09a recommends describing soil moisture content as follows:

- **Dry** – absence of moisture, dry and dusty to the touch
- **Moist** – damp but no visible water
- **Wet** – visible free water, usually soil is below the water table

The terms “**slightly moist**” (intermediate between dry and moist) and “**very moist**” (intermediate between moist and wet) may also be used.

7.9.4 **Plasticity characteristics** (for silts and clays only): describe the soil **plasticity**. If possible, also include descriptions for **consistency**, **dilatancy**, and/or **toughness** (refer to Soil Descriptive Terminology, attached). The dry strength test is generally too time-consuming to be performed.

7.9.5 **Sedimentary structures:** describe soil sedimentary structures (refer to Soil Descriptive Terminology)

7.9.6 **Anthropogenic influence:** determine if the soil is native or fill material, and describe the presence of waste materials (construction/demolition debris, solid waste, industrial wastes), hazardous substances, or petroleum (*the hand lens and magnet may be helpful*)

7.10 The following soil properties may also be included in soil descriptions at the discretion of the soil logger:

7.10.1 Secondary grain size percentages as recommended by ASTM D2488-09a:

- Trace – particles are present but estimated to be less than 5%
- Few – 5% to 10%
- Little – 15% to 25 %
- Some – 30% to 45%
- Mostly – 50% to 100%

7.10.2 Depositional environment (*Note: this is a geologic interpretation based on soil texture and sedimentary structures which should be made by a geologist or hydrogeologist.*)

7.10.3 Oxidation, leaching and/or degree of weathering

7.10.4 Other properties described in ASTM D2488-09a

7.11 The following soil description format is suggested: *consistency – color – soil classification: moisture content, plasticity characteristics, sedimentary structures, anthropogenic influence, other*

Examples:

- *firm gray lean clay with dark yellowish brown mottling: moist, medium toughness and plasticity, massive structure, solvent odor*
- *brownish yellow loam: dry to slightly moist, low plasticity, vertical fractures with iron oxide staining, broken glass and demolition debris (concrete, brick and wood fragments)*
- *dark brown sand: wet, stratified, trace fine gravel*
- *soft gray lean clay with silt: moist to very moist, low to medium plasticity, no dilatancy to slow dilatancy, varved, lacustrine (lake) deposit*

Regardless of the specific soil description format, a consistent format should be utilized for borings on the same site/property or installed for the same project.

7.12 In addition to soil descriptions, record field information associated with boring installation, soil sampling or well or probe installation on the soil logging form. Such information may include, but is not limited to the following:

- Field screening data
- Laboratory sample identification numbers for soil and ground water samples
- Ground water levels

- Relevant information recorded by the driller, e.g., changes in penetration resistance
- Monitoring well screen placement and sand pack thickness
- GPS coordinates and/or other boring location data

7.13 Properly dispose of IDW in accordance with FSOP 1.7, Investigation-Derived Wastes.

7.14 In addition to completing a field logging form for each soil boring, an Ohio Department of Natural Resources (ODNR) Well Log and Drilling Report Form may need to be filed with the ODNR Division of Soil and Water Resources. Refer to FSOP 1.8, ODNR Well Construction Logs & Well Sealing Reports.

8.0 Data and Records Management

Please refer to FSOP 1.3, Field Documentation.

9.0 Quality Control and Quality Assurance

Draft soil boring logs should be peer-reviewed by an Ohio EPA staff member with a degree in geology, hydrogeology, soil science, geotechnical engineering, or similar field experience before being finalized.

10.0 Attachments

Logging Field Form (example)

Soil Descriptive Terminology

Unified Soil Classification System Field Guidance

Presley, D. and Thien, S., September 2008, Estimating Soil Texture By Feel, Kansas State University

11.0 References

ASTM D 2488-09a, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.7, Investigation Derived Waste

FSOP 1.8, ODNR Well Construction Logs & Well Sealing Reports

Ohio EPA Division of Drinking and Ground Waters, April 2015, Technical Guidance Manual for Ground Water Investigations: Chapter 3, Characterization of Site Hydrogeology

Munsell Soil Color Chart

USDA Natural Resources Conservation Service, October 1993, Soil Survey Manual: Chapter 3, Examination and Description of Soils

U.S. EPA (D.S. Burden and J.L. Sims), April 1999, Ground Water Issue, Fundamentals of Soil Science as Applicable to the Management of Hazardous Wastes: EPA/540/S-98/500

Soil Descriptive Terminology

Page 1 of 2

Consistency: the relative ease with which a fine-grained soil (silt or clay) can be deformed. ASTM D2488-09a recommends describing consistency as follows:

- **Very soft** – thumb will penetrate soil more than 1 inch
- **Soft** – thumb will penetrate soil about 1 inch
- **Firm** – thumb will indent soil about ¼ inch
- **Hard** – thumb will not indent soil, thumbnail will indent soil
- **Very hard** – thumbnail will not indent soil

Dilatancy: volume increase under loading, or expansion (and flow) of a saturated fine-grained soil (silt or clay) in response to shaking. ASTM D2488-09a recommends describing dilatancy as follows:

- **None** – no visible change
- **Slow** – water appears slowly on the surface of the soil during shaking (and disappears slowly upon squeezing)
- **Rapid** – water appears quickly on the surface of the soil during shaking (and disappears quickly upon squeezing)

Dry Strength: the relative strength of a dried fine-grained soil (silt or clay) specimen approximately 1/2 inch in diameter. ASTM D2488-09a recommends describing dry strength as follows:

- **None** – the specimen crumbles into powder when handled
- **Low** – the specimen crumbles into powder in response to finger pressure
- **Medium** – the specimen crumbles or breaks into pieces with considerable finger pressure
- **High** – the specimen cannot be broken with finger pressure, but can be broken between the thumb and a hard surface
- **Very High** – the specimen can be broken between the thumb and a hard surface

Plasticity: the ability of a fine-grained soil (silt or clay) to deform continuously under constant stress. ASTM D2488-09a recommends describing plasticity as follows:

- **Nonplastic** – a 1/8 inch diameter thread cannot be rolled at any water content
- **Low Plasticity** – the thread can barely be rolled
- **Medium Plasticity** – the thread is easily rolled and not much time is required to reach the plastic limit (i.e., the water content at which a soil changes from a plastic state to a semisolid state)
- **High plasticity** – the thread is easily rolled and considerable time rolling and kneading is required to reach the plastic limit; the thread can be re-rolled several times after reaching the plastic limit

Soil Descriptive Terminology

Sedimentary Structure: a soil structure formed by sedimentary deposition, e.g., glacial, stream, or lake deposition (primary sedimentary structure) or by processes occurring subsequent to deposition and/or soil formation, e.g., weathering or hydrologic processes (secondary sedimentary structure). Terminology used to describe sedimentary structure includes the following:

- **Massive** – stratification (or layering) is not present; the soil appears to have a homogeneous structure which is the same in all directions
- **Stratified** – distinct near-horizontal layers (or beds) formed primarily by differences in texture (grain-size)
- **Graded** – stratified layers exhibiting grain-sizes that gradually increase or decrease with depth (usually referred to as "graded bedding")
- **Laminated** – horizontal layers less than approximately 0.2 inches thick (laminations)
- **Varved** – alternating light and dark laminations (varves) formed by seasonal sediment deposition in lakes
- **Lensed** – a soil containing small pockets or lenses one or more different soil types, e.g., pockets of sand in a clay
- **Fractured** – vertical or horizontal planes of separation formed by wetting/drying, freezing/thawing, or other physical processes to which the soil is exposed; fractures are generally near-vertical and often contain mineralization distinct from the adjacent soil (iron oxides/hydroxides, carbonates, etc.)
- **Slickenslided** – fracture planes that appear polished or glossy and sometimes slightly curved and/or striated; generally slickenslides are formed by shearing of the soil in response to loading or deformation (e.g., swelling clays)

Toughness: pressure required to roll a fine-grained soil (silt or clay) into a 1/8 inch thread. ASTM D2488-09a recommends describing toughness as follows:

- **Low** – only slight pressure is needed to roll the thread, which is weak and soft
- **Medium** – medium pressure is needed to roll the thread, which is moderately stiff
- **High** – considerable pressure is needed to roll the thread, which is very stiff

Unified Soil Classification System (USCS) Guide[1]

Page 1 of 2 (Silt and Clay)

If the soil consists of >= 50% fines (silt and clay), then the soil is a fine-grained soil. Follow these steps for field classification of silt (M) and clay (C):

1. Using manual field tests, classify the soil as a silt (ML), lean clay (CL), elastic silt (MH) or fat clay (CH) based on its plasticity characteristics:

Soil Type	Group Symbol	Dry Strength	Dilatancy	Toughness & Plasticity
Silt	ML	None to low	Slow to rapid	Nonplastic to low
Lean Clay	CL	Medium to high	None to slow	Medium
Elastic Silt	MH	Low to medium	None to slow	Low to medium
Fat Clay	CH	High to very high	None	High

Tips for classifying fine-grained soils:

- Plasticity and dilatancy may be used to differentiate silt (ML) and lean clay (CL) (*dry strength and toughness data usually aren't critical field tests*).
- Lean clay (CL) is more common than fat clay (CH) in Ohio.
- Elastic silt (MH) is rarely encountered in Ohio.
- Use "lean clay" rather than "silty clay" (CL-ML) for USCS field description of soil. Laboratory testing is necessary to classify a soil as a USCS silty clay due to its narrow plasticity index range (4-7).

2. After identifying the soil as a silt or clay, estimate the percentage of sand and gravel (S&G) ("*plus No. 200 material*" or > 0.075 mm diameter particles) in the sample:
   a. If < 15% S&G, classify the soil as a **silt** (ML), **lean clay** (CL), **elastic silt** (MH), or **fat clay** (CH)
   b. If 15%-25% S&G, add "**with sand**" if the %S >= %G or "**with gravel**" if the %G > %S, *e.g.*, **lean clay with sand** (CL), **silt with gravel** (ML)
   c. If >= 30% S&G and the %S >= %G, add the modifier "**sandy**", and if >= 15% G add "**with gravel**", *e.g.*, **sandy silt** (ML), **sandy lean clay with gravel** (CL)
   d. If >= 30% S&G and the %G > %S, add the modifier "**gravelly**", and if >= 15% S add "**with sand**", *e.g.*, **gravelly fat clay** (CH), **gravelly lean clay with sand** (CL)
3. If the fine-grained soil contains enough organic matter to influence its physical properties, *e.g.*, the soil feels "spongy" during field plasticity testing, classify it as an organic silt or clay (OL or OH). Follow step two (above) to describe the coarse-grained texture characteristics (S&G) of the soil. If the soil is mostly organic matter, classify it as peat (PT).

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[1] Based on ASTM D2488-09a, Standard Practice for Description and Identification of Soils (Visual–Manual Procedure)

Unified Soil Classification System (USCS) Guide[1]

Page 2 (Sand and Gravel)

If the soil consists of < 50% fines (silt and clay), then the soil is a coarse-grained soil (sand or gravel). Follow these steps for field classification of sand (S) and gravel (G):

1. Estimate the relative percentages of sand and gravel:
   a. If the % S >= % G, then the soil is a sand
   b. If the % G > % S, then the soil is a gravel

2. Estimate the percentage of fines (silt and clay) present in the soil:
   a. <= 5%
   b. Approximately 10%
   c. >= 15 %

3. Determine if the fines are mostly clay (plastic) or silt (nonplastic)

4. If the soil contains <= 5% fines or approximately 10% fines, then determine if the soil is well-graded (W) (*poorly sorted with a wide range of grain sizes*) or poorly graded (P) (*well-sorted with relatively uniform grain size*)

   a. If the soil contains <= 5% silt or clay, the soil is **well-graded** or **poorly graded sand** (SW or SP) or **well-graded** or **poorly graded gravel** (GW or GP)

   b. If the soil contains approximately 10% silt or clay, the soil is **well-graded** or **poorly graded sand with silt** (SW-SM, SP-SM) or **clay** (SW-SC, SP-SC) or **well-graded** or **poorly graded gravel with silt** (GW-GM, GP-GM) or **clay** (GW-GC, GP-GC)[2]

5. If the soil contains >= 15% silt or clay, then the soil is **silty** or **clayey sand** (SM or SC) or **silty** or **clayey gravel** (GM or GC); <u>the grading modifiers are not used</u>

6. If the soil is sand and contains > 15% gravel, add "**with gravel**" to the classification, *e.g.*, **poorly graded sand with gravel** (SP)

7. If the soil is gravel and contains >= 15% sand, add "**with sand**" to the classification, *e.g.*, **well-graded gravel with silt and sand** (GW-GM)

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[1] Based on ASTM D2488-09a, Standard Practice for Description and Identification of Soils (Visual–Manual Procedure)

[2] Dual symbols (two symbols separated by a hyphen, e.g., SP-SM) must be used when the soil has between 5% and 12% fines or when the liquid limit and plasticity index values plot in the CL-ML (silty clay) area of the plasticity chart. Dual symbols are not the same as borderline symbols (two symbols separated by a forward slash, e.g., CL/CH) which should be used to indicate that soil exhibits properties that do not distinctly place it into a specific group (Appendix X3).

Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods

FSOP 2.1.6 (July 9, 2020)

Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

This FSOP describes field procedures used by Division of Environmental Response and Revitalization (DERR) remedial response personnel to collect soil and other solids by bulk sampling methods for volatile organic compound (VOC) analysis (*e.g.,* using a sampling spatula to manually fill unpreserved laboratory supplied containers with soil).

1.1 Bulk sampling procedures are not compliant with U.S. EPA SW 846 Method 5035 or 5035A sampling requirements. Field procedures that are compliant with Methods 5035 and 5035A are described in FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis by U.S. EPA Methods 5035 and 5035A. Methods 5035 and 5035A are preferred for collecting soil and solid VOC samples and should be used by DERR personnel whenever possible.

1.2 DERR recognizes, however, that certain regulatory programs or laboratory certification programs may not allow or support the use of the U.S. EPA Method 5035 or 5035A procedures. If Ohio EPA Voluntary Action Program (VAP) laboratory certified data is needed, bulk containers may only be submitted for high concentration samples (>200 ppb) using SW-846 Method 8260B. If bulk containers are submitted for low level analysis (<200 ppb) using Method 8260B, the data will not be certified.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Wear appropriate personal protective equipment as specified in the project health and safety plan (HASP) while conducting sampling activities.

3.2 Conduct air monitoring as specified in the project HASP during sampling activities. Refer to Table 1 of FSOP 1.1, Initial Site Entry.

4.0 Procedure Cautions

4.1 Be familiar with all relevant program requirements, laboratory capabilities or certification requirements and project data quality objectives to ensure that the procedures described in this FSOP are appropriate for the sampling event

4.2 Sample containers should be filled to the top with no headspace.

4.3 Soil and solid samples must be collected immediately from the sampling collection device, placed in the laboratory-supplied container, and preserved on ice. Do not perform headspace screening or sample logging activities or otherwise handle or manipulate soil or other solid materials intended for laboratory analysis prior to placing the sample in a laboratory-supplied container. Sample screening may be performed on a separate portion of sample or co-located sample which is not submitted for laboratory analysis after the laboratory sample is collected and preserved. Delaying sample collection or handling the sample excessively prior to collection will likely result in a significant loss of VOCs and compromise sample integrity.

4.4 Always wear clean sampling gloves before collecting each sample.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

The following is a list of equipment and supplies that are generally required for bulk soil or solid sampling:

6.1 Chain-of-custody form
6.2 Ice
6.3 Laboratory-supplied containers
6.4 Paper towels
6.5 Sample cooler
6.6 Sample labels
6.7 Sampling gloves
6.8 Stainless steel spatula or spoon
6.9 Trip blanks
6.10 Water-proof markers and pens

7.0 Procedures

7.1 Obtain the sample directly from the sampling device (*e.g.,* direct-push core barrel, split barrel sampler, auger bucket, trowel, etc.) with a clean stainless-steel spatula or spoon and immediately place the sample in an appropriate laboratory-supplied container. Do not screen, log, homogenize or unnecessarily handle the sample before placing it into the container.

7.1 Fill the container completely so that there is no headspace visible in the container. Care should be taken not to overfill or underfill the container and to keep the lip and threads of the container free from soil, sand, debris, etc., to provide a good seal with the container lid.

7.2 Wipe any soil or debris from the outside of the container with a clean paper towel and place the lid on the container.

7.3 Immediately place the labeled sample container in a cooler with ice and trip blank samples.

7.4 Decontaminate stainless steel spatulas, spoons, and any other sampling equipment used between samples in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.5 Follow all applicable criteria in FSOP 1.5, Sample Custody and Handling, when handling or shipping/transporting samples to the laboratory.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Quality assurance/quality control (QA/QC) samples will depend on the site-specific work plan, DQOs, or laboratory requirements. QA/QC requirements need to be determined prior to ordering sample containers or devices. Trip blank samples should be included in each cooler which holds samples to be analyzed for VOCs. Inclusion and analysis of trip blanks imparts information on potential contamination of samples during sample, handling and field conditions by accompanying samples during mobilization, sampling, demobilization and shipment operations.

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.5, Sample Custody and Handling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 2.1.7, Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW-846 Methods 5035 and 5035A

Soil Sample Collection for Volatile Organic Compound Analysis Compliant with U.S. EPA SW-846 Methods 5035 and 5035A
FSOP 2.1.7 (July 9, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

U.S. EPA SW-846 Methods 5035 and 5035A, *Closed-System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples* (U.S. EPA 1996 and 2002), describe a closed system purge and trap process for analyzing volatile organic compounds (VOCs) in solid materials such as soil, sediment, and wastes. These procedures, which include field methods for sample collection, preservation, and handling, may be used in conjunction with any appropriate gas chromatographic procedure such as U.S. EPA SW-846 Methods 8260, 8021 or 8015.

This FSOP describes field procedures used by Division of Environmental Response and Revitalization (DERR) personnel to collect soil and other solids for VOC analysis that conform to the sample collection, preservation and handling procedures acceptable under Methods 5035 and 5035A. Field procedures that are compliant with Methods 5035 and 5035A are preferred to bulk sampling procedures (e.g., using a sampling spatula to manually fill unpreserved laboratory supplied containers with soil) and should be used by DERR personnel whenever possible. DERR recognizes, however, that certain regulatory or laboratory certification programs may not currently allow or support the use of Method 5035 or 5035A procedures. These programs may require bulk sampling of soil or other solids for VOC analysis. For such situations, consult FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods.

1.1 Several sample collection and preservation methods are described in Methods 5035 and 5035A. The methods specify field or laboratory preservation of samples in one or more solvents including methanol, sodium bisulfate, and organic-free reagent-grade water or laboratory preservation of the sample by freezing. Two general methods are described in this FSOP. One involves collection of the sample followed by immediate field preservation, and the other method describes collection of the sample in a headspace-free sample device and delivery to the analytical laboratory for preservation or analysis within 48 hours of sample collection. Other collection and preservation methods detailed in Methods 5035 and 5035A may also be acceptable on a case-by-case basis depending on project data quality objectives (DQOs) (U.S. EPA 1999), the site - specific work plan or laboratory or regulatory requirements.

1.2 Some of the procedures described in this FSOP may not be appropriate for Bureau of Underground Storage Tank Regulations investigations or Targeted Brownfield Assessments. Check program and laboratory certification requirements as well as laboratory capabilities prior to sampling.

1.3 The procedures listed in this FSOP are not acceptable for Toxicity Characteristic Leaching Procedure (TCLP) sampling.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Handle flammable or toxic solvent preservatives such as methanol or sodium bisulfate carefully. Refer to the appropriate safety data sheet for the preservative.

3.2 Wear appropriate personal protective equipment as specified in the project health and safety plan (HASP) while conducting sampling activities. Wear appropriate eye protection, gloves and other splash protection as appropriate when handling solvent preservatives.

3.3 Conduct air monitoring as specified in the project HASP during sampling activities. Refer to Table 1 of FSOP 1.1, Initial Site Entry.

4.0 Procedure Cautions

4.1 Be familiar with all relevant program requirements, laboratory capabilities or certification requirements and project DQOs to determine that the procedures described in this FSOP are appropriate for the sampling event.

4.2 Consult with the laboratory prior to sample collection to determine appropriate sample collection, preservation, shipping and handling and holding time requirements as these requirements may vary between laboratories. Consult the laboratory in advance to determine if the laboratory detection limits will meet project DQOs.

4.3 If a headspace-free sampling device such as the En Core® Sampler is used, then the sample must be preserved within 48 hours of collection by the laboratory. Samples need to be delivered to the laboratory as soon as possible, and the laboratory needs to receive advance notice of sample arrival. This is especially critical for Saturday delivery.

4.4 Preserve and containerize laboratory samples as soon as possible. Steps should be taken to minimize headspace screening, handling, or other manipulation of samples collected for laboratory analysis prior to sample preservation or containerization. For example, don’t submit material from headspace screening for laboratory analysis, and don’t allow soil cores to sit for an extended period prior to containerizing the sample. (Sample screening may be performed on a separate portion of sample or co-located sample which is not submitted for laboratory analysis after the laboratory sample is collected an preserved.)

4.5 If a field or laboratory solvent preservation method is used, an additional unpreserved portion of the sample must also be submitted to determine the percent moisture to calculate VOC concentration on a dry weight basis.

4.6 Soil samples from multiple sampling locations should not be collected with the same device. However, multiple aliquots of sample from the same location may be collected (into separate vials) using a device such as the Terra Core® sampler or EasyDraw Syringe®.

4.7 Samples collected using the Terra Core® sampler, EasyDraw Syringe® or similar coring device should be calibrated to ensure that the proper amount of sample material is collected. This may be achieved by adjusting the sampler to the soil density, per location, necessary to achieve 5.0 (+/- 0.5) grams of sample. Some samplers have calibrations on the cylinder of the sampler (*e.g.,* EasyDraw Syringe®, etc.). Alternatively, collect several trial samples with a clean plastic syringe. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length that corresponds to 5.0+/- 0.5 g. Discard each trial sample.

4.8 Methods 5035 / 5035A state that when practical, pre-prepared vials containing methanol should be weighed on the day of sampling to ensure that no solvent has been lost since the time of container preparation. Vials with > 0.01 g less methanol than noted on the vial should be returned to the laboratory for disposal and not used for sampling.

4.9 Use a portable analytical balance for confirming the weight of sample aliquots and pre-preserved sample vials. Limitations of using portable balances may include imprecise readings due to lack of a stable and sheltered location for the balance (*e.g.,* a mobile laboratory, fixed building, etc.) and variability in instrument precision or calibration standard weights between the laboratory's and Ohio EPA's instruments or standards. Balances should be calibrated in the field on a daily basis using an appropriate standard weight.

4.10 Always wear clean sampling gloves before collecting each sample.

4.11 Non-cohesive sample material (*e.g.,* dry sand, sediments/sludges with a high moisture content, etc.) sampled using En Core®, Terra Core® or similar devices should be collected differently than cohesive or consolidated materials, refer to Section 7.2.3. Alternate collection methods should be considered based on work plan and DQOs.

4.12 Aggregate, cemented material or material larger than the diameter of the sampler cannot be effectively collected using En Core®, Terra Core® or similar sampling devices. These materials should be collected using an alternate sampling technique.

4.13 If samples containing methanol preservative are to be shipped by common courier (*e.g.,* UPS, FedEx), air or ground, ensure that applicable U.S. DOT and/or IATA regulations are followed. The shipping of methanol is regulated by U.S. DOT, Title 49 of the Code of Federal Regulations (Parts 171 through 180).

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

The following is a list of equipment and supplies that may be required depending on the selected sampling method:

6.1 Appropriate sample handle for En Core® (T-Handle) or EasyDraw Syringe® (PowerStop Handle®)
6.2 Chain-of-custody form
6.3 Dry weight containers
6.4 En Core® samplers or similar headspace-free sample collection devices
6.5 Terra Core® or EasyDraw Syringe® samplers or similar sample collection devices
6.6 Ice
6.7 Paper towels
6.8 Preservative
6.9 Sample cooler
6.10 Sample labels
6.11 Sampling gloves
6.12 Sealable plastic bags
6.13 Trip blanks
6.14 Water-proof markers and pens
6.15 Analytical field balance and calibration weights
6.16 Pre-preserved/pre-tared sample containers, including stir bar (as applicable)

7.0 Procedures

7.1 Collection and solvent field preservation of samples followed by laboratory analysis:

7.1.1 Obtain a new unused sampler and remove the end cap. Seat the plunger on the Terra Core® or place the EasyDraw Syringe® into the PowerStop Handle® per the manufacturer's directions (Recommended Use of Terra Core®, Recommended Use of the EasyDraw Syringe® and The PowerStop Handle®, attached)

7.1.2 Expose the soil to be sampled by scraping the surface with a clean spatula or spoon. Push the device into the soil until the sample chamber is full and then extract the device.

7.1.3 Wipe any soil or debris from the outside of the sampler with a clean paper towel. Rotate the plunger 90 degrees to align with the slots in the body of the sampler.

7.1.4 Place the mouth of the sampler into a laboratory-supplied vial containing the appropriate solvent preservative and extrude the sample into the vial by pushing the plunger down. Replace the cap on the vial immediately and gently swirl (do not shake) the vial to saturate the entire sample.

7.1.5 Complete a sample label on the vial. (Note: labels should be affixed to the vials prior to weighing/reweighing the vials. Labels affixed after filling and weighing of the vials may introduce a sample weight error).

7.1.6 Place the vial with the preserved sample in a locking plastic bag and place in a cooler with ice.

7.1.7 Repeat Steps 7.1.1 through 7.1.5 to collect as many vials per sample as directed by the laboratory for VOC analysis.

7.1.8 Collect a portion of the soil sample in the same manner as above (Steps 7.1.1 through 7.1.3) and extrude the sample into an unpreserved vial or container (*e.g.,* 40mL or 60mL VOA vial) for laboratory determination of percent moisture. This data is needed for the laboratory to determine VOC concentrations on a dry weight basis.

7.1.9 Immediately place filled sample containers into a sample cooler with ice or chilled to 4°C and including trip blank samples. Samples collected by Methods 5035 / 5035A should be segregated from samples with gross contamination or free product and packed in separate coolers.

7.2 Collection of samples followed by laboratory preservation and analysis with an En Core® Sampler or similar headspace-free sample device:

7.2.1 Obtain a new sampler and place the sampler in the T-Handle per the manufacturer's directions (Disposable En Core® Sampler Sampling Procedures, attached).

7.2.2 For cohesive material, use the handle to push the sampler into the soil until the body is completely full and the O-ring rests against the tabs. Remove the sampler and wipe any excess soil from the sampler's exterior with a clean paper towel or wipe.

7.2.3 The En Core® Sampler is not recommended for non-cohesive sample material (*e.g.,* dry sand, sediments/sludge with a high moisture content). Other sampling methods should first be considering when establishing the project's data quality objectives.

7.2.4 If the En Core® Sampler is chosen as the sampling method for non-cohesive material, push the sampler plunger down into the O-ring until it rests against the tabs. Depress the locking lever on the handle and place the sampler, plunger end first, into the handle, aligning the slots on the device body with locking pins in the handle. Turn the sample upside down and fill with a clean spatula or other device.

7.2.5 Cap the sampler body while it is still in the handle. Push the cap flat and twist to lock.

7.2.6 Remove the sampler from the handle by depressing the locking lever on the handle while twisting and pulling the sampler from the handle.

7.2.7 Lock the plunger by rotating the plunger rod counterclockwise until the wings are firmly resting against the tabs.

7.2.8 Attach a sample label to the sample device and place the sampler(s) in a locking plastic bag. Place the bag in a cooler with ice.

7.2.9 Repeat the above steps to collect as many sampling devices per sample as directed by the laboratory.

7.2.10 Collect at least one portion of sample in a sample device or container (*e.g.,* 2oz jar, 40mL or 60mL VOA vial) for laboratory dry weight determination of the sample.

7.2.11 Immediately place filled sample containers into a sample cooler with ice (4°+/-2° C). Samples collected for high-level VOC analysis should be segregated from samples collected by Methods 5035 / 5035A.

7.2.12 Deliver the samples to the laboratory within 48 hours of collection. Ensure that there is sufficient ice in the cooler for preservation during sample shipment.

7.3 Follow all applicable criteria in FSOP 1.5, Sample Custody and Handling, when handling or shipping/transporting soil samples to the analytical laboratory.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Quality assurance / quality control (QA/QC) samples) will depend on the site-specific work plan, DQOs, or laboratory requirements. QA/QC requirements need to be determined prior to ordering sample containers or devices. Trip blank samples should be included in each cooler which holds samples to be analyzed for VOCs. Inclusion and analysis of trip blanks imparts information on potential contamination of samples during sample, handling and field conditions by accompanying samples during mobilization, sampling, demobilization and shipment operations.

10.0 Attachments

En Novative Technologies, Inc., Recommended Use of Terra Core®

Chemisphere, Inc., Recommended Use of the EasyDraw Syringe® and The PowerStop Handle®

En Novative Technologies, Inc., Disposable En Core® Sampler Sampling Procedures

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.5, Sample Custody and Handling

FSOP 2.1.6, Soil Sample Collection for Volatile Organic Compound Analysis by Bulk Sampling Methods

U.S. DOT, Title 49 CFR, Parts 171 through 180

U.S. EPA, July 2002, SW-846 Method 5035A: Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil And Waste Samples

U.S. EPA, December 1996, SW-846 Method 5035: Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil And Waste Samples

Well Development
FSOP 2.2.1 (July 14, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This field standard operating procedure (FSOP) describes standard monitoring well development practices used by the Ohio EPA Division of Environmental Response and Revitalization (DERR) for both newly installed wells and redevelopment of existing wells. Monitoring wells installed and/or developed by DERR are typically 0.5-inch to 2.0-inch inside-diameter wells. The practices and equipment discussed in this procedure focus on effective development of small-diameter wells used for ground water sampling.

1.2 The practices and equipment described herein may or may not be appropriate for the development of larger (> 2.0-inch inside diameter) wells used for aquifer testing, ground water remediation, gradient control, or water supply purposes (ASTM, 2018). For such situations this FSOP may serve as only a general guidance. Development of larger diameter wells may require techniques or equipment that are not discussed in this FSOP. Additional reference materials may need to be reviewed, and the site-specific work plan may need to specify additional well development procedures.

1.3 Monitoring well development is performed to (1) remove fluids that may have been added during drilling or during the well construction process, (2) remove fine sediment from the vicinity of the well screen, and (3) ensure good hydraulic interconnection between the sand filter pack and the adjacent geologic materials (formation) in which the well screen is installed. Proper development is especially critical for wells used to evaluate turbidity-sensitive ground water constituents such as metals, and for wells used to evaluate hydraulic conductivity or ground water yield (Ohio EPA TGM, February 2009).

1.4 The terms “well development” and “well purging” (the removal of water from a well) are not synonymous. While purging is an integral part of the overall well development effort, simply purging a monitoring well generally does not provide adequate development of the filter pack and surrounding formation.

1.5 For the purposes of this FSOP, development techniques include (1) surging and pumping, (2) purging with an inertial lift pump, (3) over-pumping, and (4) bailing:

1.5.1 Surging and pumping may be performed using an electric submersible pump or a bladder pump with or without a surge block. The surge block may be a separate assembly or attached to the pump assembly. If a surge block is not available, then the pump must be of sufficient diameter and weight to effectively surge the well. “Surging” means forcing the flow of water back and forth through the filter pack. This action optimizes the hydraulic interconnection between the well and surrounding formation by (1) removing fine sediments and (2) grading (sorting) and stabilizing the filter pack and adjacent (unconsolidated) formation. Pumping may be performed during or after surging. Surging and pumping is the preferred technique for wells installed in bedrock, gravel, or sand. This technique should not be used for wells installed in silt or clay.

1.5.2 Purging with a manually operated inertial lift pump (*e.g.,* a Waterra Pump™) may be used to develop monitoring wells installed in bedrock, gravel, sand, silt, or clay. This method is very effective and may be applied over a wider range of formation materials.

1.5.3 A surge block attachment may be used in wells with screens set mostly in bedrock, gravel, or sand. The attachment may also be used in wells with screens set mostly in silt if surging is performed gently for a short duration (*e.g.,* three one-minute intervals). The surge block attachment should not be used when developing wells that screen mostly clay.

1.5.4 Over-pumping is the process of repeatedly pumping the monitoring well at a relatively high rate (as compared to the well yield) to rapidly draw down the water level as far as possible, and then turning off the pump and allowing the well to recharge. Over-pumping may be performed with a submersible pump or peristaltic pump (depending on the well yield). This technique will remove fine sediments from the well casing and filter pack but does not grade (sort) the filter pack, and therefore develops the well less effectively than surging and pumping or an inertial lift pump with a surge block. In addition, it is generally less effective than an inertial lift pump at removing sediment that has accumulated at the bottom of the well screen. Over-pumping is an acceptable alternative for wells that screen mostly silt or clay.

1.6 Bailing can be used to develop monitoring wells installed in bedrock, gravel, sand, silt, and clay. However, bailing is not a very effective well development technique and should generally be avoided. Surging and pumping or purging with an inertial lift pump are much more effective techniques for wells that screen mostly bedrock, gravel, or sand. For wells that screen mostly silt or clay, purging with an inertial lift pump or over-pumping are likely to produce better results.

1.7 Development techniques and documentation should support the project data quality objectives and work plan. Requirements for well development are in part project-specific, and therefore the specific technique, level of effort, and associated data will vary between projects and sites. Not all information on the DERR Monitoring Well Development Form will be applicable to every project or site.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) before performing well development activities. The HASP should address any site-specific hazardous that may be associated with well development activities.

3.2 Due to likelihood of direct contact with ground water during well development, eye and dermal protection are strongly recommended.

3.3 If concerns exist regarding potentially toxic or explosive atmospheres within the well casings, open each monitoring well and screen the atmosphere (1) within the breathing zone above the open well casing and (2) within the well casing with a PID and/or LEL/O_2 meter.

3.4 If a portable generator is being used to operate a development pump, ensure that the generator is properly grounded to avoid electric shock.

4.0 Procedure Cautions

4.1 If a monitoring well has been installed using liquid grout to seal the annular space above the filter pack, well development activities should not be performed until the grout has set for at least 24 hours. Otherwise, development activities could damage the well by drawing uncured grout into the filter pack and well screen.

4.2 Monitoring wells that contain nonaqueous phase liquids (NAPL) should not be developed. Typically, the presence of NAPL is confirmed if an immiscible fluid layer at least 0.01 inches thick can be detected with an interface probe or clear bailer. Often, NAPL occurs in a discrete layer within the screened formation. Well development will distribute the NAPL throughout the filter pack and surrounding formation and generate purge water that is time-consuming and costly to dispose. In addition, development will likely cause subsequent NAPL recovery efforts to be more difficult and compromise any attempt to collect a representative ground water sample from the well.

4.3 Excessively or vigorously surging a monitoring well can permanently damage the filter pack. As a general rule, small-diameter wells should not be surged for a time interval longer than three minutes before pumping or manually purging sediment-laden water from the well and should not be surged for more than 15 minutes in total. Surging always should be performed slowly and gently.

4.4 As a general rule, monitoring wells that screen mostly clayey silt or clay should not be surged, because an excessive amount of fine sediment could be drawn into the filter pack and significantly reduce the hydraulic interconnection between the well and surrounding formation. Removing such sediment from the filter pack is very difficult, if not impossible. If surging is deemed necessary based on well performance concerns, it should be performed very slowly and gently and for short time intervals (*e.g.,* no more than three one-minute intervals), each followed by evacuation of at least one well volume to remove sediment from the well.

4.5 Stainless-steel, weighted non-disposable PVC or Polyethylene bailers should be used for well development. Disposable Teflon or PVC bailers designed for ground water sampling should not be used for well development.

4.6 If the measured total depth of a monitoring well indicates that more than 10 percent of the screen has filled with sediment, excess sediment should be

removed by using a bailer or inertial lift pump before lowering an electric submersible pump or bladder pump into the well. Operation of an electric submersible pump or bladder pump in a well with significant sediment accumulation may result in the pump becoming lodged ("sand locked") within the well screen or casing. Additionally, an excessive sediment load can damage the internal components of some electric submersible pumps.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard. In addition, field staff assigned to perform monitoring well development should be DERR or Division of Drinking and Ground Water personnel who have a background in hydrogeology and/or well development experience.

6.0 Equipment and Supplies

6.1 Equipment and supplies needed for every well development event regardless of technique or site-specific criteria:

6.1.1 Boring logs and well construction diagrams
6.1.2 Decontamination equipment and supplies (refer to FSOP 1.6, Sampling Equipment Decontamination)
6.1.3 Graduated bucket or other container to estimate purge volumes
6.1.4 Personal protective equipment (protective eyewear, gloves, and footwear at a minimum)
6.1.5 Plastic sheeting
6.1.6 Purge water containers
6.1.7 Watch or cell phone
6.1.8 Water level meter
6.1.9 DERR Monitoring Well Development Form

6.2 Equipment and supplies needed for well development depending on the technique or site-specific criteria:

6.2.1 Bladder pump system
6.2.2 Electric submersible pump system
6.2.3 Inertial lift pump system
6.2.4 Peristaltic pump system
6.2.5 Pump-specific tubing
6.2.6 Monitoring instruments required to evaluate the following purge water

stabilization parameters: temperature, pH, specific conductance (conductivity), oxidation/reduction potential, turbidity, or dissolved oxygen

6.2.7 Photoionization Detector (PID) and/or Lower Explosive Limit/Oxygen (LEL/O_2) meter for health and safety monitoring

6.2.8 Stainless steel or PVC bailer (and bailer rope)

6.2.9 Surge block

7.0 Procedures

7.1 Review the boring log(s) and well construction diagram(s) to determine the most appropriate well development technique.

7.2 Well development data should be recorded using the DERR Monitoring Well Development Form (attached).

7.3 Deviations from this procedure should be documented with a brief explanation of the reason(s) for the deviation.

7.4 Initial field activities:

7.4.1 If concerns exist regarding potentially toxic or explosive atmospheres within the well casings, open each monitoring well and screen the atmosphere (1) within the breathing zone above the open well casing and (2) within the well casing with a PID and/or LEL/O_2 meter.

7.4.1.1 If volatile organic compound (VOC) concentrations or the percentage LEL *in the breathing zone* exceed the health and safety action levels provided in Table 1 of FSOP 1.1, Initial Site Entry or site-specific action levels, close and secure the monitoring well. Development of the well will need to be delayed until appropriate health and safety measures can be implemented.

7.4.1.2 If VOC concentrations or the percentage LEL *in the well casing* exceed the health and safety action levels provided in Table 1 of FSOP 1.1 or site-specific action levels but VOC concentrations or the percentage LEL in the breathing zone do not, allow the well to vent. Continue monitoring the breathing zone as necessary while performing well development activities.

7.4.1.3 Record health and safety monitoring data using the DERR Monitoring Well Development Form or a field logbook or field log sheets (*e.g.,* ranges of PID and LEL measurement values).

7.4.2 Measure the static water level and total depth of each well scheduled to be developed that day. Record these data using the DERR Monitoring Well Development Form.

7.4.3 Calculate the volume of the static water column in each well scheduled to be developed. At least three well volumes must be removed from every well for development efforts to be considered complete (refer to Step

7.3.5). Further, stabilization parameters should be monitored based on well volumes (rather than arbitrary time intervals) to avoid purging too little water between successive stabilization parameter measurements and prematurely concluding that purge water stabilization has been attained (refer to Step 7.4.2).

One Well Volume (gal) = (Total Depth, ft **–** Static Water Level, ft) **x** 3.14 **x** (Well Radius, ft)^{2} **x** 7.48 gal/ft^{3}

One Well Volume (L) = (Total Depth, ft **–** Static Water Level, ft) **x** 3.14 **x** (Well Radius, ft)^{2} **x** 28.32 L/ft^{3}

The following table summarizes volume (gallons and liters) per foot (of casing/screen length) for 0.5- to 4-inch inside diameters wells:

Well Inside Diameter (inches)	Volume per Foot (gallons)	Volume per Foot (liters)
0.5	0.01	0.04
0.75	0.02	0.09
1.0	0.04	0.15
1.5	0.09	0.35
2.0	0.16	0.62
3.0	0.37	1.39
4.0	0.65	2.47

Ideally, one “well volume” should include the water contained in the filter pack surrounding the screen. However, the filter pack contribution is typically less than 25 percent of the total well volume, and therefore is not a critical consideration for well development in most situations. Either well volume calculation (with or without the filter pack contribution) may be used at the discretion of the District Office Site Coordinator (based on the recommendation of the DDAGW Geologist assigned to the site.) If the District Office Site Coordinator does not indicate a preference, SIFU staff will decide based on their best professional judgment. Calculating the well volume with filter pack contribution requires the saturated length of the filter pack interval (which is usually longer than the screen), the boring diameter, and an estimation of the filter pack porosity (typically 25 to 30 percent):

One Well Volume Including Filter Pack (gal) = [(Total Depth, ft **–** Static Water Level, ft) **x** 3.14 **x** (Well Radius, ft)^{2}] **x** 7.48 gal/ft^{3} **+** [Filter Pack Length, ft x 3.14 **x** ((Boring Radius, ft)^{2} **–** (Well Radius, ft)^{2}) **x** 0.25 or 0.30] **x** 7.48 gal/ft^{3}

7.4.4 Calibrate all field monitoring equipment that will be used for well development.

7.4.5 At each well location, set up the well development equipment on a plastic sheet to avoid possible cross contamination through direct contact with the ground. Clean 5-gallon buckets may be used to hold pump hoses, air lines, bailer rope, etc.

7.4.6 Compare the total depth measurement to the total depth shown on the well construction diagram. If the measured total depth indicates that more than 10 percent of the screen has filled with sediment, remove the excess sediment by using a bailer or an inertial lift pump before lowering an electric submersible pump into the well.

7.5 Specific procedures for development techniques:

7.5.1 Surging and pumping: start at the top of the well screen and gradually work downwards in 2 to 3 foot intervals to the bottom of the well, surging slowly with a surge block, a pump equipped with a surge block, or the pump itself. Surge for two to three minutes and then pump the well to remove at least one well volume of sediment-laden water. After repeating this process three to five times, continue to pump the well at a sustainable rate.

7.5.2 Inertial lift pump:

7.5.2.1 If using an inertial lift pump with a surge block attachment, start at the top of the well screen and gradually work downwards in 2 to 3-foot intervals to the bottom of the well, surging slowly. Surge and purge for two to three minutes to remove at least one well volume of sediment-laden water. After repeating this process three to five times, continue to purge the well at a sustainable rate. The pump foot valve should be within 2 inches of the bottom of the well during purging to remove sediment.

7.5.2.2 If using an inertial lift pump without a surge block attachment, purge the well at a sustainable rate. The pump foot valve should be within 2 inches of the bottom of the well during purging to remove sediment.

7.5.3 Over-pumping: lower the pump intake to the top of the well screen. Purge the well at a pumping rate high enough to drawdown the water level to the pump intake. Turn off the pump, allowing the water level in the well to recover to at least two feet above the pump intake. Lower the pump approximately two feet deeper into the well screen and repeat the process. After repeating this process three to five times, continue to purge the well at a sustainable rate.

7.5.4 Bailing:

7.5.4.1 If using a bailer to develop a monitoring well installed in bedrock, gravel, sand, sandy silt, or silt, surge the screened interval with the bailer, using the same method as described in paragraph 7.3.1 above. While surging, *gently* tap the bailer on the bottom of the well to remove sediment. Remove at least one well volume of water after each period of surging. Continue to bail the well at a sustainable rate; bail from the top of the water column (do not lower the bailer into the screened interval) to avoid resurging the filter pack and re-elevating the turbidity.

7.5.4.2 If using a bailer to develop a monitoring well installed in silty clay or clay, initially purge the well by lowering the bailer to the bottom of the well for each withdrawal so that it is lowered and raised through the entire length of the well screen (*do not surge as described in Step 7.3.1 above*). *Gently* tap the bailer on the bottom of the well to remove sediment. After three well volumes have been removed, continue to bail the well at a sustainable rate. Bail from the top of the water column (do not lower the bailer into the screened interval) to avoid resurging the filter pack and re-elevating the turbidity.

7.5.5 Continue well development using one or more of the procedures described above until (1) the sediment thickness remaining in the wells is less than 1 percent of the screen length or 0.1 ft (whichever is larger), (2) required purge-water stabilization parameters have stabilized, and (3) at least three well volumes of purge water have been removed.

7.5.6 Record well development procedures and the volume of water removed from the well using the DERR Monitoring Well Development Form.

7.6 Stabilization parameter monitoring:

7.6.1 The use of temperature, pH, and specific conductance as purge water stabilization parameters for well development is strongly recommended. Depending on the project data quality objectives and associated work plan requirements, stabilization parameters may include temperature, pH, conductivity, oxidation-reduction potential, turbidity, or dissolved oxygen. If the work plan does not include well development stabilization parameters, the District Office Site Coordinator will decide which, if any, stabilization parameters will be monitored (based on the recommendation of the DDAGW Geologist assigned to the site.) If the District Office Site Coordinator does not indicate a preference, stabilization parameters will be monitored at the discretion of SIFU staff.

7.6.2 Once the parameters have stabilized, collect at least three successive measurements for each parameter to evaluate stabilization criteria. At least one well volume should be purged from the monitoring well prior to each successive measurement.

The following table summarizes purge water stabilization criteria:

Purge Water Parameters	Stabilization Criteria
Temperature	0.5° C
pH	+/- 0.2 Standard Units (S.U.)
Specific Conductance	+/- 3%
Oxidation-Reduction Potential (ORP)	+/- 20 millivolts (mV)
Purge Water Parameters	**Stabilization Criteria**
Turbidity	< 10 Nephelometric Turbidity Units (NTUs) or +/- 10% for turbidity > or = 10 NTUs
Dissolved Oxygen (DO)	+/- 10% or 0.2 mg/l, whichever is greater

7.7 Water level and pumping/purging rate monitoring:

7.7.1 Monitoring the water level in the well is recommended during well development activities if possible. Record water level data using the DERR Monitoring Well Development Form.

7.7.2 Monitoring the pumping or purging rate is recommended during well development activities if possible. Record data for calculating pumping or purging rates (water volumes withdrawn over time) using the DERR Monitoring Well Development Form.

7.7.3 Water level data and pumping or purging rates can provide general information about the formation hydraulic conductivity and the well yield, which in turn may be helpful for selecting appropriate ground water sampling techniques or for locating additional monitoring wells during future assessment activities.

7.8 Upon completion of well development activities, ensure that each well is properly closed and secured.

7.9 Purge water and other waste disposal:

7.9.1 Refer to FSOP 1.7, Investigation Derived Wastes.

7.9.2 Well development water with concentrations of petroleum or hazardous substances exceeding Voluntary Action Program generic potable use standards [OAC 3745-300-08(D)(3)] must be containerized and properly disposed.

7.9.3 If well development water is suspected to be a hazardous waste, contact SIFU for assistance.

7.10 Monitoring well redevelopment is needed if more than 10 percent of the screened interval has filled with sediment. In addition, redevelopment may be needed if:

7.10.1 The well produces excessively turbid water as compared to the turbidity typically observed or measured during prior sampling events.

7.10.2 The well exhibits anomalously high or low water levels as compared to its range of historic water levels, or significantly slower recharge rates than expected.

7.10.3 The well casing or surface seal is damaged and subsequently repaired. Surface water, soil, or other foreign materials may have entered the well after it was damaged and/or during its repair. Use of a downhole camera may be used to evaluate whether a well has been damaged.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

DERR Monitoring Well Development Form

11.0 References

ASTM, D5521 / D5521M-18, Standard Guide for Development of Groundwater Monitoring Wells in Granular Aquifers, ASTM International, 2018, www.astm.org http://www.astm.org/cgi-bin/resolver.cgi?D5521D5521M

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 3.1.2, Multiple Gas Detection Meter

Ohio EPA Division of Drinking and Ground Waters, 2009, Technical Guidance Manual for Ground Water Investigations (Chapter 8: Well Development, Maintenance, and Redevelopment)

Ground Water Level Measurement
FSOP 2.2.2 (July 20, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Measurement of ground water levels from wells or piezometers is generally required to:

- Provide static water level data to prepare a potentiometric surface map and evaluate ground water flow direction
- Determine the depth to set a ground water sampling pump
- Estimate the volume of water to be purged from the well prior to sampling
- Monitor water level drawdown while purging and sampling or during aquifer testing

1.2 This FSOP is applicable to the measurement of ground water levels with an electronic water level indicator (refer to FSOP 3.1.4, Electronic Water Level Indicator) in monitoring wells, piezometers, water supply wells, soil gas probes and soil borings that intersect the water table.

1.3 Measuring water levels may be difficult in some situations, including small-diameter (< 1 inch) monitoring wells, piezometers or soil gas probes. In addition, water supply wells may not provide access for water level measurements and often contain a dedicated pump with plumbing and electrical wiring that can obstruct or entangle a water level probe or pressure transducer.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Consult the instrument’s operation manual to determine if it is intrinsically safe when working in an area where there is a potential fire or explosion hazard.

3.2 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work.

4.0 Procedure Cautions

4.1 The user should be familiar with the instrument operation. Consult the instrument manual for operating instructions prior to use.

4.2 Inspect the instrument tape for cuts or abrasions.

4.3 If concerns exist regarding potentially toxic or explosive atmospheres within the well casings, open each monitoring well and screen the atmosphere (1) within the breathing zone above the open well casing and (2) within the well casing with a PID and/or LEL/O_2 meter. (Refer to FSOP 3.1.1, Photoionization Detector and FSOP 3.1.2, and FSOP 3.1.2, Multiple Gas Detection Meter.)

4.3.1 If volatile organic compound (VOC) concentrations or the percentage LEL *in the breathing zone* exceed the health and safety action levels provided in Table 1 of FSOP 1.1, Initial Site Entry or site-specific action levels, close and secure the monitoring well. Development of the well will need to be delayed until appropriate health and safety measures can be implemented.

4.3.2 If VOC concentrations or the percentage LEL *in the well casing* exceed the health and safety action levels provided in Table 1 of FSOP 1.1 or site-specific action levels but VOC concentrations or the percentage LEL in the breathing zone do not, allow the well to vent for a few minutes and then measure the LEL again. If the LEL is less than the action level, proceed with the measurement.

4.3.3 Record health and safety monitoring data using the DERR Monitoring Well Development Form or a field logbook or field log sheets (*e.g.,* ranges of PID and LEL measurement values).

4.4 The use of electronic water level indicators to measure the depth to water in residential or other wells with pumps and associated plumbing is discouraged, because the tape may become entangled in the downhole plumbing or centralizing disks. If water level measurements must be obtained from such wells, the pump and plumbing may need to be temporarily removed first, which usually requires the services of a registered water well drilling contractor. Additional disinfection of the well and/or downhole equipment may be required by the county or local health department that has jurisdiction over the well.

4.5 Use caution when lowering and raising the tape within a well. A sharp casing edge or burr may damage the tape if it is pulled against the edge of the casing.

4.6 Do not use electronic water level indicators in wells known or suspected to contain nonaqueous phase liquids (NAPL). Use an interface meter instead (refer to FSOP 3.1.3, Interface Meter).

4.7 If using the water level indicator to measure the total depth of the well, add the length of any probe extension beyond the sensor pin (*e.g.*, 0.3 ft) to obtain an accurate measurement of the total well depth.

4.8 Be sure the instrument has charged batteries. Bring spare batteries.

4.9 Remove the batteries if the instrument is not going to be used for an extended period of time.

4.10 When reeling the tape in, be careful that the tape does not twist, kink or fold. The tape protection device (attached to the reel) should be used to prevent abrasion while the probe is in the well.

4.11 Always transport the instrument in a protective case or secure the instrument during transport.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Water level indicator with battery and operation manual
6.2 Protective case for instrument transport
6.3 Data forms or field book and pen
6.4 Well keys and tools needed to open well(s)
6.5 Decontamination equipment and supplies
6.6 Personal protective equipment appropriate for site-specific work activities

7.0 Procedure

7.1 Make sure the electronic water level indicator is functioning properly and the battery is charged. When testing the instrument, use tap water and not distilled water. Distilled water contains no dissolved solids to act as electrolytes and the alarms will not be activated.

7.2 Open the well. Allow sufficient time for the water level to equilibrate, especially if the well is installed in a confined aquifer or if air pressure is released (a "pop" is heard) when the well casing cap is removed.

7.3 Locate the designated measuring point mark on the casing. For monitoring wells this is generally marked on the highest point or north side of the top of the inner casing. If a mark is not present, use the highest visible point of the inner casing as the measuring point. If the inner casing is level (no discernible high point), use the north side of the casing. In either case mark a new measuring point.

7.4 Turn the water level indicator's switch on to the highest sensitivity position. Press the test button to ensure battery and alarm function.

7.5 Slowly lower the tape down the well, taking caution not to twist the tape or allow the tape to scrape the edge of the casing as it is being lowered. When the probe contacts water, the instrument's audible and visual alarms will be activated.

7.6 Raise the tape slightly to lift the probe out of the water. The alarm should stop. A mild shake of the tape may be necessary to remove water from the probe's sensor pin. Lower the tape slightly until the alarms activate and hold the tape firmly against the side of the casing so that the probe does not move up or down.

7.7 Carefully read the tape measurement at the well’s measuring point to the nearest hundredth of a foot (0.01 ft) and verify.

7.8 Record the water level reading.

7.9 If using the water level indicator to measure the total depth of the well, turn off the instrument. Next, lower the tape to the bottom of the well and record the tape reading at the measuring point. Remember to add the length of any probe extension to the total depth measurement.

7.10 Decontaminate the probe and the length of tape lowered into the well in accordance with the decontamination procedures specified in FSOP 1.6, Sampling Equipment Decontamination or the site specific work plan. Use deionized water and a paper towel to wipe the tape as you reel it up from the well.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 3.1.1, Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meter

FSOP 3.1.3, Interface Meter

FSOP 3.1.4, Electronic Water Level Indicator

Detection and Sampling of Nonaqueous Phase Liquids in Monitoring Wells
FSOP 2.2.3 (July 28, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure describes standard practices used by the Division of Environmental Response and Revitalization (DERR) for the detection, sampling and handling of nonaqueous phase liquid (NAPL), including light nonaqueous phase liquid (LNAPL) and dense nonaqueous phase liquid (DNAPL) that may be present in ground water monitoring wells at contaminated sites.

1.2 NAPLs are organic liquids that exist as a separate, relatively immiscible phase when in contact with water. NAPLs are divided into the general categories of LNAPL and DNAPL based on density relative to that of water:

1.2.1 LNAPL floats on the water column and accumulates on the ground water surface because its density is less than that of water (< 1.0 g/cc). Petroleum products such as gasoline, diesel fuel and motor oil are typical sources of LNAPL (U.S. EPA 1995).

1.2.2 DNAPL sinks through the water column and accumulates at the bottom of the well because its density is greater than that of water (> 1.0 g/cc). DNAPL sources include chlorinated solvents, coal tar, wood preservative wastes and pesticides (U.S. EPA 1991).

1.3 NAPL may be analyzed to determine its physical properties and chemical composition. Knowledge of physical properties such as density or viscosity is important for evaluating NAPL mobility and distribution in the subsurface and for remediation system design. Knowledge of chemical composition may be used for computing the effective solubility of NAPL components, identifying potential NAPL sources and evaluating the applicability of remedial technologies.

1.4 Refer to the Ohio EPA Technical Guidance Manual for Ground Water Investigations (Chapter 10) for additional guidance on collecting ground water samples from monitoring wells containing NAPL.

2.0 Definitions

Free Product: term sometimes used as a synonym for NAPL

3.0 Health and Safety Considerations

3.1 LNAPL typically consists of a flammable petroleum product (*e.g.,* gasoline) that releases vapors of volatile organic compounds (VOCs) known to be toxic and/or carcinogenic (*e.g.,* benzene).

3.2 DNAPL typically consists of nonflammable, volatile chlorinated solvents (*e.g.,* perchloroethylene) that are known to be toxic and/or carcinogenic.

3.3 Personal protective equipment (PPE) should be chemically resistant to organic solvents.

3.4 If NAPL (especially LNAPL) is present in a monitoring well, vapors migrating from the well casing may contaminate the work area breathing zone with VOC concentrations and/or flammable vapors that exceed health and safety action levels (Table 1, FSOP 1.1, Initial Site Entry). The work zone should be monitored using a photoionization detector (PID) for VOC concentrations and a four-gas meter for lower explosive limit (LEL) and percent oxygen (O_2). Monitoring, sampling or LNAPL recovery efforts may need to be performed using respiratory protection by qualified DERR staff.

3.5 All equipment used to monitor or sample NAPL (or ground water from wells containing NAPL) must be intrinsically safe.

3.6 NAPL samples that are flammable fluids cannot be shipped via air and must be delivered to the laboratory by an Ohio EPA staff member, a courier, or via ground shipment. Always assume that NAPL from an unknown source is flammable fluid for the purpose of sample shipment.

4.0 Procedure Cautions

4.1 Monitoring or sampling equipment that directly contacts NAPL must be resistant to organic solvents.

4.2 Excessive agitation of a monitoring well water column containing NAPL will distribute the NAPL throughout the filter pack and surrounding formation. This will cause subsequent NAPL recovery efforts to be more difficult and will compromise any attempt to collect a representative ground water sample from the well. Monitoring wells that contain NAPL generally should not be developed, purged using a bailer or pumped at a high flow rate relative to the well yield.

4.3 Measurement of NAPL layers in monitoring wells should always be performed prior to sampling or otherwise extracting ground water from the well.

4.4 Regardless of the measuring method used, the measured thickness of LNAPL or in a monitoring well rarely corresponds to that in the adjacent saturated formation, and typically exceeds the LNAPL-saturated formation thickness by approximately 2 to 10 times. This discrepancy can be caused by several factors, including but not limited to soil or bedrock capillary forces, the volume and rate of the NAPL release, fluctuation in ground water elevations or the presence of low-permeability layers above the water table. Therefore, a measured LNAPL thickness in a monitoring well should be qualified as an apparent thickness.

4.5 The measured thickness of DNAPL in a monitoring well may not correspond to that in the adjacent saturated formation depending on the placement of the well screen with respect to the DNAPL layer and the underlying impermeable layer. Therefore, a measured DNAPL thickness in a monitoring well generally should be qualified as an apparent thickness, unless well construction records indicate that the screen intercepts the DNAPL interface and the bottom elevation of the screen closely approximates the elevation of the underlying impermeable layer.

4.6 If measuring NAPL thickness using a transparent bailer, the apparent NAPL thickness in the bailer may be greater than the NAPL thickness in the well casing due to positive fluid displacement by the bailer.

4.7 DNAPL layers should be measured and sampled using double check-valve bailers rather than single check valve bailers. The second (upper) check valve on a double-check valve bailer isolates the sample as the bailer is lifted through the well water column, thereby maintaining the integrity of a DNAPL sample.

4.8 Ground water elevations in monitoring wells containing LNAPL should be corrected for the depression of the LNAPL/water interface to obtain total hydraulic head. The depression is caused by the weight of the LNAPL. The correction is performed by multiplying the measured LNAPL thickness by an estimate of the LNAPL specific gravity, and then adding the result to the elevation of the LNAPL/water interface. Approximate specific gravities at 20° C (68° F) for common petroleum product sources include the following:

- Gasoline, 0.74 g/cc
- Jet fuel or kerosene, 0.80 g/cc
- Diesel fuel, 0.85 g/cc
- Motor oil, 0.90 g/cc

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Detecting and measuring NAPL in monitoring wells:

6.1.1 Decontamination equipment and supplies (refer to FSOP 1.6, Sampling Equipment Decontamination)
6.1.2 Field logbook or field log sheets and appropriate field log forms
6.1.3 Multiple gas detection meter (aka four-gas meter), to include lower explosive limit/ oxygen LEL/O_2 sensors)
6.1.4 Oil-absorbent pads or mats
6.1.5 Interface meter (oil/water interface probe) or transparent bailers, single check valve (for LNAPL) and double check valve (for LNAPL or DNAPL)

6.1.6 Personal protective equipment (protective gloves at a minimum)
6.1.7 Photoionization detector (PID)
6.1.8 Site map with monitoring or recovery well locations
6.1.9 Water-proof pens and markers

6.2 Collecting NAPL samples from monitoring wells for laboratory analysis:

6.2.1 All equipment and supplies listed above in Section 6.1
6.2.2 Chain-of-custody forms
6.2.3 Protective eyewear and coveralls
6.2.4 Sample containers and labels as specified by the laboratory
6.2.5 Sample coolers
6.2.6 Sampling device(s), including single-check valve bailers (for LNAPL), double-check valve bailers (for LNAPL or DNAPL), or an intrinsically safe peristaltic pump

7.0 Procedures

7.1 Detecting and measuring NAPL in monitoring wells:

7.1.1 Always inspect purge water and development/monitoring/sampling equipment removed from any well for the presence of NAPL, which typically forms sheens, layers, or droplets of black, brown, yellow or clear immiscible fluid having a petroleum or solvent odor.

7.1.2 If NAPL is present or potentially present in a monitoring well, screen the atmospheres within **(a) the breathing zone above the open well casing** and **(b) within the well casing** with a PID and multiple gas detection meter with LEL and O_2 sensors. Refer to FSOP 3.1.1 for PID and 3.1.2 for multiple gas detection meter use.

7.1.2.1 If VOC concentrations or the percentage LEL **in the breathing zone** exceed the health and safety action levels provided in Table 1 of FSOP 1.1, Initial Site Entry or site-specific action levels, close and secure the monitoring well. Work will need to be delayed until appropriate health and safety measures can be implemented.

7.1.2.2 If VOC concentrations **in the well casing** exceed the health and safety action levels provided in Table 1 of FSOP 1.1 or site-specific action levels, but VOC concentrations in the breathing zone do not, work activities may continue. If LEL concentrations in the well casing exceed action levels, leave the well open and to ventilate. If LEL concentrations fall below action levels in the well casing, then continue work. Monitor the breathing zone continuously for VOC concentrations and percentage LEL. Do not work if LEL concentrations in the well casing continue to exceed action levels.

7.1.2.3 Use a logbook or field log sheets to record health and safety monitoring data (*e.g.,* ranges of PID and LEL measurement values).

7.1.3 Measure the apparent thickness of the NAPL layer in the well (the difference between the air/LNAPL and the LNAPL/water interface depths, or the difference between the water/DNAPL and well bottom depths) using one of the following techniques:

7.1.3.1 Interface meter: slowly lower the probe through the fluid column to detect and measure NAPL interfaces. Refer to FSOP 3.1.3 for interface meter use.

7.1.3.2 Transparent bailer: slowly lower the bailer through the fluid column to span the NAPL layer, slowly withdraw the bailer, and measure the NAPL thickness within it. Use double check-valve bailers to retrieve DNAPL samples. Use single-check valve or double check-valve bailers to retrieve LNAPL samples. Handle bailers over oil-absorbent pads or mats to contain NAPL that may be inadvertently spilled on the ground.

7.1.4 Measure NAPL thickness to an accuracy of +/- 0.01 ft. If the thickness is less than 0.01 ft, describe the thickness as a “sheen.”

7.2 Collecting NAPL samples from monitoring wells for laboratory analysis:

7.2.1 Collecting samples using a bailer:

7.2.1.1 To collect an LNAPL sample, slowly lower a single-check valve or double check-valve bailer through the LNAPL layer and into the underlying water column, taking care to allow as little water as possible to enter the bailer. Upon retrieval of the bailer, decant water from it by carefully opening the check valve at the bottom of the bailer. Then fill the sample containers with LNAPL by pouring from the top of the bailer. Repeat this process until all sample containers are filled or until no more LNAPL can be recovered from the well.

7.2.1.2 To collect a DNAPL sample, slowly lower a double check valve bailer to the bottom of the well. Carefully retrieve the bailer, and upon retrieval, decant water from it by pouring from the top of the bailer. Then fill the sample containers with DNAPL by opening the check valve at the bottom of the bailer. Repeat this process until all sample containers are filled or until no more DNAPL can be recovered from the well.

7.2.2 Collecting samples using a peristaltic pump:

7.2.2.1 An intrinsically safe peristaltic pump may be used to collect LNAPL or DNAPL samples provided that the NAPL is within the suction limit of the pump (generally within the upper 20 feet of the well water column).

7.2.2.2 Set the pump intake within the LNAPL or DNAPL and fill the sample containers from the pump discharge, taking care to minimize the amount of water in the sample. Repeat this process until all sample containers are filled or until no more NAPL can be recovered from the well.

7.2.3 Perform sampling activities over oil-absorbent pads or mats to contain NAPL that may be inadvertently spilled on the ground.

7.3 Decontaminate equipment in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.4 Properly containerize all wastes in accordance with FSOP 1.7, Investigation Derived Wastes. Pour waste NAPL and fluids containing NAPL into a DOT-approved container for flammable fluids and tightly seal the container. Segregate NAPL-contaminated disposable sampling equipment and personal protective equipment by double-bagging with heavy duty trash can liners. Contact the Site Investigation Field Unit (SIFU) for additional guidance on the containerization, transportation, and disposal of NAPL and media or disposal sampling equipment or personal protective equipment contaminated with NAPL.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 3.1.1, Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meter

FSOP 3.1.3, Interface Meter

Ohio EPA Division of Drinking and Ground Waters, May 2012, Technical Guidance Manual for Ground Water Investigations (Chapter 10: Ground Water Sampling)

U.S. EPA, 1995, Ground Water Issue: Light Nonaqueous Phase Liquids, EPA/540/S-95/500

U.S. EPA, 1991, Ground Water Issue: Dense Nonaqueous Phase Liquids, EPA/540/4-91-002

Ground Water Sampling (General Practices)
FSOP 2.2.4 (August 4, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This procedure describes general standard practices that should be used by the Division of Environmental Response and Revitalization (DERR) for collecting ground water samples from monitoring wells and soil borings, regardless of the technique or sampling equipment used. These procedures may be used for collecting ground water samples for screening, compliance or other objectives. Applicable ground water sampling techniques include the following:

- FSOP 2.2.5, Ground Water Sampling Using an Inertial Lift (Check Valve) Pump
- FSOP 2.2.6, Low-Flow (Low-Stress) Ground Water Sampling
- FSOP 2.2.7, Ground Water Sampling Using a Bailer
- FSOP 2.2.8, Ground Water Sampling Using a Bladder Pump
- FSOP 2.2.9, Ground Water Sampling Using a Peristaltic Pump
- FSOP 2.2.10, Ground Water Sampling Using an Electric Submersible Pump
- FSOP 2.2.11, Sampling Water Supply Systems

1.2 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA’s Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

2.0 Definitions

2.1 Ground Water Screening Sample: a ground water sample used for site assessment decision-making purposes, as opposed to a ground water compliance sample collected for modeling, risk assessment or to evaluate regulatory compliance. Ground water screening samples may be used for optimizing the location and construction of monitoring wells, selecting ground water samples for fixed-base laboratory analysis, installing additional investigatory soil borings, or as the basis for sampling other environmental media such as soil vapor. Ground water screening samples may be collected from monitoring wells, piezometers, soil borings, sumps or excavations, and do not necessarily need to meet the strict ground water purging and stabilization requirements for ground water compliance samples as described below in paragraph 2.2.

2.2 Ground Water Compliance Sample: a representative ground water sample intended to support regulatory compliance, risk assessment or modeling. Ideally, this type of sample is collected in a manner that minimizes disturbance to ambient ground water chemical and physical properties and is representative of in-situ ground water quality within the saturated zone or aquifer of interest. These samples are collected from properly constructed and developed monitoring wells and must meet strict ground water purging and stabilization requirements. Unless otherwise indicated in this FSOP, the terms “ground water sample” or “sample” refer to this type of ground water compliance sample.

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for sampling hazards before beginning work.

3.2 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector (PID), multiple gas detection meter, *i.e.,* a meter with lower explosive limit (LEL) and oxygen (O_2) measurement capabilities or other required instrument. Breathing zone action levels are provided in Table 1 of FSOP 1.1, Initial Site Entry.

3.3 Wear appropriate personal protective equipment (PPE) when performing ground water sampling activities, including but not limited to chemical-resistant gloves compatible with the contaminants of concern, and eye/face protection and coveralls for splash protection.

3.4 Use caution when handling glass sample containers and chemical preservatives.

3.5 Use caution and wear work gloves when assembling or disassembling equipment and cutting discharge tubing.

4.0 Procedure Cautions

4.1 If non-aqueous phase liquid (NAPL) is present in the well, notify the DERR site coordinator and refer to FSOP 2.2.3, Detection and Sampling of Nonaqueous Phase Liquids in Monitoring Wells.

4.2 At minimum, wells should be redeveloped when 20% of a well screen is occluded by sediments, or records indicate a change in yield and turbidity. Wells should be redeveloped per FSOP 2.2.1, Well Development to obtain a representative sample.

4.3 Use the low-flow sampling technique (FSOP 2.2.6) to sample low-yielding (100 ml/min to 500 ml/min) wells whenever possible.

4.4 For very low-yielding wells (< 100 ml/min), sample collection options include no purge sampling, purging the well dry and allowing it to recover or using a passive ground water sampling device. The SSWP should provide specific procedures for sampling very low yielding wells. If it does not and very low-yielding wells need to be sampled, contact the DERR SIFU manager and DERR site coordinator to provide sampling procedures appropriate for project objectives and DQOs.

4.5 Avoid collecting ground water samples with bailers (FSOP 2.2.7) whenever possible to prevent elevated sample turbidity and sample volatilization.

4.6 Be aware that peristaltic pumps (FSOP 2.2.9) create a vacuum to pull ground water from a well. Based on site-specific data quality objectives (DQOs), use of a peristaltic pump may or may not be appropriate for collecting ground water compliance samples for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), dissolved metals or dissolved gases.

4.7 Prolonged purging at a rate that exceeds a well's yield will result in ground water cascading within the screened interval, causing volatilization and oxidation of contaminants and inhibiting the ability to collect a representative ground water sample.

4.8 When filling pre-preserved ground water sample containers, be careful not to flush out chemical preservatives.

4.9 When collecting samples for volatile organic compound (VOC) analysis, the 40-ml sample container should be filled slowly and gently (at rate of 100 ml/min or less) to minimize sample agitation and aeration and associated loss of VOCs, regardless of the specific sampling technique used.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

- Sample containers and preservatives
- Sample coolers and ice
- Sample labels
- PPE including at a minimum, chemical-resistant gloves
- Paper towels
- Decontamination equipment and supplies
- Purge water containers
- Field forms and/or logbook
- Chain-of-custody (COC) forms
- Pens and markers

- Calculator
- Water quality meter(s) to measure pH, temperature, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen, turbidity and/or other water quality parameters
- Purging and sampling equipment (pumps, or bailers)
- Tubing (if needed)
- Electrical power source (car batteries or generator, if needed)

7.0 Procedures

7.1 Pre-sampling inspection and field monitoring

7.1.1 Document weather and other field conditions that could affect ground water sample activities and sample representativeness.

7.1.2 Inspect each monitoring well to evaluate and document the following conditions:

- Is the well secured (locked)?
- Is the well labeled?
- Are there insects (*e.g.,* wasps) or rodents (*e.g.,* mice) living inside the protective casing?
- Is the well damaged, or does it appear to have been tampered with?

7.1.3 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector (PID), multiple gas detection meter (with LEL/O^2 capabilities) or other required instrument. Breathing zone action levels are provided in Table 1 of FSOP 1.1, Initial Site Entry. Monitoring may need to continue during purging and sampling activities. Additionally, if the LEL is exceeded inside the well casing, allow the open well to ventilate and measure the LEL again. Allow the LEL concentration to drop to below the LEL before placing instrumentation or sampling devices inside the well. Refer to FSOP 3.1.1, Photoionization Detector and FSOP 3.1.2, Multiple Gas Detection Meter for use and operation of these instruments.

7.2 Static water level and total depth measurements

7.2.1 Allow sufficient time for the water level to equilibrate (at least 10 to 15 minutes) if the well is installed in a confined saturated zone, or if air pressure is released (a popping sound is heard) when the well cap is removed.

7.2.2 Measure the static water level and total depth in accordance with FSOP 2.2.2, Ground Water Level Measurement. The static water level should be measured to an accuracy of +/- 0.01 ft, and the total depth should be measured to an accuracy of +/- 0.1 ft.

7.2.3 If NAPL is present in the well, following the monitoring procedures provided by FSOP 2.2.3, Detection and Sampling of Nonaqueous Phase Liquids in Monitoring Wells. In addition, immediately notify the DERR SIFU manager and DERR site coordinator.

7.3 Purging

7.3.1 Set up ground water purging and sampling equipment ensuring that:

- The work area is organized to maximize efficiency and minimize the potential for cross contamination.
- Non-disposable down-well equipment has been decontaminated.
- Monitoring equipment is properly calibrated.
- Preserved sample containers are ready for use.
- Field forms and sample labels are ready for use.

7.3.2 Purging for volumetric sampling techniques (*e.g.* bailing or high-flow pumping) is based on well volumes, i.e., the volume of water present in the screen and well casing under static water level conditions. At a minimum, three well volumes should be purged before sampling unless the well goes dry. However, the SSWP may require collecting:

- More than three well volumes
- A specified number of well volumes (three or more) with selected water quality parameters (refer to paragraph 7.3.4)
- A variable number of well volumes (three or more) based on selected water quality parameter stabilization (refer to paragraph 7.3.4)

One well volume can be calculated based on the well depth, well diameter and ground water depth using the following equation:

One Well Volume (gallons) = $\mathbf{D}^2/4 \times 3.14 \times (\mathbf{Hd} - \mathbf{Hw}) \times 7.48\ \text{gal/ft}^3$, where

D = well diameter, ft
Hd = well depth, ft top-of-casing (TOC)
Hw = static water depth, ft TOC

Alternatively, the following well diameter-based conversion factors (see quick reference guide in table below) can be multiplied by the static water column length (**Hd** - **Hw**) to determine the well volume in gallons or milliliters (1 gallon = 3,784.41 milliliters):

Well Diameter (Inches)	Gallons Per Foot	Milliliters Per Foot
0.5	0.01	39
0.75	0.02	87
1.0	0.04	154
1.5	0.09	347
2.0	0.16	617
3.0	0.37	1,389
4.0	0.65	2,470
5.0	1.02	3,859
6.0	1.47	5,557
8.0	2.61	9,879

7.3.3 Purging for the low-flow (low-stress) ground water sampling technique is based on the stabilization of water quality parameters to determine when to begin sampling. The SSWP will indicate at least three specific stabilization parameters to be monitored. In addition, water level drawdown in the well should be minimized, with the pumping level stabilized above the screened interval (unless the static water level is within the screened interval). At least one equipment volume (pump and discharge line volume) should be evacuated between stabilization parameter measurements unless a greater volume is required by the SSWP Refer to FSOP 2.2.6, Low-Flow (Low-Stress) Ground Water Sampling.

7.3.4 The SSWP will indicate the water quality stabilization parameters that need to be monitored prior to sample collection. Ground water stabilization parameters and criteria include the following:

Stabilization Parameters	Criteria (for at least three consecutive measurements)
Temperature	+/- 0.5^{o} C
pH	+/- 0.2 standard units (S.U.)
Specific Conductance	+/- 3%
Oxidation-Reduction Potential	+/- 20 millivolts (mV)

Stabilization Parameters	**Criteria (<u>for at least three consecutive measurements</u>)**
Dissolved Oxygen	+/- 0.3 mg/L
Turbidity	< 10 nephelometric turbidity units (NTUs) is possible, or +/- 10% if > 10 NTUs

Turbidity is more susceptible to influence from poor well construction or inadequate well development than the other parameters. Therefore, if turbidity is difficult to stabilize or exceeds 100 NTUs, the well may need to be redeveloped or may be improperly constructed. A pH value exceeding 8, along with high turbidity, typically indicate that grout contamination is present in the water column/screened interval.

7.3.5 Purge the monitoring well following the SSWP-specific procedures to meet the criteria for ground water sample collection.

7.3.6 When collecting ground water screening samples using a direct push drilling unit, the ground water sampling device should be purged to lower sample turbidity and help ensure that the ground water screening sampling is representative of the depth from which it is collected. Purging requirements will vary based on site conditions and project DQOs (refer to the SSWP).

7.3.7 If the well goes dry before purging criteria are met, allow the well to recover sufficiently to collect the ground water sample as soon as possible but within 24 hours.

7.4 Ground Water Sample Collection

7.4.1 Use the purging device to collect the ground water sample, i.e., don’t remove the purging equipment (*e.g.,* a bladder pump) from the well and sample with another device (*e.g.,* a bailer) unless it is absolutely necessary in order to collect the sample.

7.4.2 Fill ground water sample containers slowly and carefully. Overfilling will dilute chemical preservatives. Fill VOC samples at a rate of 100 ml/min or less to minimize volatilization.

7.4.3 If using a volumetric sampling technique, purging to dryness or no-purge sampling, collect chemical constituents in the flowing order: VOCs, SVOCs, other extractable organics (pesticides/herbicides/PCBs), total metals, dissolved metals, and other inorganic constituents.

7.4.4 If using the low-flow technique, sample containers for constituents other than VOCs may be filled first (in no particular order) at a flow rate of 500 ml/min or less, followed by filtered samples and VOCs (last). Reduce the flow rate to 100 ml/min or less for VOCs.

7.5 Decontaminate ground water purging and sampling equipment after each use in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.6 Dispose of investigation-derived waste (purge water and used PPE, disposable sampling equipment and supplies) in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation. At a minimum, document monitoring and purging data on field ground water sampling forms or in a field logbook, and document sample collection data on a chain-of-custody (COC) form. Calibration records for water quality monitoring equipment should also be retained with site-specific purging data and COC forms.

9.0 Quality Assurance and Quality Control

9.1 Ground water quality assurance/quality control (QA\QC) samples should include duplicate samples and equipment blanks (if using non-dedicated, non-disposable equipment) at a minimum rate of 1 per 10 ground water samples. A trip blank should be included in every sample cooler with VOC samples. Field blanks should be collected as needed or as specified by the SSWP. Refer to the SSWP for site-specific QA/QC sample requirements.

9.2 Water quality monitoring instruments used to evaluate ground water stabilization parameters should be properly maintained and calibrated before each ground water sampling event per the manufacturer’s instructions. During multiple-day sampling events water quality monitoring equipment should be calibrated at the beginning of each day.

10.0 Attachments

DERR Monitoring Well Sampling Log Sheet

DERR Residential Water Supply Well Sampling Log Sheet

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.1, Well Development

FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.3, Detection and Sampling of Nonaqueous Phase Liquids in Monitoring Wells

FSOP 2.2.5, Ground Water Sampling with an Inertial Lift (Check Valve) Pump

FSOP 2.2.6, Low-Flow (Low-Stress) Ground Water Sampling

FSOP 2.2.7, Ground Water Sampling Using a Bailer

FSOP 2.2.8, Ground Water Sampling Using a Bladder Pump

FSOP 2.2.9, Ground Water Sampling Using a Peristaltic Pump

FSOP 2.2.10, Ground Water Sampling Using an Electric Submersible Pump

FSOP 2.2.11, Sampling Water Supply Systems

FSOP 3.1.1., Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meter

Ohio EPA Division of Drinking and Ground Waters, 2009, Technical Guidance Manual for Ground Water Investigations (Chapter 8: Well Development, Maintenance, and Redevelopment)

Ohio EPA Division of Drinking and Ground Waters, 2020, Technical Guidance Manual for Ground Water Investigations (Chapter 10: Ground Water Sampling)

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Ground Water Sampling Using an Inertial Lift (Check Valve) Pump
FSOP 2.2.5, August 11, 2020
Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Inertial lift pumps, commonly referred to as check valve samplers, are portable purging and sampling devices which do not require a power source. Inertial lift pumps consist of a ball valve connected to flexible tubing. Water is purged from the well by lifting and dropping the pump in a continuous up-and-down manner (manually or automatically). These tools can quickly move water and are an efficient means of purging a well.

1.2 The check valve sampler device typically used by Ohio EPA is constructed of stainless steel (Geoprobe® MN#:214061) and is most commonly used for ground water sample collection with a Screen Point Sampler. The check valve is 2.25" long and is used with 3/8" OD tubing (Teflon™ lined or LDPE tubing can be used).

1.3 Check valve samplers are used for screening purposes during the assessment phase of site investigations. The water quality results from samples collected using a check valve device are very helpful for evaluating and optimizing monitoring well locations and construction. Due to the way these devices are operated, check valve samplers should not be used to collect ground water samples for compliance, risk assessment or modeling.

1.4 A mechanical Waterra Pump™ can also be used to develop and sample monitoring wells or screen points. This method requires much less manual labor and is more efficient in deeper wells or screen points.

1.5 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling and Chapter 15, Use of Direct Push Technologies for Soil and Ground water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before beginning work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling health and safety considerations.

3.3 The manual method in this sampling procedure requires physical exertion for lifting and lowering the tubing and check valve through the water column. Sampling many wells in one day using this technique can be physically challenging.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 The up-and-down motion of the check valve and tubing within the water column may cause excessive sample turbidity, especially when sampling wells or well points in fine-grained geologic materials. Excessive turbidity may result in artificially elevated metals concentrations in a ground water sample.

4.3 The up-and-down motion of the check valve and tubing within the water column may cause off-gassing of volatile organic compounds (VOCs), resulting in sample VOC concentrations that are not representative of in-situ ground water quality.

4.4 Fine-grained sediments may get caught between the check valve wall and ball and decrease the lift capability (efficiency) of the check valve. The tubing and check valve may need to be periodically removed and cleaned.

4.5 Check valves can be used at multiple locations if properly cleaned and decontaminated in accordance with FSOP 1.6, Sampling Equipment Decontamination. However, excessive reuse of the sampler can result in oxidation (rusting) of the check valve ball and can result in the ball getting jammed or not providing sufficient seal to ensure the lift needed. Replace check valves that appear to have their seal compromised from oxidation.

4.6 Always carry extra check valve samplers and tubing to the field.

4.7 Decontaminate the check valve assembly and replace the tubing between sample locations.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Check valve sampler
6.2 Appropriately sized tubing (LDPE, Teflon™ lined tubing, etc.)
6.3 Tubing cutters
6.4 Waterra Pump™ and generator, as needed
6.5 Sample collection supplies as outlined in FSOP 2.2.4, Ground Water Sampling (General Practices)
6.6 Water quality meter(s)

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4.

7.2 Measure the water level in the well or well point, calculate the well or well point volume and determine purge volume per FSOP 2.2.4, Ground Water Sampling (General Practices).

7.3 Attach tubing to the check valve by screwing the check valve clockwise onto the tubing so that approximately ½" of tubing is inserted into the valve casing. Ensure that the connection is very snug.

7.4 Insert the check valve and tubing into the well or well point to the bottom of the screen. After ensuring the check valve is at the bottom of the screen, cut the tubing to the proper length to allow the purged ground water to easily discharge into a container.

7.5 Raise the tubing about one foot out of the well point and then lower the tubing back down (manually or using the Waterra Pump™). Continue this up-and-down motion to lift ground water to the surface.

7.6 Ensure that the open (discharge) end of the tubing remains in the purge water collection container to avoid spilling potentially contaminated water on the ground and to obtain an accurate purge volume estimate.

7.7 Begin measuring the field parameters per FSOP 2.2.4, Ground Water Sampling (General Practices) when the purge water container begins to fill with ground water.

7.8 Purging activities should be performed as required by the SSWP to meet project objectives and DQOs, and in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices). General purging practices for collecting ground water screening samples from Geoprobe® wells and screen point borings as follows:

7.8.1 GEOPROBE® WELLS: purge at least 3 well volumes or purge until the field parameters have stabilized. If collecting samples for metals or other turbidity-sensitive constituents, continue to purge until ground water turbidity is less than 10 NTUs or has stabilized to within +/- 10 percent over three consecutive measurements. In some instances, it may be appropriate to use a ground water filter to decrease turbidity if collecting samples for metals analysis.

7.8.2 GEOPROBE® SCREEN POINT BORINGS: purge the temporary point until the water clarity visually stabilizes; a turbidity meter should be used to monitor sample turbidity if required by the SSWP.

7.9 Ground water samples should not be filtered unless filtering is included in the SSWP. DERR’s Remedial Response Program and Voluntary Action Program both discourage the use of filtered ground water samples for site assessment purposes.

7.10 After purging is completed, collect and handle samples following the procedures outlined in FSOP 2.2.4, Ground Water Sampling (General Practices) and FSOP 1.5, Sample Custody and Sampling.

7.11 Decontaminate the check valve between each sampling location per FSOP 1.6, Sampling Equipment Decontamination unless using a new (dedicated) check valve at each sample location. Discharge tubing should not be reused between sampling locations.

7.12 Dispose of discharge tubing and other investigation derived waste in accordance with FSOP 1.7 Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices)

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 3.1.7, Geoprobe® Operation and Sampling

Ohio EPA Division of Drinking and Ground Waters, 2020, Technical Guidance Manual for Ground Water Investigations (Chapter 10: Ground Water Sampling)

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Low-Flow Ground Water Sampling
FSOP 2.2.6, August 19, 2020
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Low-flow ground water sampling is designed to collect ground water samples under minimal drawdown (low-stress) conditions. This technique minimizes vertical gradients and turbulence within the well and surrounding formation, thereby reducing undesired sampling-related changes to in-situ ground water quality.

1.2 Low-flow sampling assumes that under low-flow purging conditions, ground water passes continuously through a well's screened interval and does not mix with the water above the screen. The well is pumped at a rate much lower than the saturated zone yield so that drawdown is minimized and stagnant water in the casing above the screened interval remains relatively undisturbed. Fresh ground water enters the pump intake at a low velocity that minimizes turbulence in the screened interval.

1.3 In addition to effectively facilitating the collection of a representative ground water sample, low-flow sampling significantly reduces the volume of purge water generated compared to other ground water sampling techniques.

1.4 Because low-flow sampling minimizes sample volatilization and turbidity compared to other ground water sampling techniques, it is recommended for collecting ground water samples for regulatory compliance, risk assessment or modeling, especially volatile organic compound (VOC) and metal samples.

1.5 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

1.6 Ohio EPA's TGM recommends that low-flow sampling be performed using a bladder pump or variable-speed electric submersible pump. Depending on SSWP project objectives and DQOs, a peristaltic pump may also be used for low-flow sampling.

1.7 Low-flow sampling purging rates typically vary between 100 and 500 ml/min.

2.0 Definitions

Low-flow purging is also referred to as low-stress purging, low-impact purging, minimal drawdown purging, or Micropurging®.

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling and health and safety considerations.

3.3 When sampling with a bladder pump and using compressed nitrogen or carbon dioxide gas, properly secure compressed gas cylinders when transporting, using or storing them.

3.4 When carrying a 12-volt battery, lift the battery properly. Bend your hips and knees to squat down, grasp the battery, and while keeping it close to your body, straighten your legs to lift it. Do not lift the battery by bending forward, which may cause back injury.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 If NAPL is encountered in a monitoring well, do not perform ground water sampling. Immediately notify the DERR-SIFU manager and DERR site coordinator.

4.3 Low-flow sampling should not be performed using single-speed pumps. Use of a ball or gate valve with a single-speed pump to lower the flow rate is not acceptable, because the valve will cause turbulence in the sample discharge line.

4.4 Low-flow sampling cannot be performed using bailers.

4.5 Accurately measuring the static water level before beginning the low-flow sampling process is critical for evaluating water level drawdown during sampling.

4.6 Avoid drawing the water level into the screened interval during low-flow purging and sampling (if the static water level is above the screened interval). If this happens, the ground water sample will need to be collected using the volumetric (well volume) technique.

4.7 Low flow ground water samples should not be collected until drawdown has stabilized and water quality indicator parameters have stabilized.

4.8 VOC sample vials should never be filled at flow rates exceeding 100 ml/min.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Low-flow pump assembly, including control box and power supply or compressed nitrogen or carbon dioxide
6.2 Water quality meters and/or flow-through cell with data sonde to measure water quality stabilization parameters including pH, specific conductivity, temperature, dissolved oxygen (DO), oxidation reduction potential (ORP) and turbidity
6.3 Water level indicator
6.4 Stopwatch or timer (for measuring flow rate)
6.5 Graduated cylinder (for measuring flow rate)
6.6 Disposable tubing
6.7 Well construction information (total depth of well, depth to screened interval)
6.8 Other ground water sampling equipment and supplies as needed per FSOP 2.2.4, Ground Water Sampling (General Practices)

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4, Ground Water Sampling (General Practices).

7.2 Before installing the pump, measure the static water level in accordance with FSOP 2.2.2, Ground Water Level Measurement.

7.3 Slowly and carefully install the pump in a manner that minimizes disturbance to the water column in the well. The pump should be installed in the approximate center of the screened interval. Avoid placing the pump at the bottom of the well to avoid increasing turbidity.

7.4 Ensure that the flow-through cell and/or water quality meters have been calibrated and are set up and ready for use.

7.5 Start the pump at the lowest flow rate possible and measure the flow rate in a graduated cylinder (or similar device). The purge rate will depend on the well size (diameter) and yield. Typically, the purge rate will be between 100 and 500 ml/min for a two-inch inside diameter (ID) monitoring well. The purge rate for a smaller diameter well (*e.g.,* 0.75-inch ID) may be lower and the purge rate for a larger diameter well (*e.g.,* 4-inch ID) may be higher.

7.6 Monitor the water level drawdown in the well. If continuous drawdown is occurring, reduce the pumping rate until equilibrium is achieved, i.e., the water level stabilizes with the least amount of drawdown (as compared to pre-pumping static water level).

7.7 If the static water level *was initially above the screened interval* and drawdown into the screened interval cannot be avoided (despite efforts to lower the pumping rate), perform volumetric sampling by purging at least three well volumes before collecting the sample. Do not exceed a purge rate of 500 ml/min. Measure stabilization parameters as required by the SSWP.

7.8 While monitoring the water level drawdown as described above, measure and record stabilization (water quality) parameters using the flow-through cell and/or water quality meters. The SSWP will provide specific stabilization parameters, however, at least three stabilization parameters should be measured, and two of the parameters should always include specific conductance and either DO or ORP.

7.9 The time interval between successive stabilization parameter measurements should always be long enough to allow one equipment volume (pump + discharge line + flow through cell) to completely be purged from the well. Generally, a time three to five minutes is acceptable. If the pumping rate is very low (*e.g.,* 80 ml/min), the time needed between stabilization parameter measurements may need to be longer (*e.g.,* 5 to 12 minutes).

7.10 Continue low-flow purging until the water level drawdown and associated parameters have stabilized. Stabilization parameters are considered stable upon meeting the following criteria for at least three consecutive measurements:

Stabilization Parameters	**Criteria (<u>for at least three consecutive measurements</u>)**
Temperature	+/- 0.5^o C
pH	+/- 0.2 standard units (S.U.)
Specific Conductance	+/- 3%
Oxidation-Reduction Potential	+/- 20 millivolts (mV)
Dissolved Oxygen	+/- 0.3 mg/L
Turbidity	< 10 nephelometric turbidity units (NTUs) is possible, or +/- 10% if > 10 NTUs

If stabilization cannot be achieved through low-flow sampling based on SSWP DQOs and other criteria, perform volumetric sampling by purging at least three well volumes before collecting the sample. Avoid drawing the water level into the screen if possible, and do not exceed a purge rate of 500 ml/min.

7.11 After purging is completed, collect and handle samples following the procedures outlined in FSOP 2.2.4, Ground Water Sampling (General Practices) and FSOP 1.5, Sample Custody and Sampling. Disconnect the sample tubing from the flow-through cell prior to sample collection (*i.e.,* do not collect samples directly from the flow-through cell).

7.12 Collect the ground water sample by filling containers for constituents other than VOCs first (in no particular order) at a flow rate of 500 ml/min or less, followed by filtered samples (if specified by the SSWP) and VOCs (last). Reduce the flow rate to 100 ml/min or less for VOCs. If elevated turbidity is an issue, samples for metals may be collected last in an effort to minimize sample turbidity.

7.13 Decontaminate sampling equipment between each sampling location in accordance with FSOP 1.6, Sampling Equipment Decontamination. Do not reuse disposable tubing between sampling locations.

7.14 Dispose of discharge tubing and other investigation derived waste in accordance with FSOP 1.7 Investigation Derived Wastes.

8.0 Data Records and Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices)

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.4, Ground Water Sampling (General Practices)

Ohio EPA Division of Drinking and Ground Waters, 2020, Technical Guidance Manual for Ground Water Investigations (Chapter 10: Ground Water Sampling)

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Ground Water Sampling Using a Bailer
FSOP 2.2.7, August 25, 2020
Ohio EPA Division of Environmental Protection and Revitalization

1.0 Scope and Applicability

1.1 Bailers are portable, manually operated ground water sampling devices that consist of a tube with one or more check valves and an attached cord. The cord is used to lower and raise the bailer to purge water from a well. As a bailer is lowered into a well water column, the check valve(s) opens and allows the tube to fill with water. As the bailer is raised from a well water column, the check valve(s) closes and seals the ground water-filled tube that is being retrieved from the well for ground water purging or sampling.

1.2 Bailers can be constructed of virtually any rigid or flexible material. For ground water sampling purposes, Ohio EPA uses bailers constructed of materials that are inert (*i.e.,* they are neither sources of chemical contaminants nor adversely affected by chemical contaminants). Preferred materials for ground water sampling include, but are not limited to PVC, stainless steel, Teflon®, polyethylene and polypropylene. Bailers are available in a variety of diameters, volumes and lengths.

1.3 Bailer cords should be composed of contaminant-inert materials. Preferred cord materials include, but are not limited to nylon, polypropylene or Teflon®-coated wire or cord.

1.4 Given the range of material types and sizes, bailers can be used for sampling a wide variety of wells and ground water constituents. However, Ohio EPA does not consider bailers a best available technology for sampling ground water because when used, they surge the well and cause turbulence that increases turbidity and the potential for volatilization. The use of bailers to collect ground water samples for contaminants sensitive to turbidity and volatilization (especially VOCs and metals) should be avoided.

1.5 Bailers may be the only practicable option for sampling monitoring wells under the following conditions:

- The well is located in a remote area or in an area that is difficult to access
- The well is very low yielding (*i.e.,* < 100 ml/min)
- The depth to ground water is very deep (*i.e.,* > 100 ft)
- The water column is very small (*i.e.,* < 1 ft)
- NAPL is present or contaminant concentrations are very high

1.6 Use of bailers to sample contaminated ground water may require an increased level of personal protective equipment (PPE) as compared to other ground water sampling techniques, because there is a higher likelihood of purge water contact.

1.7 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

1.8 If the use of bailers for collecting ground water samples is not included in the site-specific work plan (SSWP), contact the DERR-SIFU manager and DERR site coordinator before using bailers to collect ground water samples to ensure that the use of bailers will meet project objectives and data quality objectives (DQOs).

2.0 Definitions

2.1 **Top-filling bailer:** a bailer designed such that water can enter and exit only through its top. Due to sample agitation and aeration, top-filling bailers are only appropriate for collecting light non-aqueous phase liquids (LNAPLs).

2.2 **Bottom-filling (or single-check valve) bailer:** a bailer that is open at the top with a check valve at the bottom that seals the bailer when it is withdrawn from the well water column. Ohio EPA prefers disposable bottom-filling bailers with discharge tubes when using bailers for most ground water sampling projects.

2.3 **Discharge tube:** a short section of rigid tubing with tapered cuts at both ends that is used to collect a sample from the bottom of a bottom-filling valve bailer.

2.4 **Double-check valve (or point source) bailer:** a bailer with check valves at the top and bottom that is designed to collect water samples from discrete locations within a well water column. Water flows through both ends when the bailer is lowered into the water column. When the bailer reaches the desired depth and is retrieved, both valves close and the water from the sampled interval is retained with the bailer. Double-check valve bailers can be used to collect dense non-aqueous phase liquids (DNAPLs). The SSWP should include sample collection procedures when using double-check valve bailers.

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling and health and safety considerations

3.3 Using a bailer to purge and sample is labor intensive. Two or more staff may be needed to collect ground water samples using bailers under (but not necessarily limited to) the following conditions:

- More than 8 wells need to be sampled within one day or less
- Wells that need to be sampled are large diameter (*i.e.,* > 2 inches) or very deep (> 50 ft)
- Well water columns are very large (*i.e.* > 20 ft)
- The temperature is very warm (*i.e.,* > 80^o F) or very cold (*i.e.,* < 32^o F)

3.4 Avoid splashing yourself with purge water when bailing a well. Use appropriate personal protective equipment (PPE), including chemical-resistant gloves, chemical resistant coveralls and safety glasses or goggles.

3.5 Avoid leaning over the well when purging or sampling to prevent back injuries and to prevent inhalation of organic vapors associated with VOC ground water contamination from the well casing.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 If NAPL is encountered in a monitoring well, do not perform ground water sampling unless otherwise directed. Immediately notify the DERR-SIFU manager and DERR site coordinator.

4.3 A non-slip knot such as a bowline is recommended for tying the rope to the bailer. Other knots may slip, resulting in the loss of the bailer in the well. Refer to the attached instructions on how to tie a bowline knot.

4.4 When using a bailer, do not purge quickly or allow the bailer to free fall into the well water column or “bounce” the bailer on the bottom of the well. These actions will aerate the well water column and/or cause significantly increased sample turbidity, and in some cases may damage the well,

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Bailer
6.2 Cord
6.3 Knife or cord cutter
6.4 Graduated bucket or similar container
6.5 Other ground water sampling equipment and supplies as needed per FSOP 2.2.4, Ground Water Sampling (General Practices)

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4, Ground Water Sampling (General Practices).

7.2 Before purging or sampling, measure the static water level and total depth in accordance with FSOP 2.2.2, Ground Water Level Measurement.

7.3 Calculate the well volume and determine purge volume in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices).

7.4 Don a clean pair of chemically resistant sampling gloves.

7.5 Place clean plastic sheeting adjacent to the well to prevent contamination of the bailer cord in the event it should touch the ground. Alternatively, a clean five-gallon bucket can be used to contain the bailer cord as it is removed from the well. Ideally, the cord should not touch the ground or any other potentially contaminated objects when purging or sampling.

7.6 If the well is deep (> 50 ft), the well volume is large (> 5 gallons) or the bailer is large (> 2 inches in diameter), a tripod and pulley assembly may be used to operate the bailer.

7.7 Attach the cord to the bailer using a non-slip knot such as a bowline (see attached instructions).

7.8 Slowly lower the bailer down the well to the water column. Do not allow the bailer to free-fall into the water column or touch the bottom of the well. If possible, avoid lowering the bailer into the wells screened interval to minimize sample turbidity.

7.9 Slowly withdraw the bailer and empty the purge water into the graduated container.

7.10 Lower the bailer to the same approximate depth in the well each time. Raise the bailer slowly. If the bailer is not filled with water upon retrieval, you may be purging the well dry, or you may not be lowering the bailer far enough into the water column. Continue until you meet SSWP purging and stabilization criteria (generally least three well volumes removed) or until the well purges dry.

7.11 Upon completion of purging, lower the bailer into the well to collect the ground water sample as follows:

7.11.1 If using a bottom-filling bailer with a discharge tube, hold the bailer vertically and carefully insert the discharge tube into the bottom of the bailer to displace the check valve ball. Collect the sample from the bottom of the bailer through the discharge tube, controlling the flow while adjusting the insertion depth of the discharge tube.

7.11.2 If using a bottom-filling bailer without a discharge tube, carefully and slowly decant the sample from the top of the bailer.

7.12 If using a non-disposable bailer, decontaminate the bailer between each sample location in accordance with FSOP 1.6, Sample Equipment Decontamination.

7.13 Manage ground water samples in accordance with FSOP 1.5, Sample Custody and Handling.

7.14 Dispose of used disposable bailers, cord and PPE in accordance with FSOP 1.7, Investigation Derived Waste.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices).

10.0 Attachments

Step-by-step guide on how to tie a non-slip (bowline) knot

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

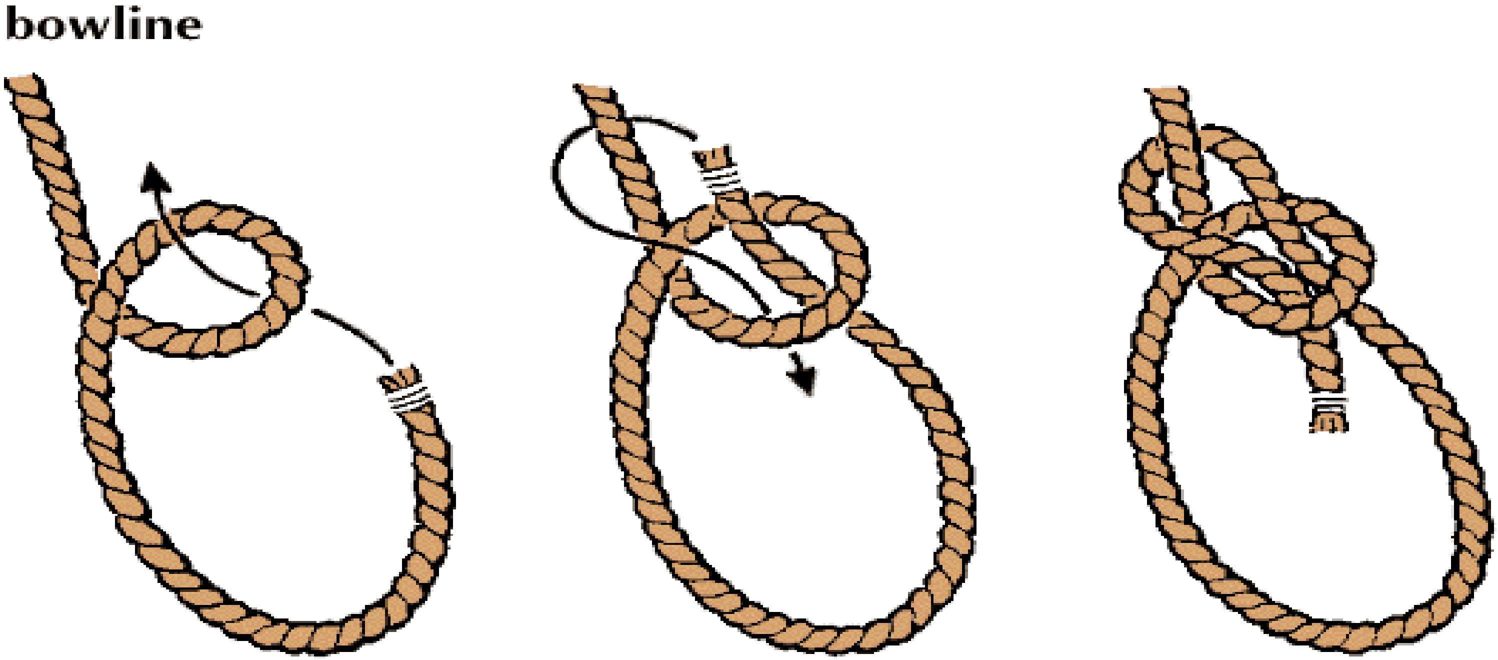
FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.4, Ground Water Sampling (General Practices)

Ohio EPA Division of Drinking and Ground Waters, 2020, Technical Guidance Manual for Ground Water Investigations (Chapter 10: Ground Water Sampling)

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

How to Tie a Bowline (Non-slip) Knot



Ground Water Sampling Using a Bladder Pump
FSOP 2.2.8 (December 3, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 A bladder pump consists of a flexible bladder inside a rigid housing with check valves at the top and bottom. Water enters the bladder through a check valve and is lifted (squeezed) to the surface through a discharge line when air or inert gas (*e.g.,* carbon dioxide) pressure is applied through an air line to the space between the inside of the housing and the outside of the bladder. An air compressor or compressed air/gas tank and regulator cycle the pressure on and off, allowing water to continuously enter the bladder and be pumped to the ground surface. The bladder chamber does not allow the ground water sample to contact the compressed air or gas. The check valves prevent backwashing from the discharge line and bladder. Flow can be readily controlled and low flow rates of 100 ml/min or less are easy to maintain.

1.2 Depending on project data quality objectives (DQOs), Ohio EPA recommends the use of polyethylene or Teflon® bladders and Teflon®/stainless steel bladder housings. Pump discharge line tubing should be composed of polyethylene or Teflon®. Both bladders and discharge line tubing are disposable.

1.3 Bladder pumps minimize ground water sample agitation, aeration and turbidity, and are generally recognized as the best overall sampling device for both organic and inorganic constituents (U.S. EPA 1992). Bladder pumps are Ohio EPA's preferred ground water sampling device, especially for the low-flow sampling technique (FSOP 2.2.6, Low-Flow Ground Water Sampling).

1.4 Ohio EPA's bladder pump can be used to sample wells up to 200 feet deep and wells with inside diameters as small as 0.75 inches.

1.5 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and DQOs. In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU supervisor and DERR site coordinator for clarification.

2.0 Definitions

2.1 Cycles Per Minute (CPM): the number of times the process of filling and discharging the bladder occurs (cycles) over one minute

2.2 Discharge: the process of the bladder closing and discharging water when pressure is applied

2.3 Refill: the process of the bladder opening and refilling with water after the pressure is released

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling and health and safety considerations.

3.3 When sampling with a bladder pump and using compressed nitrogen gas or carbon dioxide, properly secure compressed gas cylinders when transporting, using or storing them.

3.4 When carrying a 12-volt battery, lift the battery with proper form. Bend your hips and knees to squat down, grasp the battery, and while keeping it close to your body, straighten your legs to lift it. Do not lift the battery by bending forward, which may cause back injury.

3.5 Be careful when operating a 12-volt power supply under wet conditions, and if using a generator for power supply ensure that it is grounded to avoid electrical shock.

3.6 If using a generator for power supply, handle gasoline carefully. Always wear protective gloves when handling gasoline, and store gasoline containers outside of the work area.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 If NAPL is encountered in a monitoring well, do not perform ground water sampling. Immediately notify the DERR-SIFU supervisor and DERR site coordinator.

4.3 If sampling for PFAS, ensure that the bladder pump does not contain any parts containing Teflon, including includes O-rings, bladders, and tubing.

4.4 Do not lower or lift the bladder pump inside a well using the discharge tubing. Instead, use a safety cord for lowering and lifting the pump. The cord should be composed of an inert material (*e.g.,* polypropylene) that will not affect ground water quality and should be tied to the pump using a non-slip knot such as a bowline.

4.5 When using a bladder pump in a well containing high levels of turbidity or suspended solids, fine sediment may damage the bladder or cause the check valves to fail.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Stainless steel bladder pump
6.2 Dual tubing (connected air line and discharge tubing)
6.3 Disposable bladders
6.4 Aluminum lock discs
6.5 Safety cord
6.6 Knife or tubing/cord cutters
6.5 Control box and regulator
6.6 Air compressor powered by 12-volt power supply and generator or compressed air/gas tanks
6.8 Other ground water sampling equipment and supplies as needed per FSOP 2.2.4, Ground Water Sampling (General Practices)

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4, Ground Water Sampling (General Practices).

7.2 Measure the well's static water level and total depth in accordance with FSOP 2.2.2, Ground Water Level Measurement.

7.3 Assemble the pump per the manufacturer's instruction, taking care to prevent potential cross-contamination (*e.g.,* assembling the pump over a clean sheet of plastic to prevent direct contact with the ground).

7.4 Calculate the well volume, even if low-flow sampling. If the well yield is too low to stabilize the water level for low flow sampling, the volumetric sampling technique (*i.e.,* removal of three well volumes) will need to be used.

7.5 Using the safety cord, slowly and carefully install the pump in a manner that minimizes disturbance to the water column in the well. The pump should be installed in the approximate center of the screened interval. Avoid placing the pump at the bottom of the well to avoid increasing turbidity.

7.6 When low flow sampling, measure the static water level with the pump in the well. Monitor the static water level during sampling to ensure that drawdown is minimized. Follow other low-flow sampling procedures as described in FSOP 2.2.6, Low-Flow Ground Water Sampling.

7.7 Bladder pumps operate by alternating between refill and discharge cycles, which are measured in cycles per minute (CPM). Each round of refill and discharge is one cycle. Adjust the CPM control to increase or decrease the pumping or discharge rate. One CPM pressurizes for a longer time and should be used on deeper or lower yielding wells, while 4 to 6 CPM may be used on shallow or higher yielding wells.

7.8 The discharge rate may be optimized by adjusting the refill and discharge cycle lengths (measured in seconds on the control box readout).

7.9 The volume of water purged in one discharge cycle multiplied by the CPM equals the pumping rate (*e.g.,* 75 ml/cycle x 4 CPM = 300 ml/min). Measure the volume being discharged per cycle at the start of purging and periodically afterwards.

7.10 Increase the refill time or reduce the pressure to reduce the pumping rate.

7.11 Refer to the pump's manual as needed for operating instructions.

7.12 After purging criteria have been met, collect ground water samples in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices). Handle ground water samples in accordance with FSOP 1.5, Sample Custody and Handling.

7.13 Decontaminate pump between sampling locations as appropriate in accordance with FSOP 1.6, Sampling Equipment Decontamination. If using a disposable bladder replace after each use.

7.14 Dispose of investigation derived waste in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices).

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 2.2.6, Low-Flow Ground Water Sampling

Ohio EPA, 2020, Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 10, Ground Water Sampling: Ohio EPA Division of Drinking and Ground Waters

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

U.S. EPA, November 1992, RCRA Ground -Water Monitoring: Draft Technical Guidance: Office of Solid Waste

Ground Water Sampling Using a Peristaltic Pump
FSOP 2.2.9 (December 10, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Peristaltic pumps operate by creating a vacuum in the pump discharge line which draws ground water upwards to the ground surface. The vacuum is created by a series of rotating cams or rollers that compress and relax a flexible discharge line. Air or ground water in front of the rollers is pushed forward through the discharge line, and the portion of the discharge line behind the rollers rebounds to create a vacuum that continuously purges ground water from the well. Typically, these pumps are powered using an internal rechargeable 12-volt battery.

1.2 Limitations of peristaltic pumps for ground water sampling include the following:

1.2.1 Because the peristaltic pumps operate by creating a vacuum, these devices can only be used to purge ground water from depths of approximately 25 feet or less below ground surface (bgs) (the vacuum limit).

1.2.2 The application of a vacuum (negative pressure) to groundwater may promote an unacceptable amount of degassing and associated changes in ground water chemistry (see TGM Chapter 10). However, peristaltic pumps may be used for the collection of ground water compliance samples [FSOP 2.2.4, Ground Water Sampling (General Practices)] for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pH, oxidation-reduction potential, dissolved metals, dissolved gasses or other vacuum-sensitive constituents depending on the site-specific work plan (SSWP) project objectives and data quality objectives (DQOs). If use of the peristaltic pump is not supported by the SSWP objectives or DQOs, then another pump (e.g., a bladder pump) should be considered. Peristaltic pumps -are also suitable for collecting ground water screening samples or compliance samples for constituents that are not vacuum sensitive (*e.g.,* pesticides/herbicides, PCBs, nitrate, chloride, sulfate etc.)

1.2.3 Peristaltic pumps are small and are not recommended for purging large volumes of ground water.

1.3 Peristatic pumps offer the following advantages:

1.3.1 Peristaltic pumps are easily portable and relatively simple to operate compared to other ground water sampling devices.

1.3.2 The only pump components that contact ground water are the disposable discharge line and pump-head tubing, so minimal equipment decontamination is needed. No moving pump parts need to be decontaminated.

1.3.3 Sampler exposure to contaminated ground water is reduced compared to other ground water sampling techniques.

1.3.4 Peristatic pumps may be used to sample wells with inside diameters as small as 0.5 inches.

1.3.5 Peristaltic pumps may be used to perform low-flow ground water sampling at very low rates, *i.e.,* < 100 ml/min (FSOP 2.2.6, Low-Flow Ground Water Sampling).

1.4 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The SSWP will provide project objectives and DQOs. In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

2.0 Definitions

None

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling and health and safety considerations.

3.3 If the pump does not include an internal rechargeable 12-volt battery or additional battery charge is needed, an external 12-volt battery may be needed as a power source. In that case, be aware of the following health and safety considerations:

3.3.1 When carrying a 12-volt battery, lift the battery properly. Bend your hips and knees to squat down, grasp the battery, and while keeping it close to your body, straighten your legs to lift it. Do not lift the battery by bending forward, which may cause back injury.

3.3.2 Be careful when operating a 12-volt power supply under wet conditions.

3.3.3 If using a generator for power supply with a 12-volt adaptor, ensure that it is grounded to avoid electrical shock. Handle gasoline carefully. Always wear protective gloves when handling gasoline, and store gasoline containers outside of the work area.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 If NAPL is encountered in a monitoring well, do not perform ground water sampling. Immediately notify the DERR-SIFU manager and DERR site coordinator.

4.3 If the pump does not have an internal rechargeable battery, a portable 12-volt battery or 12-volt power adapters will be needed to power the pump.

4.4 Discharge line and pump-head tubing used with the peristaltic pump should not adversely affect ground water quality. For discharge line, Ohio EPA recommends the use of fluorocarbon polymer (Teflon®), polyethylene or similarly inert materials.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Peristaltic pump
6.2 12-volt battery or another power source (will need a 12-volt adaptor)
6.3 Appropriate diameter flexible tubing for pump head (cams/rollers)
6.4 Discharge line tubing (must connect to flexible pump head tubing)
6.5 Knife or tubing cutters
6.6 Other ground water sampling equipment and supplies as needed per FSOP 2.2.4, Ground Water Sampling (General Practices).

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4, Ground Water Sampling (General Practices).

7.2 Measure the well’s static water level and total depth in accordance with FSOP 2.2.2, Ground Water Level Measurement.

7.3 Place the pump near the well, connect the power source (if external) and install the flexible tubing and discharge line. The end of the discharge line should extend to the approximate center of the well's screened interval. Take care to prevent potential cross contamination of the discharge tubing. Avoid lowering the discharge tubing to the bottom of the well if possible, to avoid increased sample turbidity.

7.4 Calculate the well volume, even if low-flow sampling. if the well yield is too low to stabilize the water level for low flow sampling, the volumetric sampling technique will need to be used.

7.5 When low flow sampling, measure the static water level with the pump in the well. Monitor the static water level during sampling to ensure that drawdown is minimized If low flow sampling. Follow other low-flow sampling procedures as described in FSOP 2.2.6, Low-Flow Ground Water Sampling.

7.6 Adjust the pump speed control to increase or reduce the pumping rate to stabilize the water column drawdown. Refer to the pump's manual as needed for operating instructions.

7.7 Peristaltic pumps may be used in certain scenarios (*i.e.,* see the TGM (Chapter 10, Ground Water Sampling) and site-specific work plans) for the collection of VOC ground water samples for regulatory compliance, risk assessment or modeling.

7.8 After purging criteria have been met, collect ground water samples in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices). Handle ground water samples in accordance with FSOP 1.5, Sample Custody and Handling.

7.9 Replace the disposable discharge line and flexible pump-head tubing between each sampling location. No decontamination is necessary.

7.10 Dispose of investigation derived waste in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices).

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 2.2.6, Low-Flow Ground Water Sampling

Ohio EPA, October 2020, Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 10, Ground Water Sampling: Ohio EPA Division of Drinking and Ground Waters

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Ground Water Sampling Using an Electric Submersible Pump
FSOP 2.2.10 (December 10, 2020)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Electric submersible pumps used for ground water sampling include centrifugal submersible pumps and progressive cavity (helical rotor) pumps. Centrifugal submersible pumps are the more common and operate by using an electric motor to rotate an impeller (or series of impellers) that push ground water upward through a discharge line by centrifugal force. Ohio EPA uses variable speed centrifugal submersible pumps specifically designed for collecting ground water samples.

1.2 Electric submersible pumps are very versatile for ground water sampling. These devices can be used for low-flow sampling (< 500 ml/min or < 0.1 gpm) and quickly purging large volumes of ground water at higher pumping rates (> 5 gpm). These pumps are effective for purging deep wells (> 100 feet), larger diameter wells (> 2 inches) or wells with large water columns (> 30 feet). The use of an electrical submersible pump to sample a deep well is limited by the length of the electric cord and the amount of hydraulic head the pump is capable of lifting.

1.3 The variable speed electrical submersible pumps used by Ohio EPA for ground water sampling are constructed of stainless steel, Teflon® (fluorocarbon polymer) or other inert, non-sorptive materials. These pumps are also equipped with water-cooled motors, i.e., the electric motor is cooled by ground water flow around and through the pump. Either a portable generator or a 12-volt deep-cycle battery is used for power supply. Ohio EPA also uses disposable discharge line composed of Teflon®, polyethylene or similar materials depending on data quality objectives (DQOs).

1.4 When operated at low-flow rates (< 500 ml/min), variable-speed electric submersible centrifugal pumps may perform similarly to bladder pumps with respect to maintaining sample integrity.

1.5 Limitations of electrical submersible pumps include the following:

1.5.1 When operated at flow rates greater than 1 gpm, electrical submersible pumps may cause increased turbulence and pressure changes, which could adversely affect ground water sample quality, e.g., increased turbidity or loss of volatile constituents.

1.5.2 The heat generated by the electric motor may cause increased ground water sample temperature and loss of dissolved gasses and volatile constituents. However, this concern can be evaluated by monitoring the ground water temperature, and special devices are available (pump shrouds), depending on the well diameter, to prevent the pump motor from generating excessive heat.

1.5.3 Electric submersible pumps include intricate parts and typically result in an increase in decontamination and maintenance time compared to other ground water sampling devices.

1.5.4 Electric submersible pumps are susceptible to locking up when pumping water with excessive silt and fine sand. Caution should be exercised when purging or sampling excessively turbid wells. In some instances, an inertial lift pump and check valve should be used to remove the excessive silts and collect a sample.

1.6 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. The site-specific work plan (SSWP) will provide project objectives and DQOs. In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling and health and safety considerations.

3.3 Be careful when working with electricity under wet conditions.

3.4 If using a generator for power supply, ensure that it is grounded to avoid electrical shock. Handle gasoline carefully. Always wear protective gloves when handling gasoline, and store gasoline containers outside of the work area.

3.5 When carrying a 12-volt battery, lift the battery properly. Bend your hips and knees to squat down, grasp the battery, and while keeping it close to your body, straighten your legs to lift it. Do not lift the battery by bending forward, which may cause back injury.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for general ground water sampling procedure cautions.

4.2 If NAPL is encountered in a monitoring well, do not perform ground water sampling. Immediately notify the DERR-SIFU manager and DERR site coordinator.

4.3 If ground water is being sampled for per- and polyfluoroalkyl substances (PFAS), the pump will need to be checked to ensure that the pump components do not contain Teflon® or other PFAS (see TGM Chapter 10).

4.4 Never lower or lift the pump inside a well using the electrical power cord, especially while operating. This could result in electrocution.

4.5 The pump may be lowered or lifted using the discharge line if it is securely attached to the pump with a hose clamp. When using a hose clamp, do not overtighten the hose clamp screw if the pump is plastic. A safety cord may also be used for lowering and lifting the pump on some pumps. The cord should be composed of an inert material that will not affect ground water quality and should be tied to the pump using a non-slip knot such as a bowline. When removing the pump from the well, be sure to pull the safety line, tubing, and electrical line at the same rate. Otherwise, the lines can coil, bind, and obstruct the pump removal.

4.6 Operating an electrical submersible pump in a well with high amounts of suspended solids or turbidity may “sand lock” (seize) or damage the impellers. Carrying one or more impeller replacement kits during ground water sampling is recommended.

4.7 When operating the pump, do not allow the water level to fall below the pump intake. Otherwise, the pump will overheat.

4.8 If possible, do not operate the pump within the screened interval when purging at rates greater than 1 gpm. This may cause increased sample turbidity.

4.9 Never operate the pump at the bottom of a well. Doing so will likely cause increased sample turbidity and may sand lock the pump in the well.

4.10 Check the pump periodically to ensure the electrical wires have not loosened from the pump head or become abraded or otherwise damaged.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Electric submersible pump and controller box
6.2 Generator or 12-volt deep cycle battery
6.3 Disposable discharge tubing
6.4 Safety cord
6.5 Knife or tubing/cord cutter
6.6 Other ground water sampling equipment and supplies as needed per FSOP 2.2.4, Ground Water Sampling (General Practices)

7.0 Procedures

7.1 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector, multiple gas detection meter (with lower explosive limit/oxygen detection capabilities) or other required instrument and follow the breathing zone and well casing monitoring procedures included in FSOP 2.2.4, Ground Water Sampling (General Practices).

7.2 Measure the well's static water level and total depth in accordance with FSOP 2.2.2, Ground Water Level Measurement.

7.3 Connect the discharge tubing (and safety cord if applicable) to the pump, taking care to prevent potential cross-contamination (*e.g.,* working over a clean sheet of plastic to prevent direct contact with the ground or other potentially contaminated surfaces).

7.4 Calculate the well volume, even if low-flow sampling. (If the well yield is too low to stabilize the water level for low flow sampling, the volumetric sampling technique will need to be used.)

7.5 Using the discharge line tubing (or safety cord), slowly and carefully install the pump in a manner that minimizes disturbance to the water column in the well. The pump should be installed in the approximate center of the screened interval for low-flow sampling, and if possible, above the screened interval for volumetric sampling. Never place the pump at the bottom of the well.

7.6 When low-flow sampling, measure the static water level with the pump in the well. Monitor the static water level during sampling to ensure that drawdown is minimized. Follow other low-flow sampling procedures as described in FSOP 2.2.6, Low-Flow Ground Water Sampling.

7.7 If using a generator for power supply, the exhaust should be directed away from (downwind of) the wellhead work area where the ground water samples will be collected to avoid cross contaminating the samples.

7.8 Connect the power source to the pump controller box and the controller box to the pump.

7.9 Start the pump and adjust the flow rate using the pump speed control on the controller box. Refer to the pump's manual as needed for operating instructions.

7.10 Monitor the drawdown in the well while purging to avoid drawing the water level below the top of the well screen or to the pump intake. If this situation occurs, immediately reduce the flow rate to allow the water level to rise above the top of the well screen or the pump intake.

7.11 Monitor the purge water temperature to evaluate if the pump motor may be heating the ground water. If this situation occurs, the well will likely need to be sampled using a different device. Consult the SSWP or contact the DERR SIFU manager and DERR site coordinator for direction regarding alternative sampling procedures.

7.12 After purging criteria have been met, collect ground water samples in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices). Handle ground water samples in accordance with FSOP 1.5, Sample Custody and Handling.

7.13 Replace the discharge line between each sampling location and decontaminant the pump and electrical cord in accordance with the manufacturer's instructions and FSOP 1.6, Sample Equipment Decontamination.

7.14 Dispose of investigation derived waste in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Refer to the SSWP and FSOP 2.2.4, Ground Water Sampling (General Practices).

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.2, Ground Water Level Measurement

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 2.2.6, Low-Flow Ground Water Sampling

Ohio EPA, 2020, Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 10, Ground Water Sampling: Ohio EPA Division of Drinking and Ground Waters

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Sampling Water Supply Systems
FSOP 2.2.11 (January 5, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This FSOP provides general procedures for collecting a representative water sample from a water supply system tap (valve or faucet). The water source for the system may be ground water or surface water.

1.2 Ensuring that the public has a safe source of potable water is the primary concern for sampling water supply systems. Other reasons may include, but are not limited to the following:

- Investigating water quality concerns when directly sampling the water source is not practicable
- Characterizing the extent of a ground water contamination plume
- Evaluating the water quality at the point of use, including potential contaminants that may originate from the water distribution system components.

1.3 This FSOP does not apply when sampling directly from a water supply well using the ground water sampling techniques described in the following FSOPs:

- FSOP 2.2.7, Ground Water Sampling Using a Bailer
- FSOP 2.2.8, Ground water Sampling Using a Bladder Pump
- FSOP 2.2.10, Ground Water Sampling Using an Electric Submersible Pump

1.4 Water supply system samples may be subject to contamination from the system components including piping (*e.g.,* iron, copper, lead, plastics and solvent glues) and greases or oils from valves and pumps.

1.5 For water supply systems with ground water sources, information such as aquifer type and well depth, yield and construction may be obtained from The Ohio Department of Natural Resources (ODNR) Division of Geologic Survey water well log report (online search tools) or the local health department.

1.6 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. For this FSOP, refer to Appendix A, Additional Information for Sampling Water Supply Wells. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the TGM and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification. The procedures described in the FSOP may vary based on site-specific work plan (SSWP) project objectives or data quality objectives (DQOs).

1.7 The procedures provided by the FSOP pertain to ground water samples collected to investigate the presence of CERCLA hazardous substances and petroleum. If sampling for bacterial content, please refer to Chapter 10, Appendix A of Ohio EPA's TGM or contact the local health department or the Ohio Department of Health (ODH) for appropriate sampling procedures. If sampling for other types of constituents (*e.g.,* radionuclides), following the sampling procedures provided in the SSWP.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific hazards before performing work.

3.2 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) as applicable for general ground water sampling and health and safety considerations.

3.3 Be aware of health and safety hazards associated with residential properties including but not limited to pets, clutter, fuels, household hazardous materials, staircases, low basement ceilings, work areas with limited space, etc.

3.4 **Never** enter an OSHA-defined confined space for any reason for sampling a water supply system or during any other field activity. Only appropriately trained Agency staff are qualified to enter confined spaces for reconnaissance or sampling activities and will perform such work as necessary in accordance with Ohio EPA's Confined Space Entry Policy (OEPA-SM-10-002). The Agency Safety Program Manager is to be contacted for guidance in such situations.

3.5 Wear sample gloves and eye protection when collecting samples in pre-preserved containers or when adding sample preservatives to containers.

4.0 Procedure Cautions

4.1 Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) as applicable for general ground water sampling procedure cautions.

4.2 If NAPL (*i.e.,* sheen) is identified in purge water and/or in a water supply sample, immediately notify the DERR SIFU manager and DERR site coordinator.

4.3 Evaluate the design, age and construction of the water system before selecting a sampling location to ensure that a representative water sample is obtained and to avoid damaging the system.

4.4 Collect samples from cold water taps only.

4.5 Avoid sampling leaking taps that allow discharge from around the valve-stem handle and down the outside of the faucet or taps where water tends to flow up along the outside of the faucet lip. Samples from these taps may be contaminated with greases or oils from the valve stem, or contamination located on the outside surface of the tap.

4.6 Avoid sampling taps where the water flow is not constant.

4.7 Hoses, strainers, filters or aerators attached to the tap may be potential sources of contamination and should be removed before sampling, if possible.

4.8 Water supply samples should never be filtered.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

Refer to FSOP 2.2.4, Ground Water Sampling (General Practices) for the ground water sampling equipment and supplies needed, which will vary based on SSWP project objectives and DQOs.

7.0 Procedures

7.1 The DERR site coordinator will obtain written permission to access the property and perform water supply system sampling from the property owner and tenant (if applicable) prior to mobilizing for sampling activities.

7.2 After access permission has been granted in writing, contact the property owner and/or tenant (if applicable) to arrange a date and time to perform the sampling. Also contact the local health department or ODH for scheduling if they will be observing or participating in the sampling activities.

7.3 Before selecting a sampling point, inspect the water supply system to fully understand the location of all components and evaluate all potential sampling locations. Ideally, the tap selected for sample collection should be the closest to the water line entering the property and located upstream of any water treatment system components.

7.4 After obtaining permission from the property owner or tenant, remove any hoses, strainers, filters or aerators from the selected tap (if possible).

7.5 Open the sampling point valve (cold water only) and purge the water supply system as follows:

7.5.1 If sampling an actively used system, purge for at least 5 minutes.

7.5.2 If the system has not been actively used, purge for at least 15 minutes.

7.5.3 If the sampling location is located upstream of a pressurization or storage tank, taps inside the building (downstream of the tank) should be opened to prevent backflow from the tank to the tap being sampled.

7.5.4 In the event the water sample must be collected from a tap downstream of a pressurization or storage tank, purge enough water for a complete exchange of fresh water into the tank and at the sampling location.

7.5.5 If the sample is collected from a faucet (e.g., kitchen faucet) with an aerator, remove the aerator if possible, prior to collecting the sample.

7.6 If required by the SSWP, monitor ground water stabilization parameters.

7.7 When SSWP purging criteria have been met, collect the water sample by adjusting the flow to a moderately slow rate (*e.g.,* 0.2 to 0.5 gpm) and filling the sampling containers. Do not touch the inside of lip of the sampling containers to any part of the tap, and when filling the sample containers be careful not to flush out chemical preservatives. Do not adjust the flow rate during sampling. Chemical-resistant (*e.g.,* nitrile) gloves should be worn when sampling. Follow the sampling procedures in FSOP 2.2.4, Ground Water Sampling (General Practices) as applicable.

7.8 Handle water samples in accordance with FSOP 1.5, Sample Custody and Handling.

7.9 Dispose of any investigation derived waste in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

8.1 Document the water supply system components, configuration and condition. Take photographs as needed.

8.2 Follow FSOP 1.3, Field Documentation.

8.3 Please be aware of Personally Identifiable Information (PII) considerations when conducting residential sampling and reporting activities under federal grants.

9.0 Quality Assurance and Quality Control

QA/QC samples may include duplicate samples, trip and equipment blanks and matrix spike/matrix duplicate samples depending upon the project DQOs. In general, water supply samples should include 1 duplicate sample per 10 water supply samples collected. If VOC samples are being collected for analysis, at least one trip blank should be submitted per sample shipment.

10.0 Attachments

DERR Water Supply Well Sampling Logsheet

11.0 References

FSOP 1.3, Field Documentation.

FSOP 1.5, Sample Custody and Sampling

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.4, Ground Water Sampling (General Practices)

Ohio EPA, 2020, Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 10, Ground Water Sampling, Appendix A, Additional Information for Sampling Water Supply Wells: Ohio EPA Division of Drinking and Ground Waters

DERR Water Supply Sampling Log Sheet

Site Name: ______________________________ **Date:** ______________________________

Sample ID: ______________________________ **Time:** ______________________________

Duplicate
Sample ID #: ____________________________ **Time:** ______________________________

Sampled by: ______________________________

Sample Type: **FIELD** **DUP** **BKG** **MS/MSD**

Parameters	**VOCs**	**SVOCs**	**Metals**	**Pest**	**Cyanide**			
# Containers								
Preservative (circle)	HCL	Ice	HNO3	Ice	NaOH			

Owner's Name: **Phone:**
Owner's Address:
Number Served by Water Source (if available):
Sample Collection Point:
Water Supply System Notes (if available):
Depth of Well:
Date Well Installed:
Type of Filter or Well Treatment System:
Is the Home on Septic or Sewer?
Other:

January 2021

Field Filtering of Ground Water Samples
FSOP 2.2.12, January 5, 2021
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Field filtration of ground water samples is performed to remove the immobile sediment fraction associated with sample turbidity, which is an important concern for samples to be analyzed for total metals and other turbidity-sensitive constituents. The presence of sediment in samples preserved by field acidification may result in total metal analyses that overestimate the true concentration of mobile (dissolved plus colloidal fraction) metals species. Therefore, field filtering of ground water samples may be appropriate under certain conditions if consistent with site-specific work plan (SSWP) project and data quality objectives (DQOs), and if permitted under the regulatory program for which the samples are being collected and analyzed.

1.2 There are two types of field filtration techniques: “open system” and “in-line” (or “closed”) system. The primary difference between the two is that ground water samples filtered using the open system technique are exposed to the atmosphere and pressurized, whereas ground water samples filtered using the in-line system are not exposed. Accordingly, Ohio EPA utilizes the in-line filtering technique, which provides more representative and reliable results. The open system technique should not be used.

1.3 Ground water samples should be filtered only when all of the following conditions are present:

1.3.1 Samples are collected from monitoring wells that have been properly designed, installed and developed.

1.3.2 Samples are collected using the low-flow purging and sampling technique that is designed to minimize sample disturbance. Refer to FSOP 2.2.6, Low-Flow Ground Water Sampling.

1.3.3 Indicator parameters have been measured and stabilized before sample collection.

1.3.4 Turbidity stabilizes above 10 Nephelometric Turbidity Units (NTU), and based on professional judgment, the formation/saturated zone being sampled exhibits a high degree of sediment mobility, i.e., the turbidity is a function of natural formation conditions (e.g., clay- or silt-rich glacial deposits, karst aquifers with high flow rates).

1.4 Ground water samples collected at municipal solid waste landfills (MSW) should never be filtered. Federal regulations [40 CFR 258.53(b)] specify that metals analyses for ground water samples collected at MSW landfills be performed on unfiltered ground water samples only.

1.5 All ground water sampling techniques and associated procedures should be consistent with Ohio EPA's Technical Guidance Manual (TGM) for Hydrogeologic Investigations and Ground Water Monitoring, specifically Chapter 10, Ground Water Sampling. In addition, U.S. EPA 2002 (Yeskis and Zavala) provides ground water sampling guidance for RCRA and CERCLA sites. For Ohio EPA Voluntary Action Program (VAP) sites, field filtration procedures should be consistent with Ohio EPA VAP Technical Guidance Compendium VA30007.19.010, Ground Water Sample Filtration. The site-specific work plan (SSWP) will provide project objectives and data quality objectives (DQOs). In the event there appears to be inconsistency between the referenced guidance documents and project objectives or DQOs, please contact the DERR SIFU manager and DERR site coordinator for clarification.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Review the site-specific health and safety plan (HASP) for sampling hazards before beginning work.

3.2 Wear appropriate personal protective equipment (PPE) when performing ground water sampling activities, including but not limited to chemical-resistant gloves compatible with the contaminants of concern and eye/face protection and coveralls for splash protection, which may be more likely to occur when field filtering ground water samples.

3.3 Use caution and wear work gloves when assembling or disassembling equipment and cutting discharge tubing.

4.0 Procedure Cautions

4.1 Field filtering should only be performed for metals and other turbidity-sensitive parameters. Ground water samples for volatile organic compounds, semivolatile organic compounds, pesticides/herbicides or polychlorinated biphenyls should never be field filtered.

4.2 The appropriate filter size should be determined during the development of the SSWP. Filters with pore sizes ranging from 10 microns to 0.1 microns may be used as warranted based on project objectives, DQOs and site hydrogeologic conditions. SIFU typically uses 0.45-micron filters for non-VAP ground water sampling and 5-micron filters for VAP ground water sampling. If estimates of dissolved metals concentrations are desired, Ohio EPA recommends 0.1-micron filters.

4.3 If using filters with smaller pore sizes (*i.e.,* 0.45-micron to 0.1-micron field filters), carry at least two filters per sample in the field. These filters tend to clog quickly, and additional filters may be needed to collect the required sample volumes.

4.4 If using a flow-through cell to measure ground water stabilization parameters, an in-line field filter should never be installed directly before (directly upgradient of) the flow through cell. A “t” fitting with a stopcock valve may be installed in the discharge line before (upgradient) of the flow-through cell to provide a separate discharge line for sample filtering.

4.5 Never attempt to decontaminate or re-use a field filter.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 In-line 5-micron to 0.45-micron (or other filter pore size in accordance with SSWP) polycarbonate or cellulose acetate filters

6.2 In-line filter apparatus

6.3 Ground water sampling supplies required by FSOP 2.2.4, Ground Water Sampling (General Practices)

7.0 Procedure (In-Line Filtering Method with Low-Flow Sampling Only)

7.1 After ground water stabilization has been achieved (including turbidity stabilization), assemble the filter and install it in the sampling discharge line as recommended by the filter manufacturer. If using a flow-through cell to measure ground water stabilization parameters, the flow through cell should be disconnected and removed before installing the in-line filter. Alternatively, a “t” fitting with a stopcock valve may be installed in the discharge line before (upgradient) of the flow-through cell to provide a separate discharge line for sample filtering.

7.2 Allow at least 500 ml of ground water to pass through the filter before sample collection to help ensure that the filter has equilibrated with the ground water sample (Ohio EPA 2020 and U.S. EPA 2002). The filter manufacturer’s recommendations regarding sample equilibration should also be consulted.

7.3 Collect filtered samples for metals or and/or other turbidity-sensitive parameters as described in the SSWP and in accordance with FSOP 2.2.4, Ground Water Sampling (General Practices).

7.4 When sampling is completed, dispose of the used filters and any associated disposable apparatus in accordance with FSOP 1.7, Investigation Derived Wastes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Control and Quality Assurance

None

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.7, Investigation Derived Wastes

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 2.2.6, Low-Flow (Low-Stress) Ground Water Sampling

Ohio EPA, 2020, Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 10, Ground Water Sampling: Ohio EPA Division of Drinking and Ground Waters

Ohio EPA, January 2003 (rev. 2018), VAP Technical Guidance Compendium VA30007.19.010, Ground Water Sample Filtration

U.S. EPA (D. Yeskis and B. Zavala), May 2002, Ground Water Sampling Guidelines for Superfund and RCRA Project Managers (Ground Water Forum Issue Paper): Office of Solid Waste and Emergency Response, EPA 542-S-02-001

Surface Water Sample Collection
FSOP 2.3.1 (January 11, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This FSOP provides general procedures for surface water sample collection. The methods, procedures, and sampling equipment selected for a sampling event should always meet the site or project-specific data quality objectives (DQOs).

1.2 Surface waters include rivers, streams, lakes, ponds, wetlands, springs, and seeps. In addition, surface water may be sampled from drainage ditches, man-made lagoons or impoundments, discharge pipes/outfalls, storm sewers and associated manholes or vaults, or areas of transient ponding.

1.3 This FSOP is not necessarily applicable to field activities conducted by Emergency Response, the Office of Special Investigations, the Radiation Assessment Team, or other specialized teams.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always be conscious of hazards associated with the water body during surface water sampling, especially if sampling a lake, pond, wetland, lagoon, impoundment, river, or large stream.

3.2 Never enter a river or stream under high-flow conditions.

3.3 Be aware of trip or fall hazards along riverbanks and lagoon or impoundment slopes.

3.4 Be aware of the dangers of working near low-head dams (*e.g.,* rapid flow and undercurrents) as well as hazards that may be posed by other man-made structures such as manholes, vaults, weirs, pump houses, and associated electrical or mechanical equipment.

3.5 If sampling in swift water, near low head dams, through ice over water of unknown depth, or in other potentially dangerous situations, always wear a personal flotation device (PFD).

3.6 Never walk on a surface crust, or partially submerged debris in a lagoon or impoundment.

3.7 Do not walk on a frozen river, lake, pond, lagoon, or impoundment.

3.8 When collecting surface water samples, use the “buddy system,” with at least two persons present at all times.

3.9 Be aware of biological hazards, e.g., snakes, ticks, mosquitoes, and poison ivy, in areas around water bodies.

3.10 Never enter a permit required confined space for any reason during surface water sampling activities. Only Ohio EPA Office of Special Investigation Unit staff or other appropriately trained staff are qualified to enter confined spaces for reconnaissance or sampling activities, and will perform such work as necessary in accordance with Ohio EPA’s Confined Space Entry Policy (OEPA-SP-14-4).

3.11 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work.

3.12 When sampling in cold weather, be aware of the potential for hypothermia due to falling in or immersion in cold water. Be sure the sampling vehicle is nearby so staff can enter and turn on the vehicle heater and change clothes as necessary.

4.0 Procedure Cautions

4.1 Sample surface water before sampling sediment whenever possible.

4.2 Avoid agitating and splashing surface water during sampling. Aeration of the sampled water may cause loss of volatile organic compounds or other undesirable changes in sample quality.

4.3 Avoid disturbing sediments during surface water sampling. Incorporating excessive sediment into (increasing the turbidity of) a surface water sample often artificially elevates the concentrations of certain constituents, particularly metals and polynuclear aromatic hydrocarbons. If sediments are disturbed, allow sufficient time for the sediment to settle and the water to clear before sampling.

4.4 Avoid introducing foreign materials into surface water samples. “Foreign materials” may include vegetative debris (leaves, tree bark, plant stems, etc.) or fragments of solid waste or debris materials (paper, plastics, wood fragments, etc.)

4.5 Samples may be collected at the surface water (air/water) interface or below the water surface dependent on project DQOs.

4.6 If collecting multiple samples from flowing surface water, begin at the downstream location and work upstream to avoid compromising sample quality (*e.g.,* increasing sample turbidity or disturbing contaminated sediments).

4.7 If using pre-preserved sample containers, take care not to flush the preservative from the container during the sampling process.

4.8 Use a glass sample jar or stainless-steel dipper to collect samples for organic chemical analyses. Plastic dippers or sample containers may serve as a source of cross contamination for certain organic chemicals.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Equipment and supplies needed regardless of sampling method:

6.1.1 Chain-of-custody forms
6.1.2 Clear tape
6.1.3 Decontamination equipment and supplies (FSOP 1.6, Sampling Equipment Decontamination)
6.1.4 Field logbook, field log sheets, or activity-specific field forms
6.1.5 Method-specific analytical sample containers with waterproof labels
6.1.6 Paper towels
6.1.7 Pens and markers (preferably waterproof)
6.1.8 Personal protective equipment per the HASP including PFD
6.1.9 Sample coolers
6.1.10 Sampling gloves
6.1.11 Sample preservatives, (*e.g.,* ice, HCl, HNO_3, NaOH, H_2SO_4)
6.1.12 Stainless steel dippers or clean sample jars for sample collection
6.1.13 Water quality monitoring instruments (*e.g.,* pH/temperature/specific conductance meter, dissolved oxygen meter, turbidity meter)

6.2 Other equipment and supplies that may be needed for unique circumstances such as seep sampling and/or surface waters that are difficult to access:

6.2.1 Composite Liquid Waste Sampler (Coliwasa)
6.2.2 Disposable bailers
6.2.3 Extension rod (for stainless steel dipper or glass sample jar)
6.2.4 Hand auger, sampling spoon, or shovel
6.2.5 Inertial lift pump
6.2.6 Peristaltic pump and sampling tubing
6.2.7 Small diameter PVC well screen to construct seep sampling point

7.0 Procedures

7.1 General surface water sampling procedures (regardless of sampling method)

7.1.1 If possible, conduct site reconnaissance to identify potential sampling locations.

7.1.2 If using pre-labeled sample containers, complete each label and cover with clear tape before sampling.

7.1.3 Use decontaminated or disposable equipment to collect each sample.

7.1.4 Wear a pair of clean sampling gloves when collecting each sample.

7.1.5 Samples should be collected in the following order of sensitivity to volatility and turbidity: (1) volatile organic compounds (VOCs); (2) metals; (3) semi-volatile organic compounds (SVOC)s; (4) pesticides, herbicides and PCBs; and (5) general water quality parameters, e.g., ammonia, chloride, alkalinity, etc.

7.1.6 After filling, preserving, and labeling sample containers, place each sample container in a cooler on ice for shipment or delivery to the laboratory. Complete the chain-of-custody form.

7.1.7 Collect water quality measurements (*i.e.,* stabilization parameters) such as pH, temperature, specific conductance, dissolved oxygen, or turbidity, as required.

7.1.8 A field logbook or field log sheet may also be used to record the pertinent information if the field data form is not used (refer to FSOP 1.3, Field Documentation).

7.1.9 Decontaminate stainless steel dippers and any other sampling equipment used between samples in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.1.10 Dispose of investigation derived waste (IDW) in accordance with FSOP 1.7, Investigation Derived Wastes.

7.1.11 Follow all applicable criteria in FSOP 1.5, Sample Custody and Handling, when handling or shipping/transporting samples to the laboratory.

7.1.12 Mark the sampling locations clearly for Global Positioning System (GPS) surveying.

7.2 Sampling using a sample jar or stainless-steel dipper

7.2.1 For samples collected at the surface water interface, use a clean sample jar or a decontaminated stainless-steel dipper to fill the sample containers. Avoid overfilling pre-preserved sample containers and diluting the preservative.

7.2.2 For samples collected below the surface water interface, collect the samples as follows:

7.2.2.1 Close, invert, and completely submerge unpreserved sample containers. Pre-preserved sample containers cannot be used.

7.2.2.2 If the surface water is flowing, position the sample container opening in the upstream direction.

7.2.2.3 Fill each container by opening it under water, slowly turning it right side up, and allowing it to fill completely without breaking the water surface.

7.2.2.4 Close each filled container while still submerged.

7.2.2.5 Add preservatives to the sample container <u>after</u> the sample has been collected.

7.2.2.6 Alternatively, collect the sample from below the surface water interface using a peristaltic pump and disposable tubing. One sampler holds the tubing in the water while the other operates the pump and fills the sample containers from the bank or shore of the surface water body. This technique allows the use of pre-preserved sample containers.

7.3 Sampling from springs or seeps

7.3.1 If possible, avoid sampling springs or seeps during periods of significant rainfall.

7.3.2 Developed springs generally consist of a trench filled with buried gravel, which may include a discharge pipe and/or a concrete basin. If the spring has a flowing discharge pipe, simply fill the sample containers at the outflow (just as if collecting a water sample from an outdoor tap). If the spring consists only of a concrete basin with no discharge pipe, collect the sample directly from the basin using the techniques described in Section 7.2.

7.3.3 Collect surface water samples from seeps or undeveloped springs using the techniques described in Section 7.2 if a sufficient depth of ponded water is present. Otherwise, use any of the following techniques to provide adequate water volume for sampling:

7.3.3.1 Excavate a small area of the seep or undeveloped spring to a depth of approximately six inches using a clean sampling spoon or shovel. After allowing the excavation to fill with water (and allowing time for sediment to settle out and turbidity to drop), use the techniques described in Section 7.2 to collect a sample.

7.3.3.2 Use a sampler specifically designed to collect seep samples such as a stainless-steel scoop that has been modified to capture and contain water as it slowly discharges from a seep. Such samplers may help to reduce sample turbidity.

7.3.3.3 To collect low turbidity samples, easily purge prior to sampling, or collect multiple samples over time, install a small-diameter well screen in the seep or undeveloped spring to construct a fixed sampling sump:

7.3.3.3.1 Use a hand auger to excavate a shallow boring approximately two feet deep.

7.3.3.3.2 Install approximately 2.5 feet of PVC well screen with a sand pack. Use a PVC cap or J-plug to close the top of the screen when the sump is not being used.

7.3.3.3.3 Allow sufficient time for the sump to fill completely and for disturbed sediment to settle before sampling. If necessary, sediment-laden water may be purged from the sump after installation and prior to sampling to obtain lower turbidity samples.

7.3.3.3.4 Use a disposable bailer, peristaltic pump, or inertial lift pump to collect a sample from the sump (screen) after it fills with water.

7.4 Some surface waters may be difficult to sample due to site characteristics or health and safety concerns, such as an impoundment with steep banks or a deep storm sewer or outfalls with extremely high flows. Consider using the following equipment for these circumstances:

7.4.1 Extension rod for a stainless-steel dipper or glass sampling jar

7.4.2 Disposable bailer

7.4.3 Peristaltic pump with extended tubing

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

9.1 Quality assurance/quality control (QA/QC) sample requirements are to be specified in the site-specific work plan. QA/QC samples may include duplicate samples, trip and equipment blanks and matrix spike/matrix duplicate samples depending upon the project DQOs. In general, surface water sampling events should include 1 duplicate sample per 10 surface water samples collected. If VOC samples are being collected for analysis, at least one trip blank should be submitted per sample shipment.

9.2 If possible, collect duplicate samples at locations where contamination (or chemical(s)s of concern) is known or likely to be present at detectable concentrations.

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.5, Sample Custody and Handling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

Ohio EPA, Office of Safety and Labor, Standard Operating Procedure (OEPA-SP-14-4), Confined Space Entry Policy. Revised 08.07.2020

Sediment Sample Collection
FSOP 2.3.2 (January 11, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 This FSOP provides general procedures for sediment sample collection from shallow surface waters less than approximately two feet deep, areas of exposed sediment deposition adjacent to surface water bodies (*e.g.,* exposed mud flats during low water conditions), and seeps. The methods, procedures, and sampling equipment selected for a sampling event should always meet the site- or project-specific data quality objectives (DQOs). Surface waters include rivers, streams, lakes, ponds, wetlands, springs, and seeps. In addition, sediment may be sampled from storm sewers, drainage ditches, man-made lagoons or impoundments, or areas of transient ponding.

1.2 This FSOP is not applicable for the collection of sediment samples from surface waters deeper than approximately two feet or if sampling with specialized sampling equipment. For sediment sampling in deeper water or sediment sampling using specialized equipment (*e.g.,* dredges, coring devices, etc.), consult with SIFU and/or the Division of Surface Water for appropriate methodology and procedures.

1.3 For the purpose of this FSOP, sediments are unconsolidated organic or inorganic materials deposited by or beneath a surface water body. The physical and chemical nature of sediments is strongly influenced by particle size. Relatively fine-grained materials such as silts or clays with particle sizes less than 0.06 millimeters (60 microns) are preferred for chemical analysis. Larger sediment sizes may not retain chemical analytes of concern. Therefore, for the purpose of chemical analysis and the evaluation of chemical data, a representative sediment sample should contain a minimum of 30 percent silt and clay by volume. For a more detailed discussion of the definition of sediment and selection of sediment sampling locations and methods, consult the Ohio EPA Division of Surface Water Sediment Sampling Guide and Methodologies (3rd Edition, 2012).

1.4 Depending on project DQOs, either discrete sediment sampling or incremental sampling may be appropriate. Incremental sampling methodology is a structured composite sampling and processing protocol that reduces data variability and provides a reasonable estimate of a chemical's average concentrations for the area and volume of sediment being sampled. Please refer to FSOP 2.6.1, Multi-Incremental Sampling for Soils and Sediments, for DERR's incremental sampling procedures. If incremental sediment sampling is performed, then FSOP 2.6.1 should be used in conjunction with this FSOP.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always be conscious of water hazards during sediment sampling, especially if sampling a lake, pond, lagoon, impoundment, river, or large stream.

3.2 Never enter a river or stream under high-flow conditions.

3.3 Be aware of trip or fall hazards along riverbanks and lagoon or impoundment slopes.

3.4 Be aware of the dangers of working near low-head dams (i.e., rapid flow and undercurrents) as well as hazards that may be posed by other man-made structures such as manholes, vaults, weirs, pump houses and associated electrical or mechanical equipment.

3.5 Always wear a personal flotation device (PFD) if in the immediate vicinity of deep or swift water, near low head dams, though ice over water of unknown depth, or in other potentially dangerous situations.

3.6 Never walk on exposed sediment of unknown thickness, surface crust or partially submerged debris in a lagoon or impoundment.

3.7 Do not walk on a frozen river, lake, pond, lagoon, or impoundment.

3.8 When collecting sediment samples, use the “buddy system,” with at least two persons present at all times.

3.9 Be aware of biological hazards (*e.g.,* snakes, ticks, mosquitoes, and poison ivy areas), around water bodies.

3.10 Never enter a permit required confined space for any reason during surface water sampling activities. Only Ohio EPA Office of Special Investigation staff or other appropriately trained staff are qualified to enter confined spaces for reconnaissance or sampling activities, and will perform such work as necessary in accordance with Ohio EPA’s Confined Space Entry Policy (OEPA-SP-14-4).

3.11 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work.

3.12 When sampling in cold weather, be aware of the potential for hypothermia due to falling in or immersion in cold water. Be sure the sampling vehicle is nearby so staff can enter and turn on the vehicle heater and change clothes as necessary.

4.0 Procedure Cautions

4.1 If surface water sampling is being performed with sediment sampling, collect the surface water samples first to avoid entraining sediment into surface water samples.

4.2 If collecting multiple samples from flowing surface water, begin the sampling in a downstream direction and work upstream to avoid compromising sample quality.

4.3 Use a stainless-steel spoon or trowel to collect sediment samples for organic chemical analyses rather than plastic implements that may serve as a source of cross contamination for certain organic chemicals.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Chain-of-custody forms
6.2 Clear tape
6.3 Decontamination equipment and supplies (FSOP 1.6, Sampling Equipment Decontamination)
6.4 Field logbook, field log sheets, or activity-specific field forms
6.5 Method-specific analytical sample containers with labels (preferably waterproof)
6.6 Paper towels
6.7 Pens and markers (preferably waterproof)
6.8 Personal protective equipment per the HASP and PFD when working near water
6.9 Plastic sheeting
6.10 Sample coolers
6.11 Sampling gloves
6.12 Shovel with long handle (to reach sediments in deeper water)
6.13 Stainless steel dippers or trowels for sample collection
6.14 Stainless steel pans or bowls
6.15 Waders or rubber boots
6.16 Water quality monitoring instruments (*e.g.,* pH/temperature/specific conductance meter, dissolved oxygen meter, turbidity meter), as needed to achieve project DQOs

7.0 Procedures

7.1 If possible, conduct site reconnaissance to identify potential sampling locations. Investigate and probe for areas of adequate sediment accumulation, which are typically located in the quieter backwater or slack water areas in streams and rivers. In some areas of faster flowing water, "discrete" samples may have to be composited from several adjacent locations to obtain an adequate sample volume.

7.2 Set up a staging area on the water body bank or other dry area adjacent to each sample collection location. Place sample containers and equipment on plastic sheeting to avoid cross contamination.

7.3 If using pre-labeled containers, complete each label and seal with clear tape before sampling.

7.4 Use decontaminated or disposable equipment to collect each discrete or incremental sample.

7.5 Wear a pair of clean sampling gloves when collecting each discrete or incremental sample.

7.6 If surface water samples are also being collected for analysis at the same locations as sediment samples, collect the surface water samples first, then perform any required surface water field monitoring, and collect sediment samples last.

7.7 For the collection of discrete sediment samples:

7.7.1 For analytes other than volatile organic compounds (VOCs), collect sediment with a stainless-steel spoon, trowel, hand auger, or shovel and place it into a stainless-steel or disposable foil pan or bowl. (If sufficient fine-grained sediments (silt and clay) are not available at the selected location, then sediment samples may need to be collected from several adjacent locations to obtain adequate sample volume.) Slowly decant excess water from the pan or bowl. Remove large rocks, twigs, leaves, and other debris from the pan or bowl. Gently homogenize the sample with a stainless-steel spoon or trowel. Place the sample in an appropriate laboratory-supplied sample container(s) and preserve it as required (*i.e.,* in cooler with ice).

7.7.2 For VOC analysis, place sediment directly into the laboratory-supplied sample container and close the container. If additional sample volume is needed from adjacent location(s), reopen the container at each additional location, add additional sediment as necessary, and close the container. Preserve the sample as required (*i.e.,* in cooler with ice).

7.8 For collection of incremental samples, follow the procedures provided by FSOP 2.6.1, Multi-Incremental Sampling for Soils and Sediments.

7.9 After filling and labeling all sample containers, ensure that the chain-of-custody form has been properly completed and place each sample container in a sample cooler on ice for shipment or delivery to the laboratory.

7.10 Record all sample information on the attached Sediment Sample Collection Data Form (preferred). A field logbook or other field log sheet may also be used to record the pertinent sampling information if the attached field data form is not used (refer to FSOP 1.3, Field Documentation).

7.11 Decontaminate stainless-steel spoons, trowels, and shovels and any other sampling equipment used between samples in accordance with FSOP 1.6, Sampling Equipment Decontamination.

7.12 Dispose of investigation derived waste (IDW) in accordance with FSOP 1.7, Investigation Derived Wastes.

7.13 Follow all applicable criteria in FSOP 1.5, Sample Custody and Handling, when handling or shipping/transporting samples to the laboratory.

7.14 Mark the discrete sampling locations or incremental sampling decision unit areas clearly for global positioning system (GPS) surveying. If a sediment sample is being collected in conjunction with a corresponding surface water sample, mark the surface water location. If a discrete sediment sample is composited from several adjacent subset locations, mark the approximate center of the sample subset area.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

9.0 Quality Assurance and Quality Control

Quality assurance/quality control (QA/QC) sample requirements are to be specified in the site-specific work plan. QA/QC samples may include duplicate samples, trip and equipment blanks and matrix spike/matrix duplicate samples depending upon the project DQOs. Sediment sampling events will include 1 duplicate sample per 10 sediment samples collected.

10.0 Attachments

None

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.5, Sample Custody and Handling

FSOP 1.6, Sampling Equipment Decontamination

FSOP 1.7, Investigation Derived Wastes

FSOP 2.6.1, Multi-Incremental Sampling for Soils and Sediments

Ohio EPA, Division of Surface Water, Sediment Sampling Guide and Methodologies (3rd Edition), March 2012.

Ohio EPA, Office of Safety and Labor, Standard Operating Procedure (OEPA-SP-14-4), Confined Space Entry Policy. Revised 08.07.2020

Procedures for Active Soil Gas Sampling Using Direct-Push Systems
FSOP 2.4.1 (January 25, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Vapor intrusion is defined as vapor phase migration of volatile organic compounds (VOCs) into occupied buildings from underlying contaminated ground water and/or soil. Soil gas surveys provide information on the soil atmosphere in the vadose zone that can aid in assessing the presence, composition, source, and distribution of contaminants. The purpose of this document is to provide guidance for conducting soil gas sampling, and shall pertain to active soil gas surveys, whereby a volume of soil gas is pumped out of the vadose zone into a sample collection device for analysis.

1.2 Detection of individual constituents by active soil gas sampling is limited by the physical and chemical properties of individual contaminants of concern* and the soil characteristics of the site. In general, chemical parameters or criteria to be considered prior to selecting soil gas sampling activities are as follows:

- Vapor Pressure > 0.1 mm Hg
- Henry's Law Constant > 0.1
- Degree of soil saturation (chemical and/or water) < 80%
- Sampling zone is permeable and permits vapor migration

*Please refer to Sample Collection and Evaluation of Vapor Intrusion to Indoor Air (Ohio EPA DERR, March 2020).

1.3 Results from soil gas surveys are used in both qualitative and quantitative evaluations. The quality and application of the data is dependent upon many factors, including but not limited to: the DQO's used to develop the sampling plan, the number of sample locations and data points, the selection of the sample locations, the soil characteristics of the site, the distribution of the contaminants in both the vadose and saturated zones, the equipment and personnel used to gather the data, etc. The work plan should be finalized before any sampling is conducted. The work plan will provide specific information on the type and quality of data gathered during the soil gas sampling event. Any questions regarding data needs and usage should be resolved prior to sampling.

1.4 The evaluation of the indoor inhalation pathway at contaminated sites is a significant concern at sites/properties where contamination is known or expected to exist. As a result, procedures and technology related to evaluating the pathway continue to evolve.

NOTE: This procedure pertains to the active collection of soil gas using direct-push techniques (*i.e.,* driven probe rods/tooling). With respect to the use of other appropriate methods, procedures, and equipment for measuring concentrations of chemicals of concern in soil gas, please refer to the Vapor Intrusion Guidance: A Practical Guide (ITRC, January 2007). Please note that the ITRC web page includes a warning that this guidance has not been updated and as such it may include information that is out of date and which no longer may be applicable.

2.0 Definitions

Terms specific to soil gas sampling using direct-push systems are defined throughout this FSOP.

3.0 Health and Safety Considerations

3.1 Follow the site specific health and safety plan (HASP). If a site-specific HASP is not available, follow the health and safety procedures in FSOP 1.1, Initial Site Entry.

3.2 The use of direct push systems on a site within the vicinity of electrical power lines and other utilities requires that special precautions be taken by the operators. Underground electrical utilities are as dangerous as overhead electricity. Be aware and always suspect the existence of underground utilities (water, natural gas, cable and phone lines, fiber optic cables, storm water and sewer lines, etc.). Contacting the Ohio Utilities Protection Service (OUPS) and private utility location services will be necessary prior to initiating a field sampling plan. The LOE contractor (or in limited instances Ohio EPA) must contact OUPS prior to drilling with a direct-push drilling rig or if the LOE contractor is using another method.

REMEMBER Call 811:
Ohio Utilities Protection Service (OUPS): 800-362-2764

4.0 Procedure Cautions

4.1 A soil gas survey is only applicable to volatile contaminants. Geological barriers may exist that interfere with vapor migration such as perched water, clay or man-made structures. Interference from these geological barriers can lead to non-representative sampling with low or false negative readings or may produce localized areas of high concentrations. In addition, heavy precipitation, 24 to 48 hours prior to sampling can result in a significant reduction in volatile concentrations. Please refer to project specific DQO’s for additional procedural cautions.

4.2 Soil gas implants should generally be installed to a minimum depth of 5 feet below ground surface to prevent short circuiting to the atmosphere unless there are extenuating circumstances (*e.g.,* collecting samples along shallow utilities).

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

Personal Protective Equipment (PPE):

6.1 Hearing protection
6.2 Safety glasses
6.3 Nitrile (or similar) disposable gloves
6.4 Steel-toed boots
6.4 Hard hat

Soil Gas Sampling:

6.7 1L Evacuated canisters (i.e., Summa®), with grab flow regulators
6.8 9/16” wrench
6.9 Tubing cutter
6.10 Polycarbonate 2- & 3-way valves
6.11 Silicon connector tubing
6.12 Disposable 60cc Syringe
6.13 Photoionization detector (FSOP 3.1.1, Photoionization Detector), ppb capable
6.14 Multi-gas meter (FSOP 3.1.2, Multiple Gas Detection Meters)
6.15 Field documentation equipment and supplies, including pens, markers, field logbook and Soil Gas Data Sheets, chain-of-custody forms, camera, etc.
6.16 Hand Auger
6.17 Miscellaneous tools

7.0 Procedures: Summary of Probe Installation Methods

7.1 Using the Post-Run Tubing System for Grab Sample Collection

[This section is for informational purposes only, for Ohio EPA staff and Level of Effort (LOE) contractors.]

This is a temporary, single use application for collecting a soil gas grab sample. Using the post-run tubing system (PRT), probe rods are driven to the desired depth, and then internal tubing, with PRT fitting attached, is inserted and seated for soil gas sampling. Using the inner tubing for soil gas collection has many advantages: potential for leakage is reduced, dead air volume that must be purged is reduced, and decontamination problems are reduced as the sample does not contact the rod bore.

7.1.1 Clean all parts prior to use. Inspect all probe rods and clear them of obstructions. Install O-ring on the PRT expendable point holder and the PRT adapter.

7.1.2 Test fit the adapter with the PRT fitting on the expendable point holder to assure that the threads are compatible and fit together smoothly. Ensure the threads are clean of debris.

NOTE: PRT fittings are left-hand threaded and must be rotated counter-clockwise to engage the point holder threads.

7.1.3 Push the PRT adapter into the end of the selected tubing. Tape may be used on the outside of the adapter and tubing to prevent the tubing from spinning freely around the adapter during connection - especially when using Teflon^{TM} tubing.

NOTE: The sample will not come into contact with the outside of the tubing or adapter.

7.1.4 Attach the PRT expendable point holder (with O-ring) to the female end of the leading probe rod.

7.1.5 Attach an O-ring to an expendable soil vapor drive point and insert into the expendable point holder. Attach the drive cap to the male end of the drive rod and position rod under probe.

7.1.6 Drive the PRT rod configuration into the ground, connecting probe rods as necessary to reach the desired depth.

7.1.7 After desired depth has been achieved, disengage the expendable drive point. Using the inner extension rods, insert the expendable point popper to the bottom of the rod string and then slowly pull up on the probe rods using the rod grip pull system. Retract the rods approximately 4"- 6" up to create a void from which to sample the soil gas. Position the probe unit to allow room to work around the sample location.

7.1.8 Insert the PRT adapter end of the tubing down the inside diameter of the probe rods.

7.1.9 Feed the tubing down the rod bore until it hits bottom on the expendable point holder. Allow approximately 4-6 ft. of tubing to extend out of the hole before cutting it. Grasp the excess tubing end and lightly apply downward pressure while turning it in a counter-clockwise motion to engage the adapter threads with the expendable point holder. Continue turning until the PRT adapter O-ring bottoms out in the expendable point holder.

7.1.10 Pull up lightly on the tubing to test the engagement of the threads. Failure of the PRT adapter to thread could mean that intrusion of soil may have occurred during driving of the rods or disengagement of the expendable drive point. Once tubing has been connected, finish the surface end with a 2-way valve in the closed position.

7.1.11 Sampling at the location can commence following an equilibrium period (minimum of 15 minutes). Connect the sampling tubing and follow appropriate purging and sampling procedures. Refer to “Procedures for Collection of Indoor Air, FSOP 2.4.3” for reference for use of evacuated canisters for sample collection; and refer to Section 7.3.1 below, for sampling procedures using the bag sampler (e.g., Lung Box).

7.1.12 Prior to sample collection and screening, ensure that the implant is in a porous soil zone that will freely give up soil gas. Connect a 60-cc syringe to the implant tubing, open the 2-way tubing valve, and gently pull the plunger out to fill the syringe with gas. Let go of the plunger and observe whether it holds position where released, or if it can be observed moving back due to an induced vacuum. Should a vacuum be present, the soil zone at the end of the probe rods may be too tight to get a representative soil gas sample. Should this occur, the probe rods can be pulled up 1 to 2 feet at a time, retesting each interval until soil gas can be freely obtained. If not, abandon the location, seal the borehole with bentonite, and reposition the probe; or relocate to another position.

7.2 Installation of Soil Gas Implants

[This section is for informational purposes only, for Ohio EPA staff and Level of Effort (LOE) contractors.]

For long-term soil gas monitoring applications (multiple sampling events from the same location), a stainless steel, aluminum, polycarbonate or ceramic implant can be installed at any depth by direct push. Implants are inserted down inside the probe rods when the appropriate sampling depth has been achieved. When installing soil gas implants, knowledge of the local geology and soil types is paramount to the success of any soil gas survey. For sites where geology or soil characteristic information is not available, the collection of soil borings to target depth may be helpful in identifying zones or soil horizons in which to set soil gas implants.

7.2.1 Drive probe rods to the desired depth using the implant expendable point holder and an expendable drive point. Disengage the drive point using the point popper. Using the inner extension rods, insert the expendable point popper to the bottom of the rod string and then slowly pull up on the probe rods using the rod grip pull system. Retract the rods approximately 1”- 2” to push the expendable point out with the point popper. Remove all extension rods and point popper. Check end of last inner rod or point popper for evidence of moisture. Implants should not be installed in moist zones as these can inhibit vapor migration as well as, given enough time for water to accumulate, may result in water being drawn up and into sample containers (evacuated canister or Tedlar® bag).

7.2.2 Attach implant to one end of appropriate sample tubing (Teflon™, or nylon). Depending on implant type and diameter of sample tubing, a very short length of silicone tubing of appropriate size may be used to securely connect the implant to the sample tubing.

7.2.3 Lower the implant and tubing down the inside of the probe rods until the implant hits the top of the anchor/drive point. Note the length of the tubing to assure that proper depth has been reached. Cut the tubing flush with the top of the probe rod.

7.2.4 Using an inner extension rod, place one end of the rod on top of the fresh cut tubing. While holding the rod in place, slowly retract the rods, 4 feet at a time, and remove the drive rod. Continue this action of using the extension rod to hold the tubing in place until all the drive rods have been removed from the borehole.

7.2.5 Slowly pour sand (20/40 grade or #5) down the borehole around the outside of the tubing so that the sand extends several inches above the implant. Use the tubing to “stir” the sands into place around the implant. Do not lift up on the tubing. It should take less than 250 mL of sand to fill the space around the implant. The sand therefore will act as a grout barrier, inhibiting the grout from impacting the implant. Slowly pouring sand and bentonite will lessen the chance for the materials to bridge in the borehole.

NOTE: Implants come in various sizes and the drive rods can vary in diameter, so it is best to calculate the necessary volume of sand for each implant installation. Placement of the grout barrier by backfilling the borehole can only be performed in the vadose zone, not below the water table.

7.2.6 Once the sand is in place, slowly add the bentonite granules on top of the sand. After approximately 0.5 L of bentonite has been added, hydrate the bentonite in the hole. Hydration can be accomplished using a pump sprayer, or by using a section of tubing connected to the 60 cc syringe filled with water. Depending on borehole depth, the bentonite should be hydrated at a minimum of 3-5 intervals. Allow bentonite to come to ground surface, saturate the bentonite with water to create a bentonite “mud” and, using a finger, push this mix around the tube and back down the hole to enhance the closure. This results in a tight seal preventing gas migration down the column.

NOTE: Use caution not to over hydrate, as the water may flow out into the soil formation and travel down to the implant, causing it to become wet and potentially loose diffusivity

7.2.7 After sealing the borehole, cut the tubing to a manageable length (~12” - 18”), attach a 2-way valve connector (in the OFF position) or airtight (e.g., Swagelok®) plug, and mark the location with a pin flag or stake. Attach a label or tag to the tubing indicating the sample location identifier and depth at which the implant was set for future reference when sampling. Example: SG-3-18, meaning a soil gas point at location #3 with an implant set at 18 feet bgs.

7.2.8 Check the viability of the sample point just installed following the procedures outlined in section 7.1.12 using a 60-cc syringe. A multi-gas meter with a PID is also a very good way to purge and check the sample point’s viability and usefulness. Stable field screening measurements for VOC’s, oxygen, and hydrogen sulfide can be good indicators on a well-sealed and sampling-ready implant. Should the meter’s pump motor labor, or if the syringe plunger recedes back into syringe after pulling, a vacuum has been induced and the point is not viable for sample collection. The induced vacuum would be too much to overcome to obtain a gas sample using either an evacuated canister or a bag sampler.

7.2.9 A minimum equilibrium time should be established prior to sampling the implant (preferably stated in the work plan). While a 24-hour equilibrium period will ensure adequate equilibration, four to eight hours is generally sufficient. After equilibration, the implant is ready for sampling. Refer to Section 7.3 for sampling procedures using a vacuum canister (*e.g.,* Summa® or Silco).

7.2.10 To provide long term security to the sampling port, the installation of a flush mount or above ground protective casing with a cap can be installed and finished with a concrete pad. For temporary, short-term finishing of a sampling port, 4-6” (ID) PVC pipe sections with associated caps can be installed.

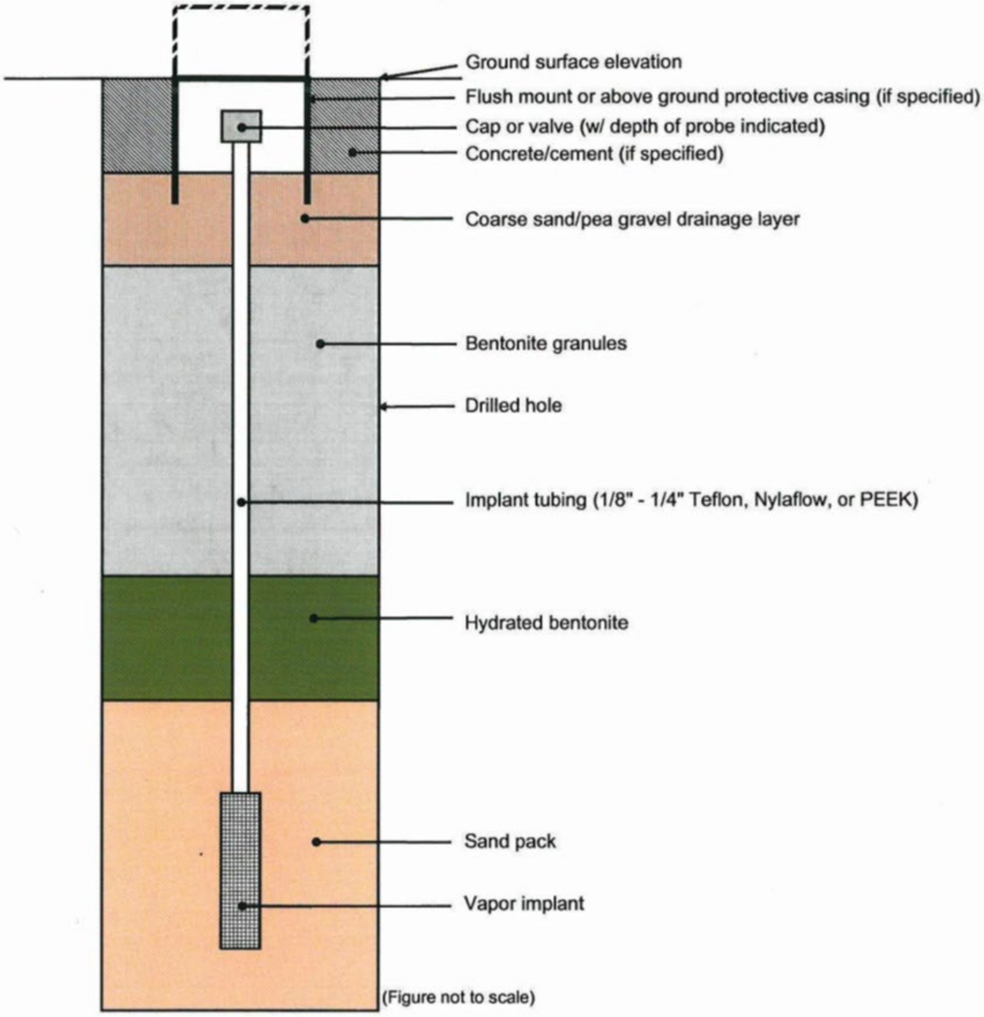


Figure 3: Permanent Soil Gas Probe Schematic

7.3 Sample Collection Methods

Three common methods of sample collection for vapor intrusion contaminants of concern (COCs) are discussed in this FSOP: 1) the lung box sampler uses Tedlar® bags as sample containers; 2) collection of samples on adsorbents is performed by using a small external pump to pull air through adsorbent media cartridges and/or tubes; and 3) collection of samples directly to stainless-steel evacuated canisters (*e.g.,* Summa®). Data Quality Objectives (DQOs) for the project will determine which sample collection method to use. Field data should be recorded on the Soil Gas Sampling Data Sheet (attached) or in a field notebook.

7.3.1 The Lung Box Sampler (Bag Samplers)

The Lung Box allows direct filling of a Tedlar® air sample bag using negative pressure without passing gas through the pump. This eliminates the risk of contaminating the pump or the sample. The Lung Box, pictured below, includes an in-line pump. Other types of bag samplers may require the use of a separate air pump or hand pump.

The recommended holding time for samples collected into Tedlar® bags is 24 to 48 hours. Therefore, soil gas samples collected in Tedlar® bags should be analyzed as quickly as practical or samples can be transferred to another container with longer holding times (i.e., Summa canister). If this method of sampling is performed, ensure that the laboratory can accept Tedlar® bags, and can meet the holding time requirements.

Semi-permanent soil gas probe location with multi-depth implants. The lung box sampler is used to collect soil gas samples using 1-liter Tedlar® bags. Note that each tube is labeled with the sampling depth; the PVC pipe is used to protect the soil gas tubing.

7.3.1.1 Prior to sampling, and after an appropriate equilibrium period (typically 8 – 24 hrs. depending on DQOs), ambient air needs to be removed from the sample train by purging. Purging of the filter pack is required if sampling occurs within 24 hours of installation. At least three volumes should be removed. For example, the sample tubing can be purged using a 60 cc syringe with an attached 3-way valve (~4 cc/ft for ¼" ID tubing/volume). Other methods may be used as long as a minimum of 3 volumes are purged from the tubing. Once purging is complete, the sample may be collected. Field screening may be performed using a direct reading instrument after sample collection.

7.3.1.2 Install new tubing in the bag sampler before collecting each sample. Place a new Tedlar® sample bag (already labeled) inside the bag sampler. Attach the inside portion of the tubing to the inlet valve on the sample bag. Open the sample valve on the sample bag following the manufacturer's instructions. Close sampler lid and secure. (DO NOT use any type of permanent marker, i.e., "*Sharpie"* pens)

7.3.1.3 Attach external part of the inlet tubing to the sample tubing. Make sure that the purge valve on the side of the box is closed (closed for fastest fill rate, open for slower fill rate).

7.3.1.4 Turn on the sample pump or initiate hand pumping. While filling, watch through the observation window of the Bag sampler as the Tedlar® bag fills with gas. Avoid filling bag more than 80% of its maximum volume. Turn the pump off when the bag has filled to the desired volume. Do not over fill sample bags. The vacuum pump may be strong enough to break a sample bag.

NOTE: Be sure to watch the sample line for the first sign of water coming up the line. Pulling water up the line is not uncommon, especially in cases where the position of the water table is unknown. This is a good reason why ample lengths of tubing should be used for the sample line. If water is drawn up the tubing, the tubing can be cut before the water reaches the sampling equipment.

NOTE: Exercise extreme caution if filling sample bags with explosive gases.

7.3.1.5 Once filling of the sample bag is complete, turn off the pump, open the purge valve to equalize the pressures, unlatch the bag sampler lid and open. Close the sample bag inlet valve by holding the side stem and turning the entire upper portion of the fitting clockwise until snug. Remove the filled sample bag from the internal inlet tubing.

NOTE: In an effort avoid any photochemical reactions, keep filled Tedlar® bags out of sunlight. Store and ship bag samples in a protective box at room temperature. Do not chill to avoid condensation.

7.3.1.6 If measurements with a portable meter are to be made (*e.g.,* oxygen), conduct measurements after collecting the soil gas sample(s).

7.3.2 Collection of Samples on Adsorbents

7.3.2.1 An alternative approach to collecting soil gas in a sample container is to concentrate the soil gas on an adsorbent media. This type of method is required for SVOCs and is often used for mercury (generally compounds heavier than naphthalene). Typically, a pump is used to draw soil gas through the adsorbent matrix, and the adsorbent is then analyzed by a laboratory.

7.3.2.2 A variety of adsorbent cartridges and pumping systems are available from commercial vendors. In addition, it is essential that the soil gas be drawn through the adsorbent by the pump, not pumped through the adsorbent to eliminate the chance for cross-contamination by the pump. It is often recommended that two tubes be used in series to avoid breakthrough losses in areas of suspected higher concentrations. The adsorbent, purge rate, and sample volume must be determined by discussion with the analytical laboratory.

7.3.3 Collection of Samples Directly to Evacuated Canisters

7.3.3.1 "Summa® Canister", a generalized trademark that refers to electropolished, passivated stainless steel vacuum sampling devices (*e.g.,* evacuated canisters). Sizes of canisters will vary with the most commonly used sizes being 6L and 1L. Canister size will depend on the predetermined time frame for sampling (*e.g.,* 24-hour v. "grab" sampling). A "Silco" canister is another name for a summa canister.

The Summa® Canister (canister) allows direct filling of soil gas into a 1-liter (or 6-liter) laboratory-supplied evacuated canister. This style of soil gas sample collection is the preferred method. Soil gas samples collected by this method are typically "grab" samples and use a supplied regulator to achieve a flow rate of approximately 200 to 250 ml/min. Sample collection time will be approximately 7 to 10 minutes to fill the 1L canister.

7.3.3.2 Prior to sampling, and after an appropriate equilibrium period (typically 15 – 30 min. depending on DQOs), ambient air needs to be removed from the sample train by purging. Purging of the tubing and filter pack is required if sampling occurs within 24 hours of installation. At least three volumes should be removed.

For example, the sample tubing can be purged using a 60-cc syringe with an attached 3-way valve (~4 cc/ft for ¼" ID tubing/volume). Other methods may be used as long as a minimum of 3 volumes are purged from the tubing. Once purging is complete, the sample may be collected. Field screening may be performed using a direct reading instrument (ppb multi-RAE) after sample collection.

7.3.3.3 Attaching/removing the flow regulator. The flow regulator/quick-connect regulator must be correctly connected to the sample canister to eliminate the potential for leaks.

- Remove the brass plug from the canister and connect the flow regulator to the canister.
- Gently tighten the connection between the flow regulator and the canister using the open-end 9/16" wrenches. Do not over-tighten this connection. Before continuing, record the canister number and the associated flow regulator number on the "Vapor Sampling Data Sheet". The canister number can be used for sample identification on the COC form.
- Attach the canister to the sample line with a slightly larger piece of silicon tubing (one that can snugly fit around the tip of the flow regulator). Open the canister/regulator valve. Record the sample start time and the canister pressure. Once the sample collection is completed, close the valve on the regulator or disconnect the quick-connect regulator from the canister. This stops the collection of any additional vapor into the canister.
- Remove the flow regulator from the canister using the 9/16" open-end wrenches. Re-install the brass plug on the canister fitting and tighten with an open-ended wrench.
- Package the canister and the flow regulator into the shipping container provided by the lab. **Note**: the canister does not require preservation.
- Complete the Soil Gas Sampling Data Sheet, and other appropriate forms and sample labels as directed by the laboratory. Use the sample start time when completing the laboratory chain of custody and double check canister identification numbers for accuracy.
- Ship the canisters to the laboratory for analysis.

7.4 Soil Gas Sample Field Screening

7.4.1 Following sample collection, field-screen the borehole or soil gas probe atmosphere with a PID in accordance with FSOP 3.1.1, Photoionization Detector, to estimate the bulk concentration of VOCs present in the soil gas sample. The PID field screening data should be recorded with the sample information on the soil gas sampling data sheet (see attached). The analytical laboratory needs to be aware of any samples potentially containing high concentrations of VOCs that may need to be diluted prior to analysis.

7.4.2 If desired, to perform the field-screening, attach an appropriate length of tubing to the PID sampling tip with a small piece of silicon tubing and extend it at least halfway into the boring or attach PID directly to tubing on a soil gas probe to obtain readings.

7.4.3 The PID field screening data may also be collected for sampler health and safety concerns or to use as real-time screening information to help evaluate the need for additional sampling or other site assessment activities while in the field.

7.4.4 In addition to a PID, a multi-gas meter (FSOP 3.1.2, Multiple Gas Detection Meters) may be used to field screen the borehole or soil gas probe atmosphere to collect gas concentration field screening data. This information may be provided to the analytical laboratory, used to monitor health and safety concerns, or used as real-time screening information to help evaluate the need for additional sampling or other site assessment activities while in the field. Parameters often include VOCs (ppb), Oxygen (% O_2), Lower Explosive Level (% LEL), Carbon monoxide (ppm CO), and Hydrogen sulfide (ppm H_2S)

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

Soil Gas Sampling Data Sheet

9.0 Quality Assurance and Quality Control

Refer to the data quality objectives (DQOs) provided in the work plan.

10.0 Attachments

Soil Gas Sampling Data Sheet

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 3.1.1, Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meters

Interstate Technology & Regulatory Council (ITRC) Vapor Intrusion Team, January 2007, Vapor Intrusion Pathway: A Practical Guideline

SOIL GAS SAMPLING DATA SHEET

GENERAL INFORMATION

Site Name:____________________________________ **Site Address:**________________________________ **City:**____ **County/District**_________________________________ **Contact Name:**_________________________________ **Phone #:**______________________________________	**Sampling Address:**_____________________________ *(if other than site address)* **Grab Sample:**________ **Canister Sample:**_________ **Sample ID #:** __________________________________ **If canister used, complete info below:** **Canister ID #:**_________________________________ **Regulator ID #:**_______________________________

SAMPLING INFORMATION

(mm/dd/yy) *(military)* **Soil Gas port installed: Date:**_______**Time:**_______ **Depth :**_______ **If canister used for sample collection, complete following info:** **Sample Collection Start: Date:**_______**Time:**_______ **Sample Collection End: Date:**________ **Time:**_______ **Regulator Calibrated for:** _____ **8-hr** _____ **12-hr** _____ **24-hr** _____ **grab (no regulator)** **Laboratory & Analytical Method:** _________________ **Sample Delivered: Date**_________ **Time:**__________ **Method of Delivery:** ____________________________ *(ex. Lab courier, UPS, delivered by sampler, etc.)*	**Canister Info:** **Initial canister vacuum:** ______ **"Hg or mm Hg** **Final canister vacuum:** _______**"Hg or mm Hg** **Temperature:** __________ **°F**	**Field Screening Info:** **PID (ppm):**__________ **% O_2 :**_______________ **CH_4 (%LEL):**_________ **CO_2:**_______________ **CO:**_________________ **H_2S:**_______________ **List instrument (and ID#) used to collect parameters:** ______________________

NOTES: (include any information on the installation of the soil gas port, or problems with sampling/canister etc.)

Signature of Sampler: ____ **Date:**________________

Note: If a diagram of the sample location(s) is sketched on the back of this data sheet, check here ☐

Installation, Sampling and Decommissioning of Sub-Slab Vapor Ports
FSOP 2.4.2 (January 28, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

Sub-slab vapor ports are used to sample the vapor contained in the interstitial spaces beneath the floor slab of dwellings and other structures for volatile organic compounds (VOCs) and other volatile chemicals. Sub-Slab vapor ports may be constructed using a custom fit stainless steel implant with Swagelok® fittings or a custom pre-manufactured Vapor Pin™ (see Section 9.0 Cox-Colvin Standard Operating Procedure, Installation and Extraction of the Vapor Pin™).

2.0 Definitions

Summa® Canister: Genericized trademark that refers to electro-polished, passivated stainless steel vacuum sampling devices (*i.e.,* evacuated canister). Sizes of canisters will vary with the most commonly used sizes being 6L and 1L. Canister size will depend on the pre-determined time frame for sampling (*e.g.*, 24-hour vs. “grab”). A “Silco” canister is another name for a summa canister.

3.0 Health and Safety Considerations

3.1 This activity involves accessing private residences and spaces in commercial buildings. Follow Ohio EPA Standard Safety Operating Procedure Number SP11-19 (Working Alone) to determine if working alone is appropriate given the site conditions and circumstances.

3.2 Never enter an OSHA-defined confined space for any reason. Only Ohio EPA Office of Special Investigation (OSI) staff or other appropriately trained staff are qualified to enter confined spaces for reconnaissance or sampling activities and will perform such work as necessary in accordance with Ohio EPA Standard Safety Operating Procedure Number SP14-4 (Confined Space Entry).

3.3 Follow the site-specific health and safety plan (HASP), which should identify the potential presence of asbestos-containing materials and other building-specific health and safety concerns. If a site-specific HASP is not available, follow the health and safety procedures in FSOP 1.1, Initial Site Entry.

3.4 This activity may result in the creation of silica dust when drilling through concrete. To prevent exposure to silica, a HEPA vacuum with an associated dust containment system must be used when drilling through concrete. Staff must be trained in the proper use of the silica dust collection equipment before installing sub-slab vapor probes.

3.5 When using electricity, be cautious of wet areas or areas with standing water, (*e.g.,* wet basement floors, sump pumps, etc.).

3.6 Be aware of potential vermin (fleas, rats, etc.)

3.7 Hearing protection should be worn while using a hammer drill.

3.8 A dust mask is to be worn in addition to using the HEPA vacuum during drilling.

3.9 Use a photoionization detector (PID) to evaluate VOC concentrations during vapor port installation in accordance with FSOP 3.1.1, Photoionization Detector.

3.10 Review available plans or documents before selecting sampling locations. Ensure that all sub-slab utilities (public and private or building specific) have been located and marked prior to installation. Contact the Ohio Utilities Protection Service (OUPS) at 811 or (800) 362-2764 to mark locations of public utilities leading to the building. For commercial buildings, it is recommended that a utility locating service be contacted to scan for and mark indoor utilities.

3.11 Do not attempt to drill through steel-reinforcement (*e.g.,* rebar) within a concrete slab without first contacting a private utility locating service.

4.0 Procedure Cautions

4.1 Review the site-specific work plan (SSWP), which should include a description of the building's size and use. In certain emergency circumstances a SSWP may not be available, and all necessary information for sub-slab vapor port installation and sampling will need to be obtained during the pre-sampling visit as described below. If a pre-sampling meeting cannot be held due to time constraints, please collect as much of the information as possible as listed below. This information can be obtained during a telephone call or in person.

4.2 A pre-sampling site visit should be conducted to meet with the building's owner and/or tenant and inspect the proposed vapor port sampling locations. During the pre-sampling visit, discuss sample location access and associated logistical concerns, including, but not limited to, lighting and electrical power, the need to temporarily move furnishings, the need to remove floor coverings (e.g., carpet or tile), the location of floor drains and/or other sub-slab utilities, and whether or not the sampling areas are occupied or unoccupied spaces.

4.3 The thickness of concrete slabs varies from structure to structure. A single structure may also have a slab with variable thickness. Drill bits of various sizes and cutting ability may be required to penetrate slabs of variable thicknesses. If a slab contains steel reinforcement (*e.g.,* rebar), a sub-slab vapor port can only be installed if SIFU can find a location where steel reinforcement can be located or is not present. SIFU cannot drill through the steel reinforcement within a concrete slab.

4.4 There is a potential for high concentrations of VOC vapors to exist under the slab. Perform work quickly to ensure minimal exposure to VOCs.

4.5 When installing sub-slab vapor ports in commercial or industrial buildings, there is the potential to encounter sub-slab utility conduits (*e.g.,* floor drains or electric, gas or water lines). Follow the procedures provided in section 7.1 for sub-slab utility clearance before installing vapor ports.

4.6 Unless approved by Ohio EPA management and the building owner, sub-slab vapor ports should never be installed in the floor of a building with an existing sub-slab vapor barrier that is a component of a vapor mitigation system because vapor port installation could penetrate the barrier. However, sub-slab vapor ports may be installed through sub-slab moisture barriers that are typically not components of vapor mitigation systems, providing that the vapor port is decommissioned in accordance with section 7.7 when it is no longer needed for sampling purposes.

4.7 When using the drill and HEPA vacuum, you will collectively exceed 15 amps which is the standard for most household outlets. Therefore, be prepared to connect the drill and the HEPA vacuum to separate outlets (*i.e.,* different circuits).

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard. Prior knowledge, training and experience with this sampling technique is strongly recommended before collecting samples.

6.0 Equipment and Supplies

General

6.1 Hammer drill or rotary hammer drill
6.2 Alternating current (AC) extension cord
6.3 AC generator, if AC power is not available on site
6.4 Hammer or rotary hammer drill bit, ⅜” diameter
6.5 Hammer or rotary hammer drill bit, 1” diameter
6.6 1 – ¾” open end wrench or 1 – medium adjustable wrench
6.7 2 – $^{9}/_{16}$” open end wrench or 2 – small adjustable wrenches
6.8 Disposable cups, 5 ounces (oz.)
6.9 Disposable mixing implement (*e.g.,* tongue depressor, etc.)
6.10 Vapor Sampling Data Sheet, Sub-Slab and Indoor Air (attached) or logbook
6.11 Pens and markers
6.12 Flashlight or equivalent head lamp
6.13 Utility knife
6.14 Disposable syringe (60 cc)
6.15 PPE appropriate for site-specific work activities (*i.e.,* mask, etc.)
6.16 Disposable mixing implement (*e.g.,* tongue depressor, etc.)
6.17 Tap water, for mixing anchoring cement/grout
6.18 Hand broom and dust pan
6.19 Small bottle brush to remove loose debris clean side walls of borehole
6.20 Portable HEPA vacuum
6.21 Dust collector
6.22 Traffic cones (to place over locations in high-traffic floor areas)

Swagelok® Equipment and Supplies

6.23 Hex head wrench, ¼”
6.24 Tubing cutter and pipe cutter
6.25 Swagelok® SS-400-7-4 female connector, ¼” national pipe thread (NPT) to ¼” Swagelok® connector
6.26 Swagelok® SS-400-1-4 male connector, ¼” NPT to ¼” Swagelok® connector
6.27 Hose barb adapter, brass, 3/16” barb x ¼” male iron pipe (MIP)
6.28 ¼” NPT flush mount hex socket plug
6.29 ¼” outer diameter (OD) stainless steel tubing, pre-cleaned, instrument grade
6.30 ¼” OD Teflon™ or nylon tubing
6.31 Teflon™ or nylon washer ID ¼”, OD ¾”
6.32 ¼” OD stainless welded tubing, 12” to 24” length
6.33 Swagelok® tee, optional (SS-400-3-4TMT or SS-400-3-4TTM)
6.34 Appropriate size tubing

Vapor Pin™ Equipment and Supplies

6.35 Cox-Colvin Vapor Pin™ Kit
6.35 Dead blow hammer
6.36 Appropriate silicon tubing
6.37 Vapor Pin™ protective cap to prevent vapor loss prior to sampling
6.38 Standard Operating Procedure Installation and Extraction of the Vapor Pin™ http://vaporpin.coxcolvin.com/wp-content/uploads/2015/02/Vapor-Pin-SOP-02-27-15-Web.pdf

7.0 Procedures

7.1 Review the SSWP, which should include a description of the building’s size and use. In certain emergency circumstances a SSWP may not be available, and all necessary information for sub-slab vapor port installation and sampling will need to be obtained during the pre-sampling visit as described below. If a pre-sampling visit is not feasible, call the owner and/or tenant prior to sampling to obtain the information.

7.2 A pre-sampling site visit should be conducted to meet with the building’s owner and/or tenant and inspect the proposed vapor port sampling locations. During the pre-sampling visit, discuss sample location access and associated logistical concerns, including but not limited to lighting and electrical power, the need to temporarily move furnishings, the need to remove floor coverings (*e.g.,* carpet or tile), the location of floor drains and/or other sub-slab utilities and whether or not the sampling areas are occupied or unoccupied spaces.

7.3 Before installing sub-slab vapor ports in a commercial or industrial building, use the following procedures for sub-slab utility clearance:

7.3.1 Perform a visual inspection of the area(s) of the building where vapor ports are to be located for potential sub-slab utility lines.

7.3.2 Discuss the presence and location(s) of sub-slab utility lines with the building owner and/or operator and review any available building construction plans that may show the location of sub-slab utility lines.

7.3.3 If the presence or location(s) of sub-slab utility lines cannot be verified following the procedures in sections 7. 1 and 7. 2, contract a private utility locating company to locate potential sub-slab utility lines before installing vapor ports.

7.4 Preparation and Drilling of the Vapor Port

7.4.1 Connect the dust collector to the HEPA vacuum. Ensure that all connections are tight.

7.4.2 Plug the HEPA vacuum into the outlet and place the dust collector on the floor. Turn on the HEPA vacuum and ensure that the dust collector has created a tight seal with the floor. If a tight seal is not present, turn off the vacuum and check to ensure that all of the connections between the vacuum and the dust collector are tight. If the connections are tight, check the filter. It may be full, and need replaced. Also make sure the rubber gasket on the dust collector is in good condition. Finally, reposition the dust collector to a smoother floor surface. Retest the seal between the dust collector and the floor.

7.4.3 After ensuring that there is a good seal between the floor and the dust collector, set-up the drill and make sure the dust collector is positioned over the location selected for the vapor port. Turn on the vacuum and then the drill.

7.5 Swagelok® Probe Assembly and Installation for Multiple Sampling Events

7.5.1 Drill a ⅜” diameter pilot hole to a depth of approximately 2” (Figure 1).

7.5.2 Using the ⅜” pilot hole as your center, drill a 1” diameter outer hole to a depth of approximately 1 ⅜” (Figure 1). Vacuum cuttings out of the hole.

Figure 1: Assembled sub-slab port ready for installation

7.5.3 Continue drilling the ⅜” inner or pilot hole through the slab and a few inches into the sub-slab material.

7.5.4 Determine the length of stainless-steel tubing required to reach from the bottom of the outer hole, through the slab and into the open cavity below the slab. To avoid obstruction of the probe tube, ensure that it does not contact the sub-slab material. Using a tube cutter, cut the tubing to the desired length.

7.5.5 Attach a measured length (typically 3”-4”) of ¼” OD stainless tubing to the female connector (SS-400-7-4) with the Swagelok® nut. Make sure that the tubing rests firmly in the fitting body and that the nut is finger tight. While holding the fitting body firmly, tighten the nut 1¼ turns.

7.5.6 Insert the ¼” hex socket plug into the female connector. If using a stainless-steel socket plug, wrap one layer of Teflon™ thread tape around the threads to prevent binding. If using a brass socket plug, Teflon™ tape is not needed. Tighten the plug slightly. Do not over tighten. If excessive force is required to remove the plug during the sample set up phase, the probe may break loose from the anchoring cement.

7.5.7 Place the completed probe into the outer hole to check fit and to ensure that stainless steel tubing is not in contact with the sub-slab material. Make necessary adjustments to the hole or probe assembly.

7.5.8 In a disposable cup or other container, mix a small amount of the anchoring cement or grout. Add water sparingly to create a mixture that is fairly stiff and moldable. Place a spoonful or two of the cement/grout around the stainless-steel tubing adjacent to the female connector nut. Mold the cement/grout into a mass around the connector nut and up around the main body of the probe assembly. Slide the Teflon™ washer onto the stainless-steel tube so that it rests next to the cement/grout mixture. The washer will prevent any anchoring cement/grout from flowing into the inner hole during the final step of probe installation.

7.5.9 Carefully place the probe assembly into the drilled hole, applying light pressure to seat the assembly. While inserting the probe assembly, work the concrete/grout mixture to fill voids. Clean up cement/grout that discharged out of the hole during placement; avoid getting any of the concrete/grout into fittings or on fitting threads. Allow the cement/grout to cure according to manufacturer's instructions before sampling (typically 24 hours). This elapsed time also allows for subsurface conditions to equilibrate prior to sampling.

7.6 Swagelok® Sample Set-Up and Collection

7.6.1 Conduct a leak test prior to sampling. Follow project-specific DQO's and/or the SSWP to determine which of the following method(s) are appropriate:

7.6.1.1 The water dam that is included in the Cox-Colvin Vapor Pin™ kit is a simple means of determining if there are any leaks (see Cox-Colvin instructions, Figure 6). To use the water dam, simply attach the water dam to the floor using putty ensuring that there are no holes between the putty and the floor. Then add water to the dam and observe whether there are any air bubbles. If there are no air bubbles, the seal is tight. If there are air bubbles, refer to Section 7.7.

7.6.1.2 Another option is to evaluate the oxygen concentration by attaching an oxygen sensor (Multi-RAE Pro meter) to the vapor pin. If the percent oxygen drops, it can be inferred that there is a tight seal. However, since this method draws in sub-slab vapor, a longer waiting period may be required before collecting the sample to allow for the sub-slab air to re-equilibrate.

7.6.1.3 A tracer gas can be used during sample collection to evaluate whether the connections between the vapor pin and the sample container have any leaks. A tracer gas is very lightly sprayed on a paper towel and the paper towel is briefly laid around the fittings. As an alternative, the tracer gas can be lightly sprayed into the atmosphere near the sample train. Do NOT spray directly on the fittings. **Note**: you will not know if there were any leaks until after the sample has been analyzed. The recommended tracer gas is 1,1-Difluoroethane, which is present in some brands of dust cleaner for electronics.

7.6.2 Wrap one layer of Teflon™ thread tape onto the NPT end of the male connector OR wrap one layer of Teflon™ tape onto the threaded end of the hose barb adapter (3/16" barb x ¼" MIP).

7.6.3 Carefully remove the ¼” hex socket plug from the female connector. Refer to Section 7.7 if the probe breaks loose from the anchoring cement/grout during this step.

7.6.4 To ensure that the sub-slab port has not been blocked by the collapse of the inner hole below the end of the stainless-steel tubing, a stainless-steel rod, ⅛” diameter, may be passed through the female connector and the stainless-steel tubing. The rod should pass freely to a depth greater than the length of the stainless-steel tubing, indicating an open space or loosely packed soil below the end of the stainless-steel tubing. Either condition should allow a soil gas sample to be collected. If the port appears blocked, the stainless-steel rod may be used as a ramrod to open the port. If the port cannot be cleared, the probe should be reinstalled, or a new probe installed in an alternate location.

7.6.5 Screw and tighten the Teflon™ taped male connector into the female connector, <u>or</u> screw and tighten the hose barb adapter (3/16” barb x ¼” MIP) into the female connector. Do not over tighten. This may cause the probe assembly to break loose from the anchoring cement/grout during this step or when the male connector/hose barb adapter is removed upon completion of the sampling event. Refer to Section 7.7 if the probe breaks loose from the anchoring compound during this step.

7.6.6 If a co-located sub-slab sample or split sample is desired, a stainless-steel Swagelok® T, may be used in place of the male connector.

7.6.7 Using a short piece of silicon tubing, attach a length of ¼” tubing (Teflon™ or nylon) to the sampling container (*e.g.,* SUMMA® canister) or system (*e.g.,* lung box for Tedlar® bag) to be used for sample collection. Connect the other end of the tubing to the male connector with a Swagelok® nut or connect directly to the barbed hose adapter.

7.6.8 Refer to site specific work plan for canister size and type of sample required (*e.g.,* 6-liter canister with regulator for either 8-hour or 24-hour sample collection or a 1-liter evacuated canister for a grab sample). After sampling, use a PID to measure the VOC concentrations to provide the laboratory with an indication of how concentrated the VOCs may be in the sample. Provide this information to the laboratory. **Note**: PID readings are not contaminant-specific quantifications. Do not assume that the PID reading equates (or approximates) the concentration of the contaminant of concern.

7.6.9 After sample collection, remove the male connector or barbed hose adapter from the probe assembly and reinstall the ¼” hex socket plug. Make sure the plug threads are wrapped with Teflon tape. Do not over tighten the hex socket plug. If excessive force is required to remove the plug during the next sampling event, the probe may break loose from the anchoring compound. Refer to Section 7.7 if the probe breaks loose from the anchoring compound during this step.

7.7 Repairing a Loose Swagelok® Probe Assembly

7.7.1 If the probe assembly breaks loose from the anchoring compound while removing or installing the hex socket plug, the Swagelok® male connector, or the barbed hose adapter, lift the probe assembly slightly above the surface of the concrete slab.

7.7.2 Hold the female connector with the ¾“ open-ended wrench.

7.7.3 Complete the step being taken during which the probe broke loose, following the instructions contained in this FSOP (*i.e.,* do not over tighten the hex socket plug, the male connector, or the barbed hose adapter).

7.7.4 Push the probe assembly back down into place and reapply the anchoring cement/grout.

Figure 2: Swagelok® port connected to canister and ready for sampling

7.8 Vapor Pin™ Probe Installation

7.8.1 Refer to attached Cox-Colvin Vapor Pin™ Standard Operating Procedure for proper vapor pin installation and removal.

7.8.2 After installing a Vapor Pin™ place the small rubber cap over the barbed inlet to prevent and gas from escaping.

7.8.3 Conduct a leak test. The project specific DQO’s or SSWP may dictate which of the following method(s) may be followed. **Note**: There are other techniques beyond those listed that may be used.

7.8.3.1 The water dam that is included in the Cox-Colvin Vapor Pin™ kit is a simple means of determining if there are any leaks (see Cox-Colvin instructions, Fig 6). To use the water dam, attach the water dam to the floor using putty ensuring that there are no holes between the putty and the floor. Then add water to the dam and observe whether there are any air bubbles. If there are no bubbles, the seal is tight. If there are air bubbles, remove the water and reset the vapor point. Test with the water dam again to see if the seal is now tight. Remove the water and dam once test is complete.

7.8.3.2 Another option is to attach an oxygen sensor (Multi-RAE Pro meter) to the vapor pin and evaluate the oxygen concentration. If the percent oxygen drops, it can be inferred that there is a tight seal. However, since this method draws in sub-slab vapor, a longer waiting period may be required before collecting the sample to allow for the sub-slab air to re-equilibrate.

7.8.3.3 A tracer gas can be used during sample collection to evaluate whether the connections between the vapor pin and the sample container have any leaks. A tracer gas is very lightly sprayed on a paper towel and the paper towel is briefly laid around the fittings. As an alternative, the tracer gas can be lightly sprayed into the atmosphere near the sample train. Do NOT spray directly on the fittings. **Note**: you will not know if there were any leaks until after the sample has been analyzed. The recommended tracer gas is 1,1-Difluoroethane, which is present in some brands of dust cleaner for electronics.

7.8.3.4 Allow a minimum of 2 hours for the sub-slab soil gas conditions to re-equilibrate prior to sample collection unless site-specific work plan requires a different equilibration time. Place traffic cone over non-recessed pins in high floor traffic areas until pin can be removed.

Figure 3: Vapor Pin™ installed and ready for sampling

7.9 Vapor Pin™ Sample Collection

7.9.1 Remove the rubber cap and attach a piece of ¼” tubing (Teflon™ or nylon) to the barbed hose adapter. The tubing must be long enough to span from the sample port to the sample container (*e.g.,* SUMMA® canister) or system (*e.g.,* lung box for Tedlar® bag).

7.9.2 Refer to site specific work plan for canister size and type of sample required (*e.g.,* 6-liter canister with regulator for either 8-hour or 24-hour sample collection or a 1-liter evacuated canister for a grab sample). After sampling, use a PID to measure the VOC concentrations to provide the laboratory with an indication of how concentrated the VOCs may be in the sample. Provide this information to the laboratory. **Note:** this number is not contaminant specific. Do not assume that your contaminant of concern equates to the reading from the PID.

7.10 Vapor Port Decommissioning

Remove the vapor pin according to the attached Cox-Colvin Vapor Pin™ Standard Operating Procedure for proper vapor pin installation and removal.

7.10.1 Prior to filling the vapor port hole, measure the slab thickness. One method is to use a “hole hook”, a section of rigid wire (such as a stiff-wire coat hanger) with a small (0.25-inch) 90-degree crimp at one end. Insert the hole hook inside the drilled hole and catch the hooked end on the underside of the concrete slab. Mark the wire where it meets the top of the slab, remove the hole hook, and measure the distance between the hooked end and marked end of the wire to determine the slab thickness. Record the measured slab thickness on the log sheet or in a field notebook. This information is necessary if a sub-slab treatment system is ever installed.

7.10.2 Gently pour dry granular bentonite into the hole to fill any void space in the gravel or soil below the underside of the slab that may have been created during the drilling of the slab or installation of the vapor port. Continue adding bentonite until the level is approximately one inch below the top of the slab.

7.10.3 Slowly add a small amount of water to hydrate the bentonite without creating a column of standing water in the hole. Use of a flashlight when adding water helps to visually determine when the bentonite stops absorbing water. If too much water is added, use a syringe or absorbent material (*e.g.,* paper towels) to remove the standing water. While adding water, try to wet the hole side walls to help create good contact with the floor tile grout that will be used to fill and seal the hole as described below.

7.10.4 Mix approximately ¼ cup of floor tile grout with a small amount of water using a disposable spoon. Add water until the consistency of the grout mixture is a little stiffer than drywall or spackling compound.

7.10.5 Use a plastic knife, putty knife, tongue depressor or similar tool to add the tile grout mixture to the hole until it is completely full. Use a concrete trowel or similar tool to remove any excess grout and finish the top of the seal so that it is smooth and even with the surrounding floor.

7.10.6 Clean up the area around the sealed hole and complete any needed field documentation, including photographs if required. Ensure all relevant information is entered in the Vapor Sampling Data Sheet.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

Vapor Sampling Data Sheet

9.0 Quality Assurance and Quality Control

9.1 Clean Vapor Pins™ and sampling ports prior to installation by washing in warm water with laboratory-grade detergent, followed by rinsing with hot water and then rinsing with deionized water. Always inspect equipment before use.

9.2 Leak testing should be conducted to document the quality of the sample.

9.3 Photographs of the sampling location and equipment may be required for project documentation.

9.4 Refer to the data quality objectives (DQOs) provided in the work plan.

10.0 Attachments

Cox-Colvin Standard Operating Procedure, Installation and Extraction of the
Vapor Pin™

Vapor Sampling Data Sheet, Sub-Slab and Indoor Air (revised May 2018)

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 3.1.1, Photoionization Detector

Ohio EPA Standard Safety Operating Procedure SP11-19 (Working Alone)

Ohio EPA Standard Safety Operating Procedure SP14-4 (Confined Space Entry)

Procedures for Collection of Indoor Air Samples
FSOP 2.4.3 (January 28, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

The collection of indoor air samples assists in the investigation of air quality within buildings for possible vapor intrusion of volatile organic compounds (VOCs) and other volatile chemicals from environmental media (*e.g.,* soil, ground water). Samples are collected from locations within buildings and structures that are occupied on a regular basis to evaluate potential exposure to VOCs. Analysis of the air samples are typically performed using U.S. EPA Method TO-15.

2.0 Definitions

"Summa® Canister", a genericized trademark that refers to electropolished, passivated stainless steel vacuum sampling devices (*i.e.,* evacuated canister). Sizes of canisters will vary with the most commonly used sizes being 6L and 1L. Canister size will depend on the predetermined time frame for sampling (*e.g.,* 24-hour v. "grab" sampling). A "Silco" canister is another name for a summa canister.

3.0 Health and Safety Considerations

3.1 This activity involves accessing private residences and spaces in commercial buildings. Follow Ohio EPA Standard Safety Operating Procedure Number SP11-19 (Working Alone) to determine if working alone is appropriate given the site conditions and circumstances.

3.2 Never enter an OSHA-defined confined space for any reason. Only Ohio EPA Office of Special Investigation (OSI) staff or other appropriately trained staff are qualified to enter confined spaces for reconnaissance or sampling activities and will perform such work as necessary in accordance with Ohio EPA Standard Safety Operating Procedure Number SP14-4 (Confined Space Entry).

3.3 Follow the site-specific health and safety plan (HASP), which should identify the potential presence of asbestos-containing materials and other building-specific health and safety concerns. If a site-specific HASP is not available, follow the health and safety procedures in FSOP 1.1, Initial Site Entry.

3.4 Be aware of potential vermin (fleas, rats, etc.)

3.5 Review available plans or documents before selecting sampling locations.

4.0 Procedure Cautions

4.1 Review the site-specific work plan (SSWP), which should include a description of the building's size and use. In certain emergency circumstances a SSWP may not be available, and all necessary information for indoor air sampling will need to be obtained during the pre-sampling visit as described below.

4.2 A pre-sampling site visit is to be conducted to meet with the building's owner and/or tenant and inspect the proposed indoor air sampling locations. Completion of the Indoor Air Building Survey and Sampling Form (attached) is recommended to ensure a comprehensive evaluation. During the pre-sampling visit, address arrangements for sampling location access and associated logistical concerns. Also, determine if the sampling areas are occupied or unoccupied spaces. Obtain a property access agreement prior to sampling.

4.3 Sampling personnel should not handle hazardous substances (such as gasoline), permanent marking pens, wear/apply fragrances, or smoke before and/or during the sampling event.

4.4 Care should be taken to ensure that the flow regulator is pre-calibrated to the appropriate sample collection time (8 hours, 24 hours, etc.). Eight (8) hour sample collection is utilized for commercial/industrial settings. Twenty-four (24) hour sample collection is used for residential and/or sensitive receptor settings (*e.g.,* day care facilities).

4.5 The flow regulator must be correctly connected to the sample canister to eliminate the potential for leaks.

4.6 The regulator should be closed shortly before the actual sampling time is completed so that a small amount of vacuum remains. If it isn't closed and no vacuum remains in the canister, extracting a sample for analysis may be very difficult. In addition, sample integrity may be compromised if the canister reaches atmospheric pressure.

4.7 An interview of the building occupants should be conducted before sampling to determine if there are any potential chemicals present that could cause interferences during sample collection. For example, paints, woodworking products, household solvents and various chemicals used in hobbies may all contain VOCs that could be detected. If possible, the building occupants should remove such products several days before sampling takes place. A copy of Instructions for Building Occupants Prior to Indoor Air Sampling Form (attached) should be provided to the resident during the interview.

4.8 If sub-slab samples are to be collected from the same building that indoor air samples are being collected, it is preferable to complete the indoor air sampling prior to installing a sub-slab vapor port (FSOP 2.4.2, Construction, Installation and Decommissioning of Sub-Slab Vapor Ports). However, if site specific reasons (*e.g.,* access or emergency conditions, etc.) dictate the need to collect both samples at the same time, care needs to be taken to install the sub-slab vapor port before beginning the indoor air sampling. In addition, the indoor air sample should be taken as far as possible from the location where the sub-slab vapor point is installed.

4.9 Indoor air samples should only be collected from the first floor/ground-level floor of the structure, unless otherwise directed in the site-specific work plan.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard. Prior knowledge, training and experience with this sampling technique is strongly recommended before collecting samples.

6.0 Equipment and Supplies

6.1 Stainless steel canister(s) (request at least one additional canister as a backup). A 6L canister will be required for this sampling activity. A 1L "grab sample" canister will not provide enough volume to sample for a timed (8 hr. or 24 hr.) sample period, refer to Section 2.0 (Definitions).

6.2 Flow regulator(s) properly calibrated for the specific sample collection duration – 8 hr. or 24 hr. (request at least one extra regulator as a back-up)

6.3 In-line filters, if needed (*e.g.,* for semi-volatile organic compounds (SVOCs)

6.4 Open-end wrenches, typically 9/16" (two wrenches are recommended to tighten the fitting in two directions at the same time)

6.5 PID (refer to FSOP 3.1.1, Photoionization Detector)

6.6 Indoor Air Building Survey and Sampling Form (attached)

6.7 Instructions for Building Occupants Prior to Indoor Air Sampling Form (attached)

6.8 Vapor Sampling Data Sheet (attached)

6.9 Field documentation supplies and equipment, including pens, markers, field logbook and additional data sheets, chain-of-custody forms, camera

7.0 Procedures

7.1 Sample Location Determination

7.1.1 Conduct a building/structure survey using the Indoor Air Building Survey and Sampling Form (attached) to determine potential target receptors and identify potential interferences to sample collection. PID screening may also help to identify VOC sampling interferences. In addition, provide the Instructions for Building Occupants Prior to Indoor Air Sampling Form to the building residents or worker for completion at this time. Potential sampling interferences need to be recognized and eliminated before sample collection begins. This should be completed at least 48 to 72 hours prior to sample collection.

7.1.2 Select indoor air sampling locations that are in inhabited or frequently used.

7.1.3 Do not place sample canisters in locations near primary-use doors or open windows.

7.1.4 Do not place sample canisters in the pathway of indoor fans.

7.1.5 If ceiling fans are in use, request that they be turned off for the duration of the sample period.

7.1.6 Note any obvious odors from scented candles, mothballs, cleaning products, gas or oils.

7.1.7 If the building has a dirt basement or dirt crawl space, an indoor air canister should be placed in this area.

7.2 Sample Set-up

7.2.1 Place the sampling canisters at breathing-zone height.

7.2.2 Remove the brass plug from the canister and connect the flow regulator (with in-line particulate filter and vacuum gauge, if needed) to the canister.

7.2.3 Gently tighten the connection between the flow regulator and the canister using the open-end 9/16” wrenches. Do not over-tighten this connection. Before continuing, record the canister number and the associated flow regulator number on the Vapor Sampling Data Sheet. The canister number can be used for sample identification on the COC form.

7.2.4 Open the canister/regulator valve. Record the sample start time and the canister pressure.

7.2.5 Photograph each canister and the surrounding areas.

Example of a canister with a regulator attached and placed in the breathing zone.

7.3 Termination of Sample Collection

7.3.1 Return to the sample collection site a minimum of 15 minutes before the end of the sample collection interval. Examine the canister to ensure it has not been moved or damaged. Document any alterations to the canister or location.

7.3.2 Examine the flow regulator to ensure that some vacuum is left on the gauge (preferably 2” to 10” of mercury on the regulator flow dial).

7.3.3 Record the vacuum pressure and stop sample collection by closing the flow regulator.

7.3.4 Remove the flow regulator from the canister using the 9/16” open-end wrenches. Re-install the brass plug on the canister fitting and tighten it with an open-ended wrench.

7.3.5 Package the canister and the flow regulator into the shipping container provided by the lab. **Note**: the canister does not require preservation.

7.3.6 Complete the Vapor Sampling Data Sheet, and other appropriate forms and sample labels as directed by the laboratory. Use the sample start time when completing the laboratory chain of custody and double check canister identification numbers for accuracy.

7.3.7 Ship the canisters to the laboratory for analysis.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

Indoor Air Building Survey and Sampling Form

Instructions for Building Occupants Prior to Indoor Air Sampling

Vapor Sampling Data Sheet

9.0 Quality Assurance and Quality Control

An ambient air sample is collected outside of the building where the indoor air is being sampled. The ambient air sample is collected at the same time as the indoor air sample and provides quality assurance/quality control (QA/QC) to help evaluate outdoor air quality. Refer to the data quality objectives (DQOs) provided in the work plan.

10.0 Attachments

Indoor Air Building Survey and Sampling Form

Instructions for Building Occupants Prior to Indoor Air Sampling

Vapor Sampling Data Sheet

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 2.4.2, Construction, Installation and Decommissioning of Sub-Slab Vapor Ports

FSOP 3.1.1, Photoionization Detector

Ohio EPA Standard Safety Operating Procedure SP11-19 (Working Alone)

Ohio EPA Standard Safety Operating Procedure SP14-4 (Confined Space Entry)

Ohio Environmental
Protection Agency

INDOOR AIR BUILDING SURVEY and SAMPLING FORM

Preparer's name: ____ Date:___________________________

Preparer's affiliation: ___________________________________ Phone #: _______________________

Site Name: ____ Case #: ________________________

Part I - Occupants

Building Address: ____

Property Contact:__________________________Owner / Renter / other: _________________________

Contact's Phone: home ( )___________ work ( )_______________ cell ( )_____________

# of Building occupants: Children under age 13 ______ Children age 13-18 _______ Adults ______

Part II – Building Characteristics

Building type: residential / multi-family residential / office / strip mall / commercial / industrial

Describe building:____ Year constructed: __________

Sensitive population: day care / nursing home / hospital / school / other (specify): ________________

Number of floors below grade:_______(full basement / crawl space / slab on grade)

Number of floors at or above grade: _______

Depth of basement below grade surface:________ft. Basement size:________ft^2

Basement floor construction: concrete / dirt / floating / stone / other (specify): _________________

Foundation walls: poured concrete / cinder blocks / stone / other (specify) __________________

Basement sump present? *Yes / No* Sump pump? *Yes / No* Water in sump? *Yes / No*

Type of heating system (circle all that apply):

hot air circulation
heat pump
hot air radiation
hot water radiation
wood
kerosene heater
steam radiation
electric baseboard
other (specify): __________________________

Type of ventilation system (circle all that apply):

central air conditioning mechanical fans bathroom ventilation fans individual air
conditioning units kitchen range hood fan outside air intake
other (specify): ___________________

Type of fuel utilized (circle all that apply):

Natural gas / electric / fuel oil / wood / coal / solar / kerosene

Are the basement walls or floor sealed with waterproof paint or epoxy coatings? *Yes / No*

Is there a whole house fan? *Yes / No*

Septic system? *Yes / Yes (but not used) / No*

Irrigation/private well? *Yes / Yes (but not used) / No*

Type of ground cover outside of building: grass / concrete / asphalt / other (specify) _______________

Existing subsurface depressurization (radon) system in place? *Yes / No* *active / passive*

Sub-slab vapor/moisture barrier in place? *Yes / No*

Type of barrier: ______________________________

Part III - Outside Contaminant Sources

Potential contaminated site (1000-ft. radius): ____

Other stationary sources nearby (gas stations, emission stacks, etc.): ________________________________

Heavy vehicular traffic nearby (or other mobile sources): ____

Part IV – Indoor Contaminant Sources

Identify all potential indoor sources found in the building (including attached garages), the location of the source (floor and room), and whether the item was removed from the building 48 hours prior to indoor air sampling event. Any ventilation implemented after removal of the items should be completed at least 24 hours prior to the commencement of the indoor air sampling event.

Potential Sources	**Location(s)**	**Removed** (Yes / No / NA)
Gasoline storage cans		
Gas-powered equipment		
Kerosene storage cans		
Paints / thinners / strippers		
Cleaning solvents		
Oven cleaners		
Carpet / upholstery cleaners		
Other house cleaning products		
Moth balls		
Polishes / waxes		
Insecticides		
Furniture / floor polish		
Nail polish / polish remover		
Hairspray		
Cologne / perfume		

Potential Sources	**Location(s)**	**Removed** **(Yes / No / NA)**
Air fresheners		
Fuel tank (inside building)		NA
Wood stove or fireplace		NA
New furniture / upholstery		
New carpeting / flooring		NA
Hobbies - glues, paints, etc.		

Part V – Miscellaneous Items

Do any occupants of the building smoke? *Yes / No* How often? _______________

Last time someone smoked in the building? _____________ hours */ days ago*

Does the building have an attached garage directly connected to living space? *Yes / No*

If so, is a car usually parked in the garage? *Yes / No*

Are gas-powered equipment or cans of gasoline/fuels stored in the garage? *Yes / No*

Do the occupants of the building have their clothes dry cleaned? *Yes / No*

If yes, how often? weekly / monthly / 3-4 times a year

Do any of the occupants use solvents in work? *Yes / No*

If yes, what types of solvents are used? _______________________________________

If yes, are their clothes washed at work? *Yes / No*

Have any pesticides/herbicides been applied around the building or in the yard? *Yes* / No

If so, when and which chemicals? ____

Has there ever been a fire in the building? *Yes / No* If yes, when? ______________

Has painting or staining been done in the building in the last 6 months? *Yes / No*

If yes, when____________________ and where? ______________________________

Has there been any remodeling done (flooring/carpeting) in the building in the last 6 months? *Yes / No*

If yes, when ___________________ and where? ______________________________

Part VI – Sampling Information

Sample Technician:_______________________________Phone number: ( )________- ___________

Sample Source: Indoor Air / Sub-Slab / Near Slab Soil Gas / Exterior Soil Gas

Sampler Type: Tedlar bag / Sorbent / Stainless Steel Canister / Other (specify): __________________

Analytical Method: TO-15 / TO-17 / other:___________ Cert. Laboratory: __________________

Field ID #______-____________________________ Field ID #_____- ______

Were “Instructions for Occupants” followed? Y*es / No*

If not, describe modifications: ____

Additional Comments:

Provide Drawing of Sample Location(s) in Building

Part VII - Meteorological Conditions

Was there significant precipitation within 12 hours prior to (or during) the sampling event? *Yes / No*

Describe the general weather conditions: ____

____

Part VIII – General Observations

Provide any information that may be pertinent to the sampling event and may assist in the data interpretation process.

____

____

____

Ohio Environmental Protection Agency

Instructions for Building Occupants Prior to Indoor Air Sampling

Representatives from the Ohio EPA – Division of Environmental Response and Revitalization (DERR) - will be collecting one or more indoor air samples from your building on__________- beginning @__________and ending @________. Your assistance is requested during the sampling program in order to collect an indoor air sample that is both representative of indoor conditions and avoids the common background indoor air sources associated with occupant activities and consumer products.

Please follow the instructions below starting at least 48 hours (2 days) prior to and during the indoor air sampling event:

- ☐ Do operate your furnace and whole house air conditioner as appropriate for the current weather conditions
- ☐ Do not use wood stoves, fireplaces or auxiliary heating equipment
- ☐ Do not use window air conditioners, fans or vents
- ☐ Do not use paints or varnishes (up to a week in advance, if possible)
- ☐ Do not use cleaning products (e.g., bathroom cleaners, furniture polish, appliance cleaners, all-purpose cleaners, floor cleaners)
- ☐ Do not use hair spray, nail polish remover, perfume, etc.
- ☐ Do not store containers of gasoline, oil or solvents within an attached garage.
- ☐ Do not operate or store automobiles within an attached garage
- ☐ Do not open windows or keep doors open
- ☐ Do not smoke in the building
- ☐ Do not apply pesticides
- ☐ Do not use air fresheners or odor eliminators
- ☐ Do not engage in indoor hobbies that use solvents (e.g. gun cleaning)
- ☐ Do not operate gasoline powered equipment within the building, attached garage or around the immediate perimeter of the building
- ☐ Do not bring freshly dry cleaned clothes into the building

You will be asked a series of questions about the structure, consumer products you store in your building, and occupant activities typically occurring in the building. These questions are designed to identify "background" sources of indoor air contamination. While this investigation is looking for a select number of chemicals related to the known or suspected subsurface contamination, the laboratory will be analyzing the indoor air samples for a wide variety of chemicals. As a result, chemicals such as tetrachloroethene that is commonly used in dry cleaning or acetone, which is found in nail polish remover might be detected in your sample results.

Your cooperation is greatly appreciated. If you have any questions about these instructions, please feel free to

contact____at_________________________________.

VAPOR SAMPLING DATA SHEET
SUB-SLAB AND INDOOR AIR

General Information

Site Name / Address: ____

Sampling Location / Address: ____
(if other than site address)

Contact Name: __________________________________ **Phone:** _______________________________

Laboratory & Analytical Method: __________________ **Method of Delivery:** __________
(Courier, UPS, delivered by sampler, etc.)

Sampling Team Members: ____

Met with resident/business on (date) ____________ **to provide information on VOC inventory and sampling cross-contamination concerns. If not, explain why:**____
____
____

Indoor Air Samples

Sample ID #: ___________________ **Canister ID #:**__________________ **Regulator ID #**__________________

Start: Date: ___________________ **Time:** __________ **Initial canister vacuum:** ________ **mm Hg**

End: Date: ___________________ **Time:** __________ **Final canister vacuum:** _________ **mm Hg**

Regulator Calibrated for: 8 hr _____ **24 hr** _____ **grab (no regulator)**______

Canister/ Regulator Leak Checked: Yes ______ **No**______

Sub-Slab Samples

Sample ID #: _________________ **Canister ID #:**________________ **Regulator ID #**________________

Size of canister: __________ **Thickness of sub-slab (inches)** _________ **Port install time:** __________

Sampling Start: Date: ________________ **Time:** __________ **Initial canister vacuum:** ________ **mm Hg**

Sampling End: Date: ________________ **Time:** __________ **Final canister vacuum:** _________ **mm Hg**

Regulator Calibrated for: 8 hr _____ **24 hr** _____ **grab (no regulator)** ______

Canister/ Regulator Leak Checked: Yes No **Sub-Slab Port Leak Checked: Yes No**

Type of sub-slab port: Swagelok __________ **Vapor Pin:** __________

Sub-Slab Port Installed by: _________________________ **Sub-Slab Port Sealed: Yes No**

PID Reading: VOC ppb___________ **% 02**_____________ **PID ID#:** __________________

NOTES: (sampler/canister problems, other significant sampling details, or FSOP deviations)

Note: If a diagram of the sample location(s) is sketched on the back of this data sheet, check here ☐

Revised: 05.2018

Photoionization Detector
FSOP 3.1.1 (January 27, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

The photoionization detector (PID) is a portable instrument used to detect the real-time presence and relative concentration of certain ionizable compounds in gaseous or vapor states. This instrument is typically used for both health and safety monitoring of the work area breathing zone and for the screening of environmental samples. Other uses may include screening of soil gas probes or leak detection (*e.g.,* tanks, vessels, process lines). Consult FSOP 1.1, Initial Site Entry and FSOP 2.1.4, Sample Headspace Screening prior to using a PID for health and safety monitoring or sample headspace screening procedures, respectively.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Hazardous vapors or explosive gases may be present in concentrations requiring use of personal protective equipment (PPE) such as respiratory protection (Table 1, FSOP 1.1, Initial Site Entry) when work area breathing zone air conditions need to be monitored. Only personnel cleared to wear respiratory protection can enter the work area breathing zone if respiratory protection is required.

3.2 Prior to use in potentially flammable atmospheres, consult the instrument manual to determine if the PID is intrinsically safe.

3.3 PIDs only measure the relative concentration of molecules in gases or vapors that are ionizable (*i.e.,* those with an ionization potential (IP) less than that of the ionization energy (IE) of the instrument's ultraviolet lamp). Refer to paragraph 3.3 below for additional information. PIDs may not detect the presence of toxic or explosive gases or vapors with relatively high IPs, including carbon monoxide, chlorine, hydrogen, hydrogen cyanide, hydrogen sulfide or methane. PIDs do not detect or measure the concentration of atmospheric oxygen or the presence of explosive atmospheres. Be sure to use the correct instrument(s) for health and safety monitoring. (Refer to FSOP 1.1, Initial Site Entry.)

3.4 Many instruments are equipped with audio and visual alarms that may be set at threshold limits for the gas or condition of concern. Default alarm levels are generally set by the manufacturer but should be set in accordance with the specified limits in the site-specific health and safety plan.

4.0 Procedure Cautions

4.1 The user should be familiar with the operation of the instrument being used. Consult the instrument manual for operating and calibration instructions specific to the instrument prior to use.

4.2 PID readings are not compound-specific. The instrument must be calibrated using a relatively non-toxic gas such as isobutylene and zeroed to a known clean or background air source. Readings are relative to the calibrant gas, and although the instruments display “ppm” or parts per million readings, the readings are actually ppm-calibration gas equivalents. The PID’s display concentration may be lower or higher than the actual concentration. There are correction factors that can be applied if the compound detected is known and the calibration gas is known.

4.3 PIDs only detect molecules that can be ionized. PIDs are equipped with ultraviolet lamps of different IEs, typically 9.8 electron volts (eV), 10.2 eV, 10.6 eV, and 11.7 eV. The IE of the lamp must be higher than the ionization potential (IP) of the compound(s) being screened. Consult the instrument manual or other reference for the ionization potential of the constituent(s) to be monitored to determine the proper lamp (or if a PID is appropriate for the proposed monitoring task).

4.4 PID performance may be adversely affected by temperature fluctuations, and PID readings are significantly affected by the presence of water vapor and methane due to their high IEs (> 12 eV). If using a PID in extremely wet or cold conditions, store the instrument in a relatively warm, dry location such as the front seat of a field vehicle with the heater running. A flame ionization detector may be better suited for use in these conditions and generally is preferred in situations where large temperature fluctuations, very moist or humid conditions or high methane concentrations are anticipated. Elevated methane concentrations may be encountered in subsurface areas at or adjacent to solid waste landfill disposal units.

4.5 Excessively dusty environments may overwhelm a PID inlet filter and reduce performance by fouling the ionization chamber or lamp. Filters should be inspected and changed after use in excessively dusty environments, and the lamp or ionization chamber should be cleaned if the instrument begins exhibiting a weak response to calibration gas.

4.6 If used for sample headspace screening, never allow the instrument probe to draw in liquid or solid material from a sample container, which may damage the instrument.

4.7 PIDs should be calibrated before each use and at any time the proper performance of the instrument appears to be questionable.

4.8 Always use a regulator with an appropriate flow rate to calibrate a PID. Information on calibration and regulator flow rate should be included in the operator’s manual.

4.9 Never use a source of highly concentrated organic vapors to check whether a PID is responding properly (*e.g.,* never insert a PID probe into the fill port of a vehicle fuel tank, as doing so could damage the instrument).

4.10 Take care when using a PID to screen atmospheres with highly concentrated organic vapors (*e.g.,* opening of a drum containing solvent- or petroleum-contaminated soil). Screening in this manner may contaminate the instrument's lamp or filter to the point that the PID must be serviced or removed from the area of elevated vapor concentrations until it can equilibrate or may otherwise damage the instrument.

4.11 PIDs should be cleaned, inspected, and internally calibrated annually by a service center authorized by the instrument manufacturer.

4.12 Always transport the instrument in a protective case or secure the instrument during transport.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Calibrant gas (*e.g.,* isobutylene)
6.2 Regulator for calibrant gas cylinder
6.3 Clean containers such as sealable plastic bags or jars with foil or film covers (if using for headspace screening)
6.4 Field logbook, field log sheets, or appropriate field form
6.5 Pens or markers
6.6 PPE appropriate for site-specific work activities
6.7 Inert tubing with "tee" connector
6.8 Instrument with operation manual
6.9 Protective case for instrument transport
6.10 Tedlar® bag
6.11 Calibration log sheet

7.0 Procedures

7.1 Consult the instrument manual for both general procedures and instrument-specific operating functions prior to using the instrument.

7.2 Make sure instrument is fully charged before use. Bring a backup battery if necessary.

7.3 Turn the instrument on and allow it to warm up. Some instruments will give a "ready" prompt in the instrument display when ready for use. Make sure pump is running and lamp is on. Check for warnings on instrument display during warm up. Check alarm levels to be sure they are consistent with site specific health and safety plan.

7.4 Calibrate the instrument according to the manufacturer's instructions with a relatively non-toxic span gas (*e.g.,* isobutylene) before each use.

7.4.1 Calibrate the instrument directly from the cylinder using a flow regulator of appropriate flow rate (equal to or slightly higher than the pump capacity) or a pressure demand regulator. Use a piece of tubing to connect the regulator to the instrument probe. If the regulator flow rate is significantly higher than the pump flow, then install a "tee" fitting in the tubing to bleed of excess calibrant gas.

7.4.2 For an alternate calibration method, fill a clean Tedlar® bag with the calibrant gas by first connecting the cylinder to the bag with the regulator and tubing and allowing the bag to inflate after opening the valve on the bag. Next, close the valve on the bag, attach the instrument probe to the bag with a length of tubing and open the bag valve when ready to calibrate.

7.4.3 Record calibration data, including operator name, location, instrument make and model, date, time, calibration gas type, and result on the calibration log sheet.

7.5 Zero the instrument with a clean air source such as a cylinder of certified clean air, or to ambient (background or off-site) air, and ensure that the instrument is zeroed or recording background readings before use.

7.6 Use the instrument for health and safety monitoring or headspace screening in accordance with the site-specific health and safety plan and FSOP 1.1, Initial Site Entry and/or site-specific work plan and FSOP 2.1.4, Sample Headspace Screening as appropriate.

7.7 Observe and record the instrument readings as appropriate.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 2.1.4, Sample Headspace Screening

Multiple Gas Detection Meters
FSOP 3.1.2 (January 27, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Multiple gas detection meters are a class of portable instruments used to monitor the presence or absence of several classes of atmospheric gases or conditions in real time. These instruments are typically used for initial site entry and health and safety monitoring at a site (FSOP 1.1, Initial Site Entry). Other uses may include screening of soil gas probes or leak detection (*e.g.,* tanks, vessels, process lines).

1.2 Although there is a wide range and combination of detection sensors available, instruments owned or used by the agency are typically equipped with sensors for the detection of oxygen, explosive atmospheres (*e.g.*, LEL) and two other gases, generally carbon monoxide and hydrogen sulfide. These instruments are commonly referred to as “four gas meters” because they typically have four detection sensors, however, the number of sensors may vary. For example, several multiple gas meters are available with a built-in photoionization detector for the detection of ionizable molecules in addition to the four sensors listed above (FSOP 3.1.1, Photoionization Detector). In addition, some instruments may be designed to measure the temperature and pressures from solid waste landfill gas monitoring or extraction wells.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Hazardous vapor or explosive gases may be present in concentrations requiring use of personal protective equipment (PPE) such as respiratory protection (Table 1, FSOP 1.1, Initial Site Entry) when work area breathing zone air conditions need to be monitored. Only personnel cleared to wear respiratory protection can enter the work area breathing zone if respiratory protection is required.

3.2 Consult the instrument manual to determine if the instrument is intrinsically safe prior to use in potentially flammable atmospheres.

3.3 Combustible gas indicator (CGI) or lower explosive limit (LEL) sensors are designed to operate under normal atmospheric oxygen concentrations (20.9% v/v) and will not function properly in oxygen-deficient or oxygen-enriched environments. When using a CGI/LEL sensor, the user should concurrently monitor the ambient percentage of oxygen. If oxygen monitoring data are not available, the CGI/LEL readings cannot be considered reliable.

3.4 Many instruments are equipped with audio and visual alarms that may be set at threshold limits for the gas or condition of concern. Default alarm levels are generally set by the manufacturer but should be checked and re-set as needed, in accordance with the specified limits in the site-specific health and safety plan.

3.5 If a CGI/LEL sensor indicates potentially explosive atmospheric conditions, or other sensors indicate the presence of oxygen-deficient, oxygen-enriched or toxic atmospheres, evacuate the area immediately. (Refer to Table 1 of FSOP 1.1, Initial Site Entry, and to the site health and safety plan for action levels and responses.)

4.0 Procedure Cautions

4.1 The user should be familiar with the operation of the instrument being used. Consult the instrument manual for operating and calibration instructions specific to the instrument prior to use.

4.2 Instrument should be serviced and/or cleaned and calibrated annually by a service center authorized by the instrument manufacturer.

4.3 Do not use calibrant gas (“mixed gas”) for “zero” calibration as the oxygen content of the calibrant gas may be less than normal atmospheric oxygen content (20.9%).

4.4 Always transport the instrument in a protective case or secure the instrument during transport. Multiple gas meter performance may be adversely affected by temperature fluctuations, and readings are significantly affected by the presence of water vapor and methane. If using a multiple gas meter in extremely wet or cold conditions, store the instrument in a relatively warm, dry location such as the front seat of a field vehicle with the heater running.

4.5 Excessively dusty environments may overwhelm a multiple gas meter inlet filter and reduce performance by fouling the instrument. Filters should be inspected and changed after use in excessively dusty environments if the instrument begins exhibiting a weak response during calibration.

4.6 If used for sample headspace screening, never allow the instrument probe to draw in liquid or solid material from a sample container, which may damage the instrument.

4.7 Multiple gas meters should be calibrated before each use and at any time the proper performance of the instrument appears to be questionable.

4.8 Always use a regulator with an appropriate flow rate to calibrate a multiple gas meter. Information on calibration and regulator flow rate should be included in the operator’s manual.

4.9 Never use a source of highly concentrated organic vapors to check whether a multiple gas meter is responding properly (*e.g.,* never insert a probe into the fill port of a vehicle fuel tank, as doing so could damage the instrument).

4.10 Take care when using a multiple gas meter to screen atmospheres with highly concentrated organic vapors (*e.g.,* opening of a drum containing solvent- or petroleum-contaminated soil). Screening in this manner may contaminate the instrument's sensors, filters, or lamp (when meter contains PID) to the point that the multiple gas meter must be serviced or removed from the area of elevated vapor concentrations until it can equilibrate or may otherwise damage the instrument.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Calibrant gas (*e.g.,* mixed gas consisting of known concentrations that instrument sensors may detect)
6.2 Regulator for cylinder
6.3 Logbook, log sheets, or appropriate field form
6.4 Pens or markers
6.5 PPE appropriate for site-specific work activities
6.6 Instrument with operation manual
6.7 Protective case for instrument transport
6.8 Inert tubing with “tee” connector
6.9 Tedlar® bag
6.10 Calibration log sheet

7.0 Procedures

7.1 Consult the instrument manual for both general procedures and instrument-specific operating functions prior to using the instrument.

7.2 Make sure instrument is fully charged before use. Bring a spare battery if necessary.

7.3 Turn the instrument on and allow it to warm up. Some instruments will indicate a “ready” prompt in the instrument display when ready for use. Make sure the pump is running. Check for warnings on instrument display during warm up. Check the alarm levels to be sure they are consistent with site specific health and safety plan.

7.4 Calibrate the instrument according to manufacturer's instructions before use:

7.4.1 The instrument may be calibrated directly from the cylinder using a flow regulator of appropriate flow rate (equal to or slightly higher than the pump capacity) or a pressure demand regulator. Use a piece of tubing to connect the regulator to the instrument probe. If the regulator flow rate is significantly higher than the pump flow, then a “tee” may be inserted in the tubing to bleed of excess calibrant gas.

7.4.2 An alternate calibration method is to fill a clean Tedlar® bag with the calibrant gas by first connecting the cylinder to the bag with the regulator and tubing and allowing the bag to inflate after opening the valve on the bag. Next, close the valve on the bag, attach the instrument probe to the bag with a length of tubing and open the bag valve when ready to calibrate.

7.5 Zero the instrument with a clean air source or to ambient or background air and ensure that the instrument is zeroed or record background readings before use. If using a cylinder of clean air for zeroing, make sure cylinder contains 20.9% oxygen. Calibrate the instrument with cylinder of mixed gas of known concentration. When calibrating with a cylinder of mixed gas, an oxygen content of less than atmospheric percentage (e.g., 18.0 – 19.5 %) is recommended to verify that the instrument is accurately detecting oxygen-deficient conditions.

7.6 Record calibration data, including operator name, location, instrument make and model, date, time, calibration gas type, and result on the calibration log sheet.

7.7 Use the instrument for monitoring in accordance with the site-specific health and safety plan and FSOP 1.1, Initial Site Entry or site-specific work plan.

7.8 Observe and record the instrument readings as appropriate.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 3.1.1, Photoionization Detector

Interface Meter
FSOP 3.1.3 (February 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

Interface meters (also referred to as oil/water interface probes) are used to measure the depth and thickness of light and dense non-aqueous phase liquid (LNAPL and DNAPL) and depth to ground water in wells. [Use FSOP 2.2.3, NAPL Detection and Sampling, in conjunction with this FSOP.] Typically, interface meters consist of a reel, graduated tape and sensor. The reel has an alarm, control switches and a battery pack. The tape has a wire or series of wires encased within it. The sensing probe is connected to the end of the tape which is lowered into the well. When the probe contacts water or NAPL, audible and/or visual alarms will be activated. The probe utilizes an infrared beam and detector. When the probe is lowered into a liquid, the infrared light is refracted triggering audible (buzzer) and visual (light) alarms. In general, if the liquid is relatively non-conductive, such as oil, a steady audible alarm tone will sound, and a steady alarm light will be displayed. If the liquid is conductive, such as water, then an intermittent (beeping) alarm will sound, and a flashing light will be displayed.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Consult the instrument’s operation manual to determine if it is intrinsically safe when working in an area where there is a potential fire or explosion hazard.

3.2 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work.

3.3 If NAPL or high concentrations of VOCs are suspected to be present in the well, use a photoionization detector (PID) or a flame ionization detector (FID) to screen the breathing space above the well casing before taking measurements. Monitoring, sampling or LNAPL recovery efforts may need to be performed using respiratory protection by qualified DERR staff.

3.4 If NAPL is suspected to be present in the well, monitor the well for lower explosive limit (LEL) and percent oxygen (O_2) for a potentially explosive atmosphere with a multiple gas detection meter. If the LEL is exceeded inside the well casing, allow the open well to ventilate and measure the LEL again. Allow the LEL concentration to drop to below the LEL before placing instrumentation or sampling devices inside the well.

4.0 Procedure Cautions

4.1 The user should be familiar with the operation of the instrument being used. Consult the instrument manual for operating instructions specific to the instrument prior to use.

4.2 Inspect the instrument tape to make sure there are no cuts or abrasions that may impair the function of the tape.

4.3 The use of an interface meter to measure the depth to water or NAPL in residential or other wells with pumps and associated plumbing is generally discouraged because the tape may become entangled in the downhole plumbing or centralizing disks. If water level measurements must be obtained from such wells, the pump and plumbing may need to be temporarily removed first, which generally requires the services of a registered water well drilling contractor. Additionally, for residential or other water supply wells, there may be additional sanitary requirements for disinfection of the well and/or downhole equipment required by the county or local health department that has jurisdiction over the well.

4.4 Use caution when lowering and raising the tape within a well. A sharp casing edge or burr may damage the tape if the tape is allowed to rub against the edge of the casing.

4.5 Be sure the instrument has new or charged batteries. Replace old or weak batteries as necessary.

4.6 Remove instrument batteries if the instrument is not going to be used for an extended period of time.

4.7 Always transport the instrument in a protective case or secure the instrument during transport.

4.8 When reeling the tape back in, be careful that the tape does not twist, kink or fold.

4.9 If NAPL is encountered, follow the decontamination procedures in FSOP 1.6, Equipment Decontamination before reusing the instrument.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA’s hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Interface meter with battery and operation manual
6.2 Protective case for instrument transport
6.3 Field log sheet (attached) or field book and pen
6.4 Well keys or tools to open well
6.5 Decontamination equipment and supplies
6.6 Personal protective equipment appropriate for site-specific work activities

6.7 Photoionization Detector (PID)
6.8 Multi Gas detection meter, as necessary
6.9 Spare replaceable battery

7.0 Procedures

7.1 Make sure the interface meter is functioning properly and the battery is charged. (**Note:** when testing the instrument, use tap water and not distilled water. Distilled water contains no dissolved solids to act as electrolytes and the alarm may not activate.)

7.2 Open the well by removing the lock and cap.

7.3 If required by the SSWP or HASP, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector (PID), multi gas detection meter (with LEL/O2 capabilities) or other required instrument. Breathing zone action levels are provided in Table 1 of FSOP 1.1, Initial Site Entry. Monitoring may need to continue during purging and sampling activities. Additionally, if the LEL is exceeded inside the well casing, allow the open well to ventilate and measure the LEL again. Allow the LEL concentration to drop to below the LEL before placing instrumentation or sampling devices inside the well. Refer to FSOP 3.1.1, Photoionization Detector and FSOP 3.1.2, Multiple Gas Detection Meter for use and operation of these instruments.

7.4 Locate the measuring point elevation mark on the casing. A surveyed measuring point will need to be established if not already present. For monitoring wells, this is generally marked on the highest point or north side of the top of the inner casing. If a mark is not present, then use the highest visible point of the inner casing as the measuring point.

7.5 Turn the instrument’s switch on to the highest sensitivity position. Adjust the sensitivity as necessary.

7.6 Slowly lower the tape down the well taking care not to twist the tape or allow the tape to scrape the edge of the casing as it is being lowered. If LNAPL is present in a measurable thickness (generally 0.01 foot), the instrument’s audible alarm (buzzer) will emit a steady tone and visual (light) alarm will display a steady light. When the instrument’s probe contacts water, the audible alarm will emit a beeping tone and the visual alarm will flash. If the instrument is lowered through the water column and encounters DNAPL, then the instrument will sound a continuous alarm similar to when it encounters LNAPL.

7.7 Raise the tape slightly so that the probe is out of the water or LNAPL/DNAPL. The alarm signals should stop or change. A mild shake of the tape may also be necessary to remove water from the probe sensor pin. Lower the tape slightly until the alarms activate and hold the tape firmly against the side of the casing so that the probe does not move up or down.

7.8 Carefully read the tape measurement at the well's measuring point to the nearest 0.01 foot.

7.9 Record the water level reading, NAPL reading(s) and supporting information (site, date, time, notes) on the attached field log sheet or in a field logbook.

7.10 For apparent LNAPL thickness, subtract the LNAPL reading from the water level reading. For apparent DNAPL thickness, subtract the DNAPL reading from the total depth of the well (measured from the top of casing).

7.11 Ground water elevations in monitoring wells containing LNAPL should be corrected for the depression of the LNAPL/water interface to obtain total hydraulic head. The depression is caused by the weight of the LNAPL. The correction is performed by multiplying the measured LNAPL thickness by an estimate of the LNAPL specific gravity, and then adding the result to the elevation of the LNAPL/water interface. Approximate specific gravities in grams per cubic centimeter (g/cc) at 20^o C (68^o F) for common petroleum product sources include the following:

- Gasoline, 0.74 g/cc
- Jet fuel or kerosene, 0.80 g/cc
- Diesel fuel, 0.85 g/cc
- Motor oil, 0.90 g/cc

The water level correction for LNAPL is very important for determining apparent ground water elevations and preparing accurate potentiometric surface maps.

7.12 Decontaminate the instrument probe and the length of tape lowered into the well in accordance with the decontamination procedures specified in FSOP 1.6, Sampling Equipment Decontamination. The probe should be cleaned as follows: wash probe thoroughly with a non-abrasive mild detergent. DO NOT use any solvents. Use a soft cloth around the pins on the end of the probe to remove all product and a soft bristle brush to remove all product from the inner part of the probe. Use lukewarm water, hot water may result in damage to the probe. Rinse the probe thoroughly with distilled water and wipe dry.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

Field Log Sheet for Depth to Ground Water and Depth to Nonaqueous Phase Liquids (NAPL) Measurements in Monitoring Wells and Piezometers

11.0 References

FSOP1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 2.2.3, NAPL Detection and Sampling

FSOP 3.1.1, Photoionization Detector

FSOP 3.1.2, Multiple Gas Detection Meter

Field Log Sheet for Depth to Ground Water and Depth to Nonaqueous Phase Liquids (NAPL) Measurements in Monitoring Wells and Piezometers

Site Name:

Well or Piezometer	Date	Time	LNAPL Depth (ft TOC)	Water Depth (ft TOC)	DNAPL Depth (ft TOC)	Notes:

Electronic Water Level Indicator
FSOP 3.1.4 (February 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Electronic water level indicators are used to measure the depth to ground water in monitoring wells and other types of wells. [Frequently, FSOP 2.2.2 Ground Water Level Measurement is used in conjunction with FSOP 3.1.4.] Typically, electronic water level indicators consist of a reel, tape and sensor. The reel generally has an alarm, control switches and a battery pack. The tape has a wire or series of wires encased within it. The tape is connected to the reel and graduated in tenths and hundredths of feet. The sensing probe is connected to the end of the tape which is lowered into the well. When the tape is lowered into the well and the probe contacts water, an audible or visual alarm is activated.

1.2 This FSOP is only applicable to electronic water level indicators. While other types of water level indicators are available, electronic water level indicators are the environmental industry standard and are preferred by Ohio EPA.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Consult the instrument's operation manual to determine if it is intrinsically safe when working in an area where there is a potential fire or explosion hazard.

3.2 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work

4.0 Procedure Cautions

4.1 The user should be familiar with the operation of the instrument being used. Consult the instrument manual for operating instructions specific to the instrument prior to use.

4.2 Inspect the instrument tape to make sure there are no cuts or abrasions that may impair the function of the tape.

4.3 The use of electronic water level indicators to measure the depth to water in residential or other wells with pumps and associated plumbing is generally discouraged. This is because the tape may become entangled in the downhole plumbing or centralizing disks. If water level measurements must be obtained from such wells, the pump and plumbing may need to be temporarily removed first. This generally requires the services of a registered water well drilling contractor. Additionally, for residential or other water supply wells, there may be additional sanitary requirements for disinfection of the well and/or downhole equipment required by the county or local health department that has jurisdiction over the well.

4.4 Use caution when lowering and raising the tape within a well. A sharp casing edge or burr may damage the tape if the tape is allowed to rub against the edge of the casing.

4.5 Do not use electronic water level indicators in wells known or suspected to contain nonaqueous phase liquids (NAPL). Use an interface meter instead (refer to FSOP 3.1.3, Interface Meter.)

4.6 If using the water level indicator to measure the total depth of the well, add the length of any probe extension beyond the sensor pin (*e.g.,* 0.3 ft) to obtain an accurate measurement of the total well depth.

4.7 Be sure the instrument has fresh batteries. Replace old or weak batteries as necessary.

4.8 Remove instrument batteries if the instrument is not going to be used for an extended period of time.

4.9 Always transport the instrument in a protective case or secure the instrument during transport.

4.10 When reeling the tape back in, be careful that the tape does not twist, kink or fold.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Water level indicator with battery and operation manual
6.2 Protective case for instrument transport
6.3 Field data sheet (attached) or field book and pen
6.4 Well keys or tools (*e.g.,* ratchet, bolt cutter, screwdriver) to open well
6.5 Decontamination equipment and supplies
6.6 Personal protective equipment appropriate for site-specific work activities

7.0 Procedures

7.1 Make sure the electronic water level indicator is functioning properly and the battery is functioning. (**Note:** when testing the instrument, use tap water and not distilled water. Distilled water contains no dissolved solids to act as electrolytes and the alarms will not be activated.)

7.2 Open the well by removing the lock, if present, and cap. Allow sufficient time for the water level in the well to equilibrate, especially if the well is installed in a confined aquifer or if air pressure is released (a “popping” sound is heard) when the well casing cap is removed.

7.3 Locate the designated measuring point mark on the casing. For monitoring wells this is generally marked on the highest point or north side of the top of the inner casing. If a mark is not present, use the highest visible point of the inner casing as the measuring point. If the inner casing is level (no discernible high point), use the north side of the casing.

7.4 Turn the water level indicator’s switch on to the highest sensitivity position.

7.5 Slowly lower the tape down the well taking caution not to twist the tape or allow the tape to scrape the edge of the casing as it is being lowered. When the tape’s probe contacts water, the instrument’s audible (buzzer) and visual (light) alarms will be activated.

7.6 Raise the tape slightly to lift the probe out of the water. The alarm should stop. A mild shake of the tape may also be necessary to remove water from the probe’s sensor pin. Lower the tape slightly until the alarms activate and hold the tape firmly against the side of the casing so that the probe does not move up or down.

7.7 Carefully read the tape measurement at the well’s measuring point to the nearest hundredth (0.01) foot.

7.8 Record the water level reading and supporting information (site, date, time, notes) on the attached field log sheet or in a field logbook.

7.9 If using the water level indicator to measure the total depth of the well, turn off the instrument. Next, lower the tape to the bottom of the well and record the tape reading at the measuring point. Remember to add the length of any probe extension to the total depth measurement.

7.10 Decontaminate the probe and the length of tape lowered into the well in accordance with the decontamination procedures specified in FSOP 1.6, Sampling Equipment Decontamination. The probe should be cleaned as follows: wash probe thoroughly with a non-abrasive mild detergent. DO NOT use any solvents. Use a soft cloth around the pins on the end of the probe to remove all product and a soft bristle brush to remove all product from the inner part of the probe. Use lukewarm water, hot water may result in damage to the probe. Rinse the probe thoroughly with distilled water and wipe dry.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

Field Log Sheet for Depth to Ground Water Measurements in Monitoring Wells and Piezometers

11.0 References

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 3.1.3, Interface Meter

Field Log Sheet for Depth to Ground Water Measurements in Monitoring Wells and Piezometers

Site Name: ____

Well or Piezometer	Date	Time	Water Depth (ft TOC)	Total Depth (ft TOC)	Notes:

Water Quality Meters
FSOP 3.1.5 (February 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Water quality meters are a class of portable instruments used to determine surface water or ground water chemistry in the field. These "field parameter" measurements may be collected to evaluate:

- General water quality/chemistry
- Ground water stabilization during monitoring well development or sampling
- Regulatory standards for surface water analytes that are dependent on pH, temperature or other parameters.

1.2 There are many models and manufacturers of water quality meters. Meters are typically equipped with sensors to measure field parameters including pH, specific conductance, temperature, total dissolved solids, salinity, dissolved oxygen, oxidation-reduction potential and/or turbidity. Some meters are equipped with "flow-through" cells that allow multiple parameters to be continuously measured over time. Flow-through cells are very useful for evaluating ground water stabilization when continuously purging a monitoring well with a pump.

1.3 DERR owns several water quality meter models. The user should be familiar with the capabilities and operation of a particular meter prior to use and should always review the manufacturer's instruction manual prior to use.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Always review the site-specific health and safety plan (HASP) for site-specific sampling hazards before beginning work.

3.2 Always be conscious of hazards associated with the water body during surface water sampling, especially if sampling a lake, pond, wetland, lagoon, impoundment, river or stream. Never enter a river or stream under high-flow conditions.

3.3 Be aware of slip, trip or fall hazards along riverbanks and lagoon or impoundment slopes.

3.4 Be aware of the dangers of working near low-head dams (*e.g.,* rapid flow and undercurrents) as well as hazards that may be posed by other man-made structures such as manholes, vaults, weirs, pump houses and associated electrical or mechanical equipment.

3.5 If sampling from a boat, always wear a personal flotation device (PFD) and follow Ohio EPA's Boating Safety SOP (SP10-12).

3.6 Never walk on a surface crust or partially submerged debris in a lagoon or impoundment.

3.7 Do not collect samples from a frozen lake, pond, lagoon, or impoundment unless authorized by a site-specific health and safety plan. Never collect samples from atop of a river, stream or any other flowing water body that is frozen over.

3.8 When collecting surface water samples, use the "buddy system," with at least two people present at all times.

3.9 Be aware of biological hazards (*e.g.,* snakes, ticks, bees, mosquitoes and poison ivy).

3.10 For ground water sampling from wells, refer to the health and safety precautions in FSOP 2.2.4, Ground Water Sampling (General Procedures).

4.0 Procedure Cautions

4.1 The user should be familiar with the capabilities and operation of the meter. Consult the user's manual for operation and calibration instructions prior to use.

4.2 Remove old batteries to prevent potential damage if the meter is not going to be used for an extended period of time.

4.3 Always transport the meter in its protective case.

4.4 Do not to drop the meter or immerse the body of the meter in a surface water body. Some meters are not waterproof.

4.5 Clean meter cells and sensors with distilled water after each use or as otherwise indicated in the user's manual.

4.6 For meters equipped with a pH probe that has a bulb-type sensor with a cap or cover, be sure to place a small amount of pH storage solution, slightly acidic pH solution (*e.g.,* pH 4.0), or tap water (depending on manufacturer instructions) in the probe's cap or cover to keep the pH probe bulb moist during storage. Allowing the pH probe bulb to dry out will shorten its life.

4.7 Don't use expired calibration standard fluids to calibrate a meter.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

Equipment and Supplies

5.1 Water quality meter with a copy of the operation manual
5.2 Standard calibration fluids
5.3 Spare batteries
5.4 Equipment and supplies to decontaminate and clean meter after each use, including spray bottles, distilled or deionized water, paper towels, etc.
5.5 Log book, log sheets (see FSOP 2.2.4), or appropriate field forms with pens or markers
5.6 Personal protective equipment appropriate for site-specific work activities

6.0 Procedures

6.1 Consult the user's manual for both general procedures and meter-specific operating functions prior to using the meter.

6.2 Be sure the meter battery is functioning.

6.3 Calibrate the meter according to the manufacturer's instructions before use with the appropriate standard calibration solutions.

6.4 If the meter has a measurement cup cell, rinse the cell three times with the standard solution or the sample to be measured.

6.5 If the meter has a flow-through cell, allow three volumes of purge water to pass through the cell before recording water quality parameter measurements.

6.6 If the meter has a probe, fill a clean jar with the sample to be measured or, in surface water bodies, place the probe directly in the water body.

6.7 Allow the meter readings to stabilize before recording.

6.8 For temperature readings, make sure the probe is placed in a sufficient volume of water to account for the temperature of the probe body on very hot or cold days. If the sample jar is small, water may need to be added to the sample jar several times to achieve an accurate temperature measurement.

6.9 Record water quality parameter readings as appropriate.

6.10 Decontaminate the meter between sampling locations in accordance with the user’s manual and/or FSOP 1.6, Sampling Equipment Decontamination as appropriate.

7.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

8.0 Quality Assurance and Quality Control

Not applicable

9.0 Attachments

None

10.0 References

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 2.2.4, Ground Water Sampling (General Practices)

FSOP 2.3.1, Surface Water Sample Collection

Radiation Detection Meters
FSOP 3.1.6 (February 26, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Radiation detection meters are used to monitor for the presence of alpha, beta and primarily for gamma radiation. These instruments are used by DERR personnel for health and safety monitoring during initial site entry at former landfills or other potentially contaminated sites where radioactive materials may be present, or at potentially contaminated sites with a poorly documented history.

1.2 If, based on historical knowledge of the site, radioactivity is expected to be present, the initial site entry team will consult with management prior to entry, and with the Ohio Department of Health (ODH) Bureau of Environmental Health and Radiation (BEHR). For initial site entry purposes, the team will utilize a radiation detection meter.

1.3 ODH BEHR regulates nuclear materials and has jurisdiction over radiologic assessment in Ohio (OAC 3701:1-38-13, general radiation protection standards). Except for members of Ohio EPA’s Radiation Assessment Team (RAT), DERR staff only monitor radiation for personal health and safety and not to assess or investigate radiation at sites. If radioactive materials are encountered during the initial site entry or gamma radiation measured at any location exceeds 2 millirem/hr (0.002 rem/hr), leave the site immediately and contact the ODH BEHR at (614) 466-1390. Background radiation levels for the State of Ohio range from 0.008 millirem/hr to 0 .019 millirem/hr.

1.4 There are many manufacturers and models of radiation meters available. Some radiation meters function as survey meters often equipped with separate probes to measure radiation in the surrounding area or on specific surfaces. Other meters function as personal monitors with a built-in audible alarm which will sound if given a dose or dose rate is exceeded.

1.5 This FSOP applies to DERR district and site investigation field unit (SIFU) staff. This FSOP does not apply to Ohio EPA’s RAT staff.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Some meters are equipped with audio and visual alarms that may be set at threshold limits for radiation. Default alarm levels should be set at 2 millirem/hr.

3.2 Consult the meter’s user manual to determine if the instrument is intrinsically safe prior to use in potentially flammable atmospheres.

3.3 A radiation meter does not monitor for hazardous/toxic vapors or gases, potentially explosive atmospheres or oxygen-deficient/oxygen-enriched atmospheres. Monitoring for these atmospheric hazards should be performed in accordance with FSOP 1.1, Initial Site Entry as necessary based on anticipated site conditions.

3.4 If radioactive materials are encountered during the initial site entry, or if gamma radiation measured at any location exceeds 2 millirem/hr, leave the site immediately and contact ODH BEHR.

3.5 Monitor for radiation in accordance with FSOP 1.1, Initial Site Entry and the site-specific health and safety plan (if one is available).

4.0 Procedure Cautions

4.1 Review the meter's manual for operating and calibration instructions prior to use.

4.2 The meter should be cleaned and calibrated annually by an equipment service center authorized by the State of Ohio emergency management agency (EMA) or recommended by the meter's manufacturer.

4.3 Always transport the meter in its protective case.

4.4 Remove the batteries to prevent potential damage if the meter is not going to be used for an extended time period.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Instrument with operation manual
6.2 Spare batteries
6.3 Logbook, log sheets or appropriate field form
6.4 Pens or markers
6.5 PPE appropriate for site-specific work activities

7.0 Procedures

7.1 Consult the user's manual for both general and instrument-specific operating procedures prior to using the meter.

7.2 Be sure the meter is functional (*i.e.,* batteries are fresh) before use.

7.3 Prior to site entry, turn on the instrument and check the display, calibration date, and operation (using a reference source, if available). If the instrument is equipped with an alarm, ensure the alarm is set at 2 millirem/hr.

7.4 Establish background by taking readings prior to site entry.

7.5 Initiate monitoring upon initial site entry and continue to monitor during the site visit. If gamma radiation is less than 2 millirem/hr, continue monitoring. If gamma radiation measured at any location exceeds 2 millirem/hr, leave the site immediately and contact the ODH BEHR at (614) 466-1390.

7.6 Observe and record the instrument readings as appropriate.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

None

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

Ohio Administrative Code 3701:1-38-13

X-Ray Fluorescence Analyzer
FSOP 3.1.7 (February 26, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 The X-Ray Fluorescence (XRF) Analyzer is a handheld energy dispersive X-Ray fluorescence spectrometer. The XRF easily and quickly identifies and quantifies elements over a wide dynamic concentration range.

1.2 This instrument is a screening tool for the identification and quantitative analysis of the following elements:

titanium (Ti)
chromium (Cr)
manganese (Mn)
iron (Fe)
cobalt (Co)
nickel (Ni)
copper (Cu)
zinc (Zn)
mercury (Hg)
arsenic (As)
lead (Pb)
selenium (Se)
rubidium (Rb)
strontium (Sr)
zirconium (Zr)
molybdenum (Mo)
silver (Ag)
cadmium (Cd)
tin (Sn)
antimony (Sb)
barium (Ba)

XRF is suggested to be used with confirmatory analysis using other techniques, (*e.g.,* flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

1.3 The method sensitivity or lower limit of detection depends on several factors including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects and interelement spectral interferences.

1.4 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each operator/analyst must demonstrate the ability to generate acceptable results with this method. Each operator/analyst must be enrolled in a radiation monitoring program and issued a personal dosimeter.

1.5 The primary guidance for the performance of field-portable XRF analysis is U.S. EPA Method 6200, Field Portable X-RAY Fluroescence Spectrometry For The Determination Of Elemental Concentrations In Soil and Sediment.

2.0 Definitions

2.1 XRF: X-Ray fluorescence

2.2 Ionizing Radiation: high-energy radiation capable of producing ionization in substances through which it passes. It includes nonparticulate radiation, such as X-rays, and radiation produced by energetic charged particles, such as alpha and beta rays and neutrons.

2.3 Dosimeter: a device carried on the person for measuring the quantity of ionizing radiation to which one has been exposed, such as gamma rays.

2.4 In-situ: in its original place

3.0 Health and Safety Considerations

3.1 The X-ray source can emit dangerous levels of ionizing radiation.

3.2 When operating the instrument, operators must wear a dosimeter ring on the hand closest to the beam port. The dosimeter ring will measure any accumulated radiation received while using the analyzer. The dosimeter is a means to assure the device is being used in a safe manner. The dosimeter will be exchanged with a new dosimeter quarterly. The dosimeter will be analyzed for radiation levels and the results given to the operator.

3.3 The X-ray beam comes out of the front nose of the analyzer. Always be aware of the direction of the analyzer's X-ray beam. Never point the instrument at yourself or anyone else when operating the device.

3.4 The X-ray tube is emitting X-rays when the trigger is depressed and the "X-Ray – ON" lights are illuminated. These lights should go off when the analysis is completed and the trigger is released. If they stay on, immediately cease using the device, disconnect the battery, and contact the manufacturer.

3.5 Never put any part of your body forward of the trigger during the test.

3.6 Never activate the device with anyone within a three-foot radius of the device. If anyone enters this zone, immediately cease testing until the three-foot radius is established.

3.7 NEVER TEST A SAMPLE BY HOLDING IT IN YOUR HAND!

3.8 If any operational irregularities are experienced with the device, immediately cease its use, disconnect the battery, and contact the manufacturer.

3.9 Untrained personnel and minors are forbidden from operating the device.

4.0 Procedure Cautions

4.1 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the XRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup (*i.e.,* against the cup window), the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.2 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by air drying the samples or drying in a convection or radiant oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between XRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.3 Inconsistent positioning of samples in front of the probe window is a potential source of error because the X-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.4 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as X-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. Arsenic concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., < 300 ppm) for As, regardless of the actual concentration present.

5.0 Personnel Qualifications

5.1 Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

5.2 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

6.0 Equipment and Supplies

6.1 XRF Analyzer
6.2 Polyethylene sample cups, 31 to 40 mm in diameter with collar or 4" x 4" plastic weight boats
6.3 X-ray window film Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 µm thick.
6.3 Stainless steel grinder for grinding soil and sediment samples
6.4 Sieves – No. 10-mesh (0.25 mm), stainless-steel, nylon, or equivalent for preparing soil and sediment samples
6.5 Plastic bags for collection and homogenization of soil samples
6.6 Drying oven – may be a standard radiant or a convection oven, for soil and sediment samples that require drying
6.7 Logbook, data sheets, marker, etc.

7.0 Procedures

7.1 Sample Prepartion

7.1.1 The XRF may be used to analyze in-situ samples, bagged samples and processed samples. In-situ and bagged testing can efficiently generate data very quickly, but generally are not as accurate as processed soil testing. Processed soil samples offer the best accuracy, but require more time for sample preparation.

7.1.1.1 For in-situ analysis, the XRF is placed directly onto the ground. Operators must remove any plant growth or foreign objects so that the analyzer probe is flush to the soil surface.

7.1.1.2 For bagged analysis, a soil sample is collected in a thin plastic bag and testing occurs directly through the bag. Except for a few elements – namely Cr and Ba testing through the thin plastic bag has little affect on the test result. However, concentration results for Cr and Ba may be underestimated by 20 to 30 percent.

7.1.1.3 Processed sample testing generally provides the most accurate results, because it provides the most uniform sample for testing. The greatest source of error for XRF (and all analytical techniques) is non-uniform samples. Processed sample tests require a sample to be collected, dried if necessary and sieved and ground into a powder. The processed sample is placed into a plastic bag, plastic weigh boat or XRF cup for analysis.

7.1.2 Detailed sample preparation procedures are provided in U.S. EPA Method 6200, Field Portable X-RAY Fluroescence Spectrometry For The Determination Of Elemental Concentrations In Soil and Sediment.

7.2 General Operation

7.2.1 Turn on the device by depressing the on button at the top of the analyzer. The device can only be activiated for testing after the user has logged on to the software. A system standardization test is required before any sample tesing is done.

7.2.2 The trigger must be depressed for the test to begin. The analyzer is actively testing whenever the indicator lights are blinking.

7.2.3 You must have a sample present in front of the window of the device in order to perform a test. If a sample moves from the window during a test, the instrument aborts the test. This will prevent accidental exposure to the user and bystanders to the open X-ray beam.

7.2.4 See Users Manual for additional information and detailed instructions.

8.0 Data and Records Management

8.1 An instrument log book is updated every time the instrument is used.

8.2 Data results are downloaded to a Ohio EPA’s computer network for review, evaluation, and records management purposes.

8.3 Data is presented in an electronic spreadsheet (Excel) format and allows for editing based on the user’s specific needs and/or project Data Quality Objectives.

8.4 All data are reported in parts per million (ppm) which is equivalent to milligrams/kilogram (mg/kg).

8.5 Project-specific field log sheets are created based on specified Data Quality Objectives (DQO’s).

9.0 Quality Assurance and Quality Control

9.1 Follow project-specific DQO's as defined in the site-specific work plan.

9.2 Operators do not need to calibrate the analyzer for soil testing. The analyzer is delivered with a factory calibration, generally based upon the Compton Normalization (CN) method. The CN method has been proven over the past several years to provide a robust calibration generally independent of site-specific soil matrix chemistry.

9.3 Operator-recommended quality assurance consists of periodically testing known standards to verify calibration, as well as testing blank standards to determine limits of detection and to check for sample cross-contamination or instrument contamination. Components of instrument QC:

- 9.3.1 An energy calibration check sample at least twice daily
- 9.3.2 An instrument blank for every 20 environmental samples
- 9.3.3 A periodic calibration verification check
- 9.3.4 A precision sample at least one per day
- 9.3.5 A confirmatory sample for every 10 to 20 environmental samples

9.4 Energy Calibration Check: The XRF analyzer performs this automatically; this is the purpose of the standardization check when the analyzer is started. The software does not allow the analyzer to be used if the standardization is not completed.

9.5 Instrument Blank: The operator should use the SiO_2 (silicon dioxide) blank provided with the analyzer. The purpose of this test is to verify that there is no contamination on the analyzer window or other component that is seen by the X-rays. The manufacturer recommends an instrument blank at least once per day, preferably every 20 samples.

9.6 Calibration Verification: The manufacturer provides standard reference samples for periodic calibration checks by operator. The operator should perform a test on a standard to verify relative response is within acceptable range. The difference between the XRF result for an element and the value of the standard should be 20 percent or less. As a result of the factory calibration, the calibration verification frequency will vary. This verification will take place on a daily basis when the instrument is in use.

9.7 Precision Verification: At least one precision sample run per day should be performed by conducting from 7 to 10 replicate measurements of the sample. The precision is assessed by calculating a relative percent difference (RPD) of the replicate measurements for the analyte. The RPD values should be less than 20 percent for most analytes, except chromium, for which the value should be less than 30 percent. The frequency of the precision verification may be based on project-specific needs.

9.8 The manufacturer strongly recommends that operators compare only processed sample results to fixed-base laboratory results. This is because processed-sample results yield the best possible accuracy with a portable XRF.

9.9 To compare XRF and fixed-base laboratory analytical results, use the following procedure:

9.9.1 Collect and prepare the sample as follows:

9.9.1.1 Collect at least 100 g of sample.

9.9.1.2 Dry the sample (air dry or use an oven).
9.9.1.3 Remove any obvious rocks, pebbles and organic material (*e.g.,* wood).

9.9.1.4 It may be necessary to break apart clumps of soil with a rubber mallet.

9.9.1.5 Sieve the ground sample through a No. 10 (2 mm) sieve.

9.9.1.6 Grind the dried sample using a grinder or a mortar and pestle.

9.9.1.7 Sieve the ground sample through a No. 60 (250 um) sieve.

9.9.2 Take a sub-sample (5-10 grams) of the fully-prepared sample, place it into an XRF cup and perform at least two analyses on the sample.

9.9.3 Send the same XRF sample to the fixed-based laboratory for analysis.

9.9.4 The laboratory must use a total-digestion method for sample prep. If the laboratory does not use this method all of the elemental metal from the sample may not be extracted. In this case, the lab result will be lower than the XRF result. Incomplete sample digestion is one of the most common sources of laboratory error, thus it is very important to request a total digestion method.

10.0 Attachments

None

11.0 References

User Manual Delta™ Family: Handheld XRF Analyzers

U.S. EPA Method 6200, Field Portable X-RAY Fluroescence Spectrometry For The Determination Of Elemental Concentrations In Soil and Sediment

Global Positioning System Receivers
FSOP 4.1 (March 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Global Positioning System (GPS) technology is an effective method to memorialize sample locations and site features, establish elevations, refine site topography, estimate material volumes, create sample grids and locate historic land features. These are advanced applications and require consultation with the appropriate user manual (see Section 11.0) and/or training sessions with an authorized trainer. Coordinates for sampling locations should be established and recorded when possible.

Ohio EPA-DERR utilizes two grades of GPS devices manufactured by Trimble®, Survey Grade and Mapping Grade. The site-specific work plan and/or data quality objectives will determine which grade of instrument is required for the project.

1.1.1 Survey Grade: A Trimble® R8 GPS is used to collect coordinates which require sub-centimeter accuracy. It is utilized to collect elevations and topography data, to estimate earth or fill material volumes and to create sample grids. For samples that are very close together, or where accurate elevations are important, the R8 is the preferred GPS instrument. Advanced training is required to operate this instrument.

1.1.2 Mapping Grade: A Trimble® Geo Series handheld unit is used when performing general mapping functions where sub-centimeter accuracy is not needed. Accuracy for this instrument ranges from sub-meter to sub-foot. Historic background aerial images can be loaded into this unit to help locate historic features in the field. Current aerial images are also helpful for sample planning and placement.

2.0 Definitions

Global Positioning System (GPS): A satellite-based system that transmits signals received by ground based receivers to establish location.

3.0 Health and Safety Considerations

3.1 GPS units may be mounted on metal antenna masts or backpacks. Due to lightning strike hazards, do not use GPS when thunderstorms are expected.

3.2 Be aware of trip and fall hazards when performing a GPS survey.

3.3 Refer to the site health and safety plan (HASP) for site-specific safety concerns.

4.0 Procedure Cautions

4.1 Handle the antenna and mast with care, especially when transporting the instrument.

4.2 Tree canopies and buildings may block satellite signals making it difficult to collect GPS survey data.

5.0 Personnel Qualifications

5.1 Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

5.2 Ohio EPA staff who perform GPS surveying must receive specialized training to operate and maintain GPS equipment, and in particular survey grade equipment.

6.0 Equipment and Supplies

6.1 GPS instrumentation
6.2 Antenna mast or backpack if required
6.3 Mobile hotspot if required for dialing into correctional network

7.0 Procedures

7.1 Turn the GPS on under an unobstructed view of the sky. Attach the antenna head to mast if using the R8 GPS. Refer to the manufacturer's manual for establishing connections between datalogger, wireless hotspot and GPS receiver or for general operation.

7.2 Create a new electronic file in which to collect your data. Software may vary depending on what is loaded. Typically for mapping grade units, the software is Terrasync™. For survey grade units, it is Trimble Access™. Follow the instrument manual for detailed data collection.

7.3 The GPS will initialize and start collecting satellite data. Ensure that the coordinate projection is set properly (*i.e.,* latitude/longitude, state plane). Most GIS systems at Ohio EPA accept the Ohio State Plane map datum. The projection used should be consistent with the GPS data user's needs.

7.4 Refer to the instrument manual for detailed operation instructions.

8.0 Data and Records Management

8.1 Data management is initially performed within the GPS datalogger while in the field. Upload and process raw GPS data by using Trimble Pathfinder™ (Section 11.0) or Trimble Business Center™ software. Special training by Trimble® is highly recommended to utilize Trimble® Business Center Software.

8.2 Store processed files the Ohio EPA computer network in accordance with agency document retention schedules.

9.0 Quality Assurance and Quality Control

Follow project specific data quality objectives as described in the site-specific work plan.

10.0 Attachments

Not applicable.

11.0 References

GPS:
Trimble® R8 GNSS Receiver User Guide
Trimble® GeoExplorer 6000 Series User Guide
Trimble® Geo-7X User Guide

Software:
TerraSync™ Software, Getting Started Guide
GPS Pathfinder™ Office Software, Getting Started Guide

Down-Hole Well Cameras
FSOP 4.2 (March 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Down-hole well cameras are used to record video and photographs in well casings or open boreholes. Ohio EPA DERR owns a Well-VU™ 1.75-inch diameter down-hole camera attached to 300 feet of coaxial cable which is connected to a Digital Video Recorder (DVR). The DVR can digitally record photos and video. The procedures in this FSOP are for the Well-Vu™ camera.

1.2 The well camera is used for viewing open boreholes or inspecting the integrity of monitoring, remediation or ground water supply wells. The downhole well camera can be used to quickly and accurately identify the following conditions in wells and open borings:

- Foreign objects or obstructions
- Damaged or obstructed well casings
- Silted/clogged screened or open-borehole intervals (in bedrock wells)
- Biofilms on well screens
- Changes in bedrock type and bedrock fracture zones

This information can be used to help evaluate the following concerns:

- If a well is in proper hydraulic communication with an aquifer or saturated zone
- If a representative ground water sample can be collected from a well
- When a well should be redeveloped
- Whether or not a damaged well can be repaired or needs to be replaced
- How a well should be constructed, especially with regards to screen interval placement

2.0 Definitions

Secure Digital (SD) Card: computer card designed to provide high-capacity memory for digital recording devices

3.0 Health and Safety Considerations

3.1 Refer to the site health and safety plan (HASP) for site-specific safety concerns.

3.2 If concerns exist regarding potentially toxic or explosive atmospheres within a well, open the well and screen the atmosphere (1) within the breathing zone above the open well casing and (2) within the well casing with a photoionization detector (PID) and/or lower explosive level/oxygen (LEL/O_2) meter.

4.0 Procedure Cautions

4.1 Well casings or open boreholes must be at least 2 inches inside diameter to use the camera.

4.2 Do not lower the camera into a water supply wells or other wells containing potential objects that may tangle or bind the well camera cable (*e.g.,* pump, piping, electrical wire, stabilizers, etc.). If the camera must be used in such wells, the pump and plumbing may need to be temporarily removed first, which usually requires the services of a registered water well drilling contractor. Additional disinfection of the well and/or downhole equipment may be required by the county or local health department that has jurisdiction over the well.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 Well camera and reel
6.2 DVR
6.3 Tripod and associated accessories
6.4 Tools to open wells
6.5 Decontamination supplies

7.0 Procedures

7.1 If required by the site-specific work plan or health and safety plan, or if concerns exist regarding potentially toxic or explosive atmospheres within the well, monitor the breathing zone above the open well casing and the well casing atmosphere with a photoionization detector (PID), multiple gas detection meter (with LEL/O^2 capabilities) or other required instrument. Breathing zone action levels are provided in Table 1 of FSOP 1.1, Initial Site Entry. Monitoring may need to continue during purging and sampling activities. Additionally, if the LEL is exceeded inside the well casing, allow the open well to ventilate and measure the LEL again. Allow the LEL concentration to drop to below the LEL before placing instrumentation or sampling devices inside the well. Refer to FSOP 3.1.1, Photoionization Detector and FSOP 3.1.2, Multiple Gas Detection Meter for use and operation of these instruments.

7.2 Connect the well camera to the DVR. Refer to the Well-Vu™ Setup Guide for camera set-up and use.

7.3 Position the tripod over the well and hang the pulley from the tripod.

7.4 Run the coaxial cable through the pulley and position the camera at top of the well casing or near the top of the open borehole.

7.5 Turn on the DVR and make sure the camera lights are on.

7.6 The well camera should be in “Viewing Mode”.

7.7 To collect video:

7.7.1 A video icon should be visible in the upper left-hand corner of the screen. If not, press “Menu” / “Recorder Settings” / “Work Mode” and select “Video”.

7.7.2 Return to “Viewing Mode” and press the “Record” button.

7.7.3 Slowly lower the camera into well while recording.

7.8 To take photographs:

7.8.1 Press the “Menu” button.

7.8.2 Press “Recorder Settings.”

7.8.3 Press “Work Mode” and switch to “Camera.” The video icon in the upper left corner of the screen changes to a camera icon.

7.8.4 Return to “Viewing Mode”, lower the camera and press the “Record” button to take a photograph.

7.8.5 For additional detailed instructions refer to the Well-Vu™ Digital Command Console User’s Guide.

7.9 Decontaminate the downhole camera and coaxial cable between well or boring locations in accordance with FSOP 1.6, Sampling Equipment Decontamination.

8.0 Data and Records Management

Video and photo data is recorded onto an SD card. Download videos and photos from this card. Follow FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Follow project specific data quality objectives as described in the site-specific work plan (SSWP).

10.0 Attachments

Not applicable.

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.3, Field Documentation

FSOP 1.6, Sampling Equipment Decontamination

FSOP 3.1, Photoionization Detector

FSOP 3.2, Multiple Gas Detection Meter

Well-Vu™ Setup Manual

Well-Vu™ Digital Video Command Console User’s Guide

Magnetic Locating Instruments
FSOP 4.3 (March 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

Magnetic locating instruments are used to detect ferrous (iron or steel) objects such as buried drums, pipes, survey markers, manholes, septic tanks, well casings and scrap metal. Ohio EPA owns a Schönstedt GA-52C magnetic locator. This unit can detect objects to a depth of approximately 10 feet below the ground surface. The detector will not detect nonmagnetic metals such as aluminum, copper, chromium, lead or zinc. The procedures described in this FSOP are for magnetic locators in general and the Schönstedt GA-52C magnetic locator in particular. Procedures for other magnetic locators may vary. The owner's manual for each instrument should be consulted.

2.0 Definitions

Not applicable

3.0 Health and Safety Considerations

3.1 Magnetic locators are never to be used for subsurface utility clearance. The GA-52C locator is not designed for this purpose, and DERR staff are neither authorized nor trained to perform utility clearance. Refer to FSOP 1.2, Utility Clearance, to clear locations for drilling or excavation.

3.2 The GA-52C is not intrinsically safe.

3.3 The instrument should not be immersed in water or allowed to become excessively wet.

3.4 Follow manufacturer's recommendation for safe use of this product (refer to the operation manual).

3.5 Refer to the site-specific health and safety plan for any site-specific concerns.

4.0 Procedure Cautions

4.1 The user should be familiar with the operation of the instrument. Refer to the attached instrument manual for operating instructions prior to use.

4.2 If possible, the instrument operator should remove any ferrous metal (iron or steel) objects from themselves prior to using the instrument as the metal may interfere with an accurate reading. This may include protective work boots that have steel components ("steel toed" or "steel shank") as opposed to plastic or other materials.

5.0 Personnel Qualifications

Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

6.0 Equipment and Supplies

6.1 The Schönstedt GS-52C unit
6.2 Four “C” size batteries
6.3 Field book or log sheet and pen

7.0 Procedures

7.1 Turn the unit on using the circular knob and adjust the volume by rotating the control in a clockwise direction.

7.2 Using the wedge-shaped sensitivity control, adjust the sensitivity to mid-range. Calibration is not necessary.

7.3 Hold the detector by the detecting tube just below the control box.

7.4 Gently sweep the detector from side to side at approximately ground level. Hold the detector away from your feet if wearing steel-toed boots.

7.5 When detector comes within range of an iron or steel object, a gradual increase in signal frequency and intensity will be heard from the instrument speaker. After a metal object is detected, hold the locator vertically (with the control box up) and move it back and forth over the suspected area in an "X" pattern. The highest frequency signal will be heard directly over a vertically oriented target and over the ends of a horizontal target. Refer to Figure 1:

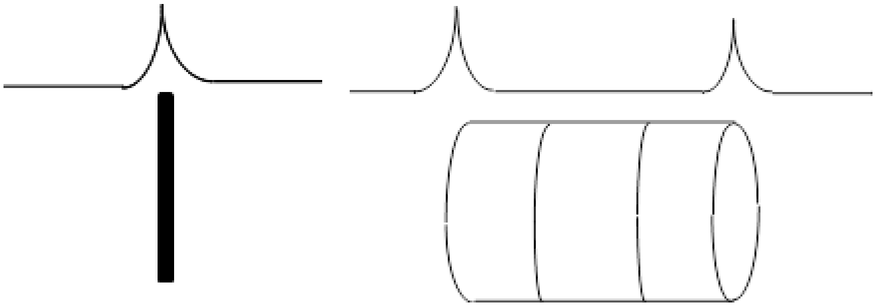


Figure 1: Frequency Spikes

7.6 If there is excessive background noise from small objects such as nails, raise the tip of the detector further above the ground to reduce the background noise and focus on larger buried objects.

7.7 Mark the locations of the buried metal either using a flag or marking paint or collect GPS coordinates with a hand-held GPS unit in accordance with FSOP 4.1, Global Positioning Systems.

7.8 When surveying is completed, turn off the unit, remove the batteries and return the instrument to its protective case.

7.9 The instrument does not require any maintenance except for battery changes.

8.0 Data and Records Management

Refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

Not applicable

10.0 Attachments

An electronic copy of the Model GA-52Cx instruction manual is available upon request.

11.0 References

FSOP 1.2, Utility Clearance

FSOP 1.3, Field Documentation

FSOP 4.1, Global Positioning Systems

Schönstedt Instrument Company Instruction Manual, Model GA-52Cx

Electromagnetic Geophysical Sensors
FSOP 4.4 (March 16, 2021)
Ohio EPA Division of Environmental Response and Revitalization

1.0 Scope and Applicability

1.1 Electromagnetic geophysical sensors can be used to identify areas of elevated soil conductivity that may be associated with buried waste materials or releases of hazardous substances. Ohio EPA owns a Geophex Ltd. GEM-2 electromagnetic sensor. The procedures described in this FSOP are for electromagnetic sensors in general and the GEM-2 in particular. Depending on circumstances and site conditions, GEM-2 geophysical surveys may help facilitate the following site assessment activities:

- Locating suspected underground storage tanks (USTs) and other buried objects or structures (*e.g.,* drums, voids or foundations)
- Placing soil borings and monitoring wells where waste materials or hazardous substances are more likely to be present (*e.g.,* the presence of landfilled material)
- Understanding site geology (*e.g.,* differentiating fill from native soil, identifying lateral changes in soil type)

1.2 The GEM-2 operates by transmitting a low frequency electromagnetic field into the ground. When contacted by the primary field, subsurface materials spontaneously generate secondary electromagnetic fields that are measured by the GEM-2 receiver (Figures 1 and 2). Based on the relationship between the transmitted field and the received field, GEM-2 data can be used to estimate the bulk (apparent) conductivity of soil or fill materials. In addition, GEM-2 data can be used to estimate magnetic susceptibility, which is a measure of the ability of soil or fill materials to become magnetized. Magnetic susceptibility data are similar to magnetometer data and can be used to locate materials or structures that contain ferrous (iron-bearing) metal.

1.3 GEM-2 data is to be used be used for site screening purposes only. Geophysical data are open to interpretation and do not typically provide definitive answers regarding subsurface conditions.

1.4 GEM-2 surveys are performed by DERR-SIFU staff who have received specialized training to properly operate and maintain the instrument. GEM-2 data evaluation and reporting are performed by DERR personnel who have received specialized training in geophysical surveying techniques.

2.0 Definitions

2.1 Anomaly: an area of relatively high or low conductivity (compared to background conditions) that may be related to a target of interest (*e.g.,* buried drums)

2.2 Apparent Conductivity: conductivity measured in millisiemens per meter (mS/m) at a given height above the earth; in general, apparent conductivity is less than the conductivity measured at the ground surface due to the airspace between the GEM-2 and the ground; apparent conductivity is also a measure of the bulk conductivity of the earth below the instrument

2.3 Conductivity: the ratio of electrical current flow to the applied voltage per unit length, measured mS/m.

2.4 Electromagnetic Induction: a geophysical technique in which the primary electromagnetic field of a transmitter induces an electrical current in the earth, which produces a secondary electromagnetic field that is measured by a receiver

2.5 Magnetic Susceptibility (or Permeability): a response from the reorientation of the magnetic domains in the earth induced by the primary field of the GEM-2 receiver, which is a measure of the ability of the earth to become magnetized (dimensionless property)

2.6 Primary Field: the electromagnetic field transmitted into the ground by the GEM-2

2.7 Secondary Field: the electromagnetic ground response received by the GEM-2

3.0 Health and Safety Considerations

3.1 Follow the site-specific health and safety plan (HASP) if one is available. Otherwise follow the health and safety procedures provided by FSOP 1.1, Initial Site Entry.

3.2 Dress appropriately for anticipated weather conditions, and always have ample drinking water available when working in hot weather due to the extensive walking involved (*e.g.,* survey grid pattern). Insect repellant may be needed for protection from ticks, mosquitoes, and other biting insects in heavily wooded areas.

3.3 Use caution when clearing brush or removing other obstacles from survey areas, and wear appropriate personal protective equipment (PPE), including but not limited to safety glasses or goggles and hard hats. Steel-toed boots may induce an anomaly during data collection.

4.0 Procedure Cautions

4.1 The GEM-2 must never be used for subsurface utility clearance. The instrument is not designed for this purpose, and DERR staff are neither authorized nor trained to perform utility clearance. Refer to FSOP 1.2, Utility Clearance to clear locations for drilling or excavation.

4.2 The GEM-2 may not operate properly under rainy weather conditions or high humidity.

4.3 GEM-2 surveys are difficult to perform (and may not provide usable data) under the following site conditions:

- Steep slopes
- Heavily wooded areas with thick brush
- Areas within buildings or other structures

- Areas with high levels of electromagnetic interference (*e.g.,* junkyards or the central areas of landfills)
- In close vicinity to large metal objects/structures or operating equipment that create high levels of electromagnetic interference (*e.g.,* vehicles, metal buildings, generators[1]).

5.0 Personnel Qualifications

5.1 Ohio EPA personnel working at sites that fall under the scope of OSHA's hazardous waste operations and emergency response standard (29 CFR 1910.120) must meet the training requirements described in that standard.

5.2 Personnel must receive specialized training to operate and maintain the GEM-2 or to evaluate GEM-2 data and prepare reports.

6.0 Equipment and Supplies

6.1 GEM-2 electromagnetic sensor and associated equipment (Trimble® GPS receiver, additional charged batteries)
6.2 Field laptop computer with cables to download GEM-2 data files
6.3 Geophysical field notebook, GEM-2 electromagnetic survey field forms, pens and markers
6.4 Power inverter (to run laptop)
6.5 Traffic cones
6.6 300 ft measuring tapes (at least four)
6.7 Flags, survey pins and marking paint
6.8 Hand tools to clear brush (axes, saws, machetes)
6.9 Tool box
6.10 Other surveying supplies as needed based on site conditions
6.11 GPS unit

7.0 Procedures

7.1 Scope of Work Development and Project Planning

7.1.1 Prior to performing a GEM-2 survey, the survey requestor needs to develop project objectives and a scope of work. DERR-SIFU staff can assist with this task and scheduling a project pre-meeting (or conference call) is recommended. The initial contact is the DERR-SIFU supervisor.

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[1] Electrical fields from overhead power lines and transformers do not adversely affect GEM-2 surveys because the frequencies used by the instrument are out-of-phase with power line frequencies.

7.1.2 The survey requestor will arrange site access and provide DERR-SIFU staff a copy of the access agreement. Geophysical survey work cannot be performed until consent to access is obtained.

7.1.3 The survey requestor and DERR-SIFU will agree on survey and deliverable (report) dates.

7.2 Surveying

7.2.1 GEM-2 surveys will be conducted on the agreed-upon dates unless surveying cannot be performed due to inclement weather (heavy rain), site access or other unforeseen circumstances.

7.2.2 DERR-SIFU staff will design and perform the survey based the requestor's objectives and scope of work. Surveys are performed in a manner that maximizes the potential for locating targets of interest (anomalies) while minimizing potential electromagnetic interference. Typically, survey areas are gridded using measuring tapes and traffic cones or flags. The GEM-2 is capable of simultaneously running multiple frequencies (primary fields) to evaluate multiple depth intervals, and DERR-SIFU staff select frequencies based on the project objectives and site conditions. The maximum depth of investigation ranges between 15 and 100 feet depending on the frequencies used and the site conditions. DERR-SIFU staff generally can survey between two and four acres of area per eight-hour day, depending on site conditions.

7.3 Data Evaluation and Reporting Options

7.3.1 Field-Screening Only:

The "field-screening only" option includes in-field evaluation of GEM-2 data using a laptop computer. DERR-SIFU staff can prepare "real time" maps of apparent conductivity and magnetic susceptibility during surveying to locate anomalies (examples provided in Figures 3 and 4). A report is not prepared, but maps generated during the survey can be provided to the requestor in electronic format if requested. If requested, copies of raw data files will also be provided in electronic format.

7.3.2 Field Screening with Report:

The "field-screening with report" option includes field-screening activities as described above and a short report that includes a brief narrative describing the results of the survey, maps of apparent conductivity and magnetic susceptibility, photographs (as needed for supporting documentation), and copies of field notes. The report will be provided in electronic format. If requested, copies of raw data files will also be provided in electronic format.

8.0 Data and Records Management

Please refer to FSOP 1.3, Field Documentation.

9.0 Quality Assurance and Quality Control

9.1 DERR SIFU follows the manufacturer's (Geophex) recommendations for GEM-2 maintenance and repair.

9.2 DERR management and staff provide peer-review of draft reports.

10.0 Attachments

Not applicable

11.0 References

FSOP 1.1, Initial Site Entry

FSOP 1.2, Utility Clearance

FSOP 1.3, Field Documentation

Geophex GEM-2 User's Manual

Huang, H., 2005, Depth of investigation for small broadband electromagnetic sensors: Geophysics, Vol. 70, No. 6 (November-December), pp. G135-G142

Won, I.J., Keiswetter, D.A., Fields, George R.A. and Sutton, L.C., 1996, GEM-2: A New Multifrequency Electromagnetic Sensor: Journal of Environmental and Engineering Geophysics, Vol. 1, Issue 2 (August), pp. 129-137

Won, I.J., and Huang, H., May 2004, Magnetometers and electro-magnetometers (Tutorial): The Leading Edge

U.S. EPA, September 1993, Use of Airborne, Surface and Borehole Geophysical Techniques at Contaminated Sites – A Reference Guide: EPA/625/R-92/007, pp. 4-1 through 4-32

U.S. EPA, June 1984, Geophysical Techniques for Sensing Buried Wastes and Waste Migration: prepared by TECHNOS, Inc. (subcontractors to Lockheed Engineering and Management Services Company, Inc.) for the Environmental Monitoring Systems Laboratory, Office of Research and Development under contract no. 68-03-3050, NTIS PB84-198449, pp. 63-90

Figure 1: GEM-2 Electromagnetic Induction Survey in Progress

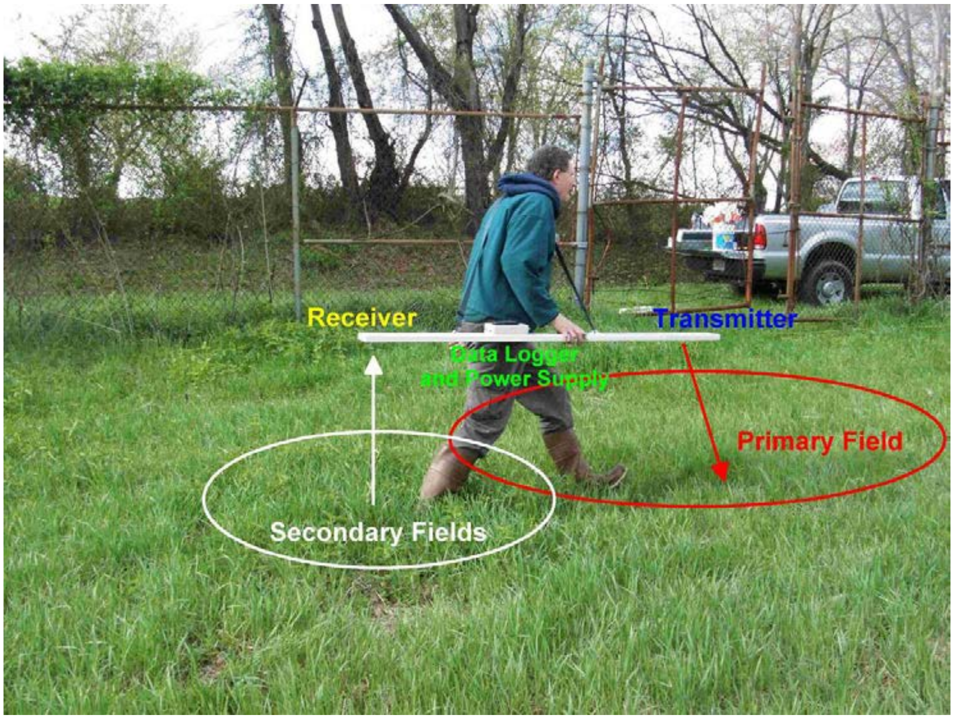
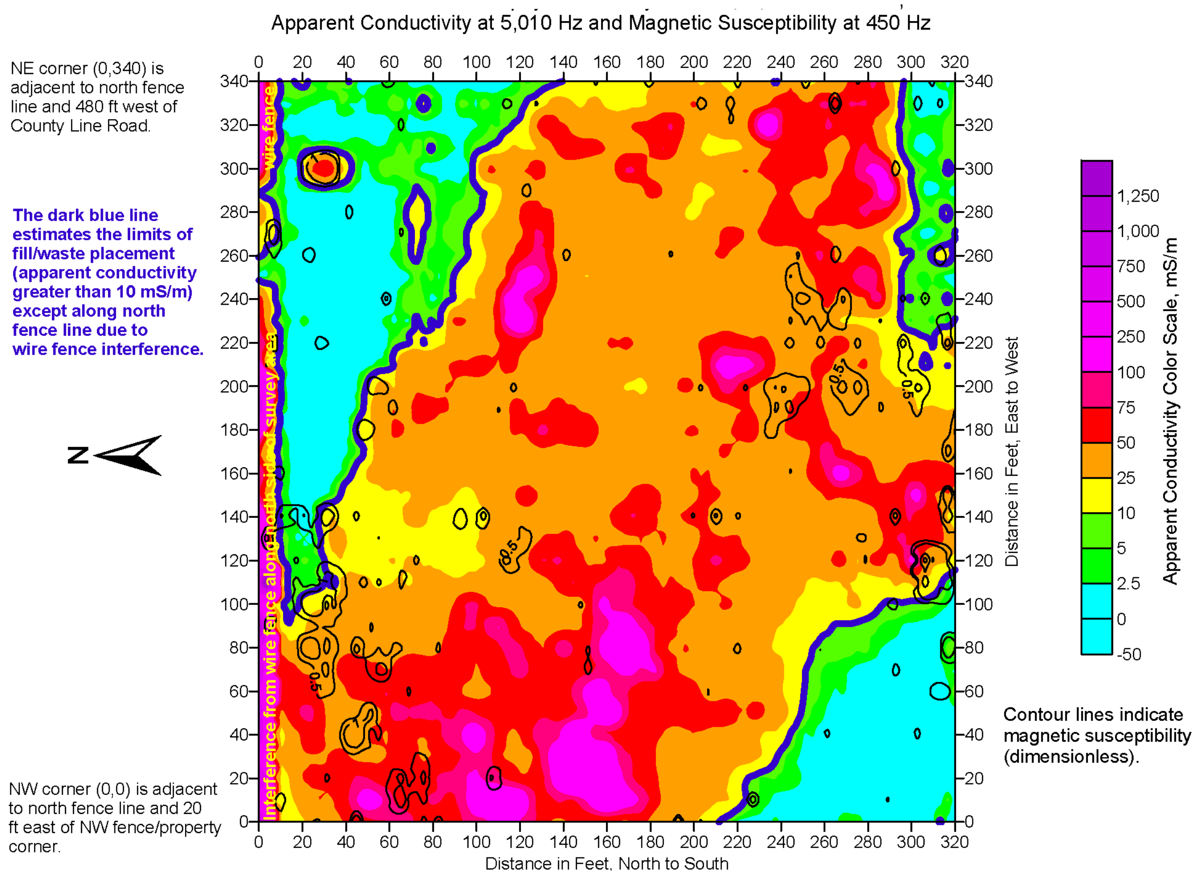


Figure 2: GEM-2 Electromagnetic Induction Survey in Progress



Apparent Conductivity at 5,010 Hz and Magnetic Susceptibility at 450 Hz

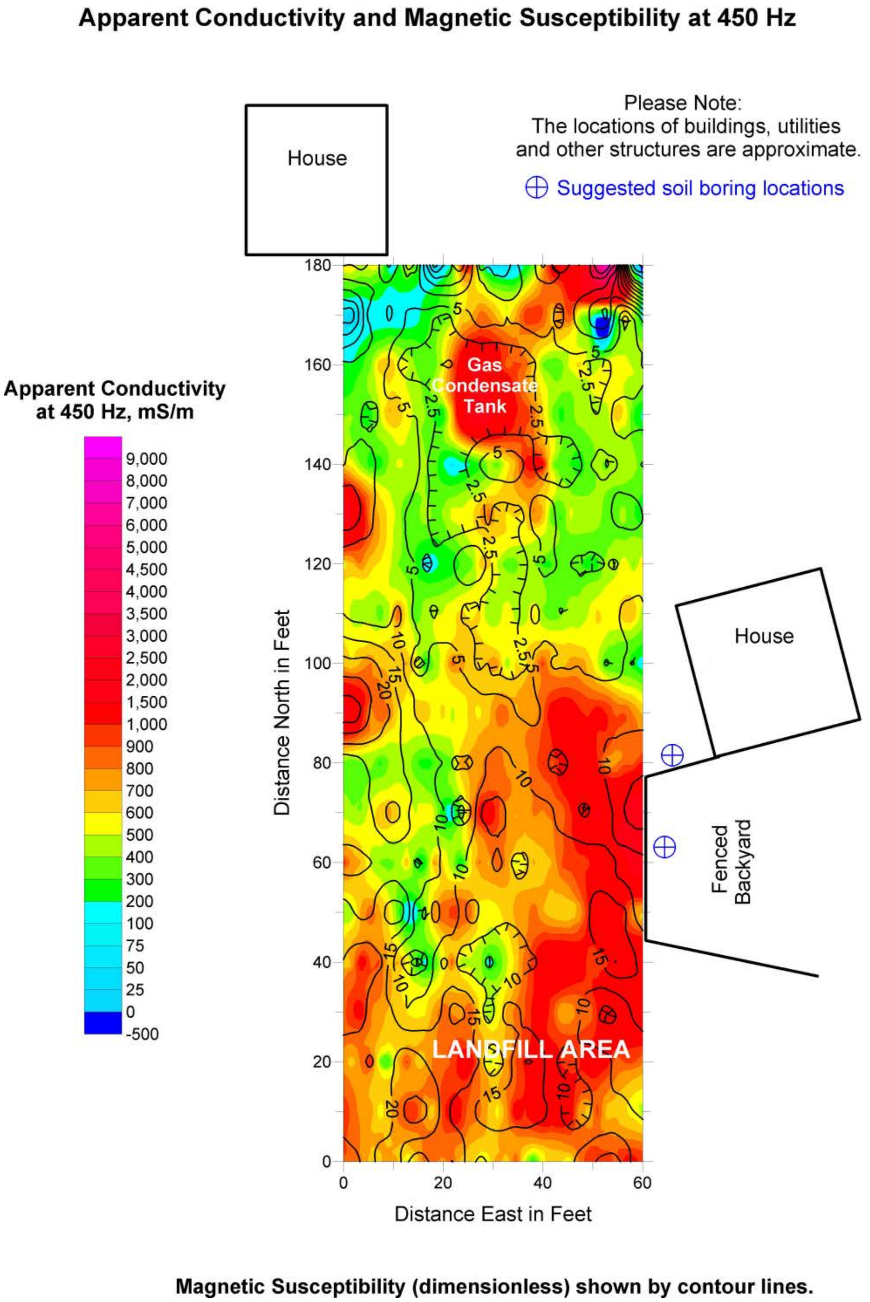
NE corner (0,340) is adjacent to north fence line and 480 ft west of County Line Road.

The dark blue line estimates the limits of fill/waste placement (apparent conductivity greater than 10 mS/m) except along north fence line due to wire fence interference.

NW corner (0,0) is adjacent to north fence line and 20 ft east of NW fence/property corner.

Contour lines indicate magnetic susceptibility (dimensionless).

Figure 3: Example GEM-2 Geophysical Survey Map (Evaluating Former Landfill Limits of Waste Placement and High-Conductivity Target Areas for Sampling)



Apparent Conductivity and Magnetic Susceptibility at 450 Hz

Please Note:
The locations of buildings, utilities and other structures are approximate.

⊕ Suggested soil boring locations

Magnetic Susceptibility (dimensionless) shown by contour lines.

Figure 4: Example GEM-2 Geophysical Survey Map (Evaluating High-Conductivity Target Areas for Sampling, Residential Neighborhood Constructed over Former Landfill Area)

Ohio EPA, *Technical Guidance Manual for Ground Water Investigations*. Ohio Environmental Protection Agency, Department of Drinking and Ground Waters available at

DERR Ground Water and Hydrogeology Support | Ohio Environmental Protection Agency

TECHNICAL GUIDANCE COMPENDIUM
VA30007.14.022

TITLE: **Sampling and Analysis of Fraction Organic Carbon (f_{oc}) in Soils**

DATE EFFECTIVE: January 2014

HISTORY: Update of VA30007.14.001 – Revision was necessary to reflect changes in the rule citations that became effective in August 2014.

KEYWORDS: Organic carbon (OC), property-specific soil standards, sampling

RULE/ AUTHORITY: OAC 3745-300-07(F)(4), 3745-300-07(G)(4), 3745-300-09(D)(3)(b)(iv) and 3745-300-09(H)(5)

QUESTION: If a property-specific f_{oc} for soils is measured at a property, what considerations are necessary for sampling and analysis?

BACKGROUND: Fraction organic carbon (f_{oc}) is a dimensionless ($\text{mass}_{(carbon)}/\text{mass}_{(soil)}$), mass measure of soil organic carbon (OC) relative to soil. The measurement is used to estimate the capacity of a soil to adsorb or bind certain contaminants. The f_{oc} is needed when calculating property-specific soil standards for various exposure pathways, including but not limited to: direct contact with soil, determination of soil saturation limits; OAC 3745-300- 09(H)(5)), leaching to ground water (OAC 3745-300-07(F)(4)), and volatilization to indoor air (OAC 3745-300-07(G)(4) and 3745-300- 09(D)(3)(b)(iv)). Due to its important role in binding contaminants in soil media, the f_{oc} can affect the analysis of exposure pathways and migration of the contaminants to other environmental media. In order to accurately determine f_{oc} of soil at a property, it is important to consider the geologic setting of the property, the heterogeneity of the soil profile, the presence of hydrocarbons or other sources of organic carbon in the soil, and the purpose for which the determination is being made.

ANSWER: Sampling Considerations

The determination of f_{oc} must be based on sampling locations that are not impacted by releases of petroleum or other organic chemicals of concern.
Sampling depth and location may be dependent on the geologic features of the property, such as topography, soil type and the possible incorporation of non-native fill material. It is very important that the reason f_{oc} is being determined is taken into consideration when choosing a sample location(s) - it must be representative of the

pathway of concern.

The surface organic layer (typically the top 6 inches/ 15 cm) should not be used to represent the OC composition of soils at the property. The number of samples and the horizontal and vertical distribution of sampling are dependent on the heterogeneity of the subsurface and the purpose for which the determination is being made. If the property-specific **f_{oc}** is measured to determine a property-specific soil saturation concentration (as described in OAC 3745-300-09(H)(5)), an **f_{oc}** value representative of the vadose zone as described in OAC 3745-300-07(I)(1)(a)(ii) should be used. **For leaching and vapor intrusion assessments, a set of samples should be collected at varying depths to adequately represent the vadose zone.** The minimum number of samples (8, per US EPA's ProUCL software: http://www.epa.gov/osp/hstl/tsc/software.htm) should adequately describe the distribution of values. The final input value for **f_{oc}** should be the lower 95% confidence interval of the mean. US EPA has several methods and guidance documents that can be consulted for this determination, including US EPA (1989), *Methods for the Attainment of Cleanup Standards* (EPA 230/01-89-042), RCRA Waste Sampling Draft Technical Guidance (EPA530-D-02-002; http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/rwsdtg.pdf) and within the assessment criteria in USEPA's ProUCL software (http://www.epa.gov/osp/hstl/tsc/software.htm). Ohio EPA (OEPA) recommends that additional samples be taken during field operations to prevent unnecessary costs for remobilization of sampling equipment.

Studies have shown that differences in soil bulk density (ρ) can skew final calculation of **f_{oc}** within the soil profile, and lead to overestimation of this parameter. For this reason, it is recommended that a method to normalize **f_{oc}** values based on ρ at depth be employed. Calculation of a depth weighted average or a composite sampling regime, such as described in OEPA TGC 300007.14.002 can be utilized.

Because of the variability of the distribution of soil OC, only site samples should be used. In lieu of determining a property-specific **f_{oc}**, the VAP will accept default values for various pathways. The defaults are 0.6% (0.006) for direct contact, 0.2% to 0.3% (0.002 to 0.003) for the leaching to ground water pathway, and 0.2% (0.002) for volatilization into indoor air. See OEPA's Support Documentation for the Development of Generic Numeric Standards (March 2009), OEPA's Derived Leach-Based Soil Values, Appendix Technical Support Document (October 2008), and Users Guide for the Johnson and Ettinger Model for Subsurface Vapor Intrusion into Buildings

(February 2004).

Sample Processing

After sampling, using the appropriate protocol, samples should be processed by removing roots, sticks, rocks and other debris that could influence the $\mathbf{f_{oc}}$ analysis, air dried, ground and sieved to a standard size (i.e.< 2 mm) prior to analysis (IDEM, Determining the Fraction of Organic Carbon, OLQ-General-ID-0119, September 2007; http://www.in.gov/idem/files/Foc_Guidance_070925_Final.pdf).

Method of Analysis

The method of analysis must be capable of measuring a $\mathbf{f_{oc}}$ value that is representative of the concentration of OC within the soil matrix. Care must be taken to differentiate between OC and total carbon (TC). Simple pyrolytic methods which do not quantitate the CO_2 that is produced, but simply record the loss on ignition (LOI) of the sample are not appropriate for environmental remediation purposes. **These methods should be avoided for determination of $\mathbf{f_{oc}}$ since it can lead to large overestimation of organic carbon content (Schumacher, 2002).** The second general category of soil organic matter analytical methods is wet chemical oxidation.

Additional analytical methods for determining TC and OC values by dry and wet combustion (acid digestion) are presented in “Total Carbon, Organic Carbon, and Organic Matter,” by D. W. Nelson and L. E. Sommers, from Methods of Soil Analysis, Part 3.Chemical Methods, SSSA Book Series No. 5. 1996.

Because soil analytical methods don’t distinguish between inorganic carbon (IC) and OC sources, the laboratory must provide assurances that IC does not bias the analytical results. Consequently, OEPA recommends that soil be pretreated to remove IC prior to analysis by pyrolitic methods, as an integral procedure to any analytical method. A detailed procedure of the pre-treatment procedure for wet chemical oxidation is found in Nelson and Sommers (1996). If the actual Walkley-Black method is used, it is recognized that incomplete oxidation of OC may occur without modification to the original method. **Because of this, the unmodified Walkley-Black Method is not recommended, due to uncertainty associated with unoxidized organic fractions.** Instead, a modification, such as described in Nelson and Sommer (1975; A rapid and Accurate Procedure for Estimation of Organic Carbon in soil, Proc. Indiana Acad. Sci., 84:456-462) is suggested. For pyrolytic methods, similar pretreatment procedures can be used, but HCl may be substituted for H_2SO_4 to remove inorganic carbon sources.

Reporting and Documentation

Ohio EPA recommends that data reports from the laboratory contain the following information in order to facilitate review and interpretation of the results:

- Laboratory SOP (should include a rationalization of the method and sampling procedures)
- Laboratory internal Chain of Custody
- Sample identification
- Laboratory reagents and standards (NIST)
- Sample pre-treatment and/or particle size reduction
- Date and time of analysis
- Lab sheets showing
    - Weight of sample
    - Volume and normality (or Molarity) of dichromate solution
    - Volume and normality (or Molarity) of titrant
    - Reaction time
    - Reaction temperature
    - Calibration results (appropriate for determinative method)
- Blank results determining concentration of titrant
- Laboratory control samples (NIST) and duplicate results
- Moisture content of soil samples
- Bulk density of soil samples
- Average of each $\mathbf{f_{oc}}$ sample (triplicate analyses) in dry weight
- Average $\mathbf{f_{oc}}$ of each soil strata

SUMMARY:

Due to its important role in binding contaminants in soil media, the $\mathbf{f_{oc}}$ can affect the analysis of exposure pathways and migration of the contaminants to other environmental media. In order to accurately determine $\mathbf{f_{oc}}$ of soil at a property, it is important to consider the geologic setting of the property, the heterogeneity of the soil profile, the presence of hydrocarbons or other sources of organic carbon in the soil, and the purpose for which the determination is being made. To accurately determine the $\mathbf{f_{oc}}$ of soil at a property, VAP recommends use of a method which clearly delineates organic carbon concentration from inorganic carbon.

OHIO EPA CONTACT:

For any questions concerning this issue, please contact the VAP Central Office at (614) 644-2942.

METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 4.1

Edited by J.W. Munch (1995)

A. Alford-Stevens, J.W. Eichelberger, W.L. Budde - Method 524, Rev. 1.0 (1983)

R.W. Slater, Jr. - Revision 2.0 (1986)

J.W. Eichelberger, and W.L. Budde - Revision 3.0 (1989)

J.W. Eichelberger, J.W. Munch, and T.A. Bellar - Revision 4.0 (1992)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment (1,2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Analyte	Chemical Abstract Service Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide*	75-15-0
Carbon tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
trans-1,4-Dichloro-2-butene*	110-57-6
Dichlorodifluoromethane	75-71-8

1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene chloride	75-09-2
Methyl iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-pentanone*	108-10-1
Methyl-t-butyl ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6

m-Xylene	108-38-3
p-Xylene	106-42-3

* New Compound in Revision 4.0

1.2 Method detection limits (MDLs) (3) are compound, instrument and especially matrix dependent and vary from approximately 0.02 to 1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02 to 200 µg/L when a wide-bore thick-film capillary column is used. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and noninterfering quantitation ions (Table 1), can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar (Sect. 11.6.2). Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect. 11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (> 2% solubility) and compounds with boiling points above 200°C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated using procedural standard calibration (Sect. 3.14). The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory.

The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in <u>exactly</u> the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS -- 40-mL to 120-mL screw cap vials each equipped with a Teflon faced silicone septum. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column. The use of a moisture control device is recommended to prohibit much of the trapped water vapor from entering the GC/MS and eventually causing instrumental problems.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 9, and <u>provided the purge and desorption procedures specified in Section 11 of the method are not changed</u>. Specifically, the purging time, the purge gas flow rate, and the desorption time may not be changed. Since many of the potential alternate sorbents may be thermally stable above 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in Section 11. If higher temperatures are used, the analyst should monitor the data for possible analyte and/or trap decomposition.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 lb/in^2 across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. If the column oven is to be cooled to 10°C or lower, a subambient oven controller will likely be required. If syringe injections of 4-

bromofluorobenzene (BFB) will be used, a split/splitless injection port is required.

6.3.2 Capillary GC Columns. Any gas chromatography column that meets the performance specifications of this method may be used (Sect. 10.2.4.1). Separations of the calibration mixture must be equivalent or better than those described in this method. Four useful columns have been evaluated, and observed compound retention times for these columns are listed in Table 2.

6.3.2.1 Column 1 -- 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 µm film thickness.

Column 2 -- 30 m x 0.53 mm ID DB-624 (J&W Scien-tific, Inc.) fused silica capillary with a 3 µm film thickness.

Column 3 -- 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 µm film thickness.

Column 4 -- 75 m x 0.53 mm id DB-624 (J&W Scien-tific, Inc.) fused silica capillary with a 3 µm film thickness.

6.3.3 Interfaces between the GC and MS. The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore columns 1, 2, and 4 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface (7) or an all-glass jet separator is an acceptable interface. Any interface can be used if the performance specifications described in this method (Sect. 9 and 10) can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 When narrow bore column 3 is used, a cryogenic interface placed just in front of the column inlet is suggested. This interface condenses the desorbed sample components in a narrow band on an uncoated fused silica precolumn using liquid nitrogen cooling. When all analytes have been desorbed from the trap, the interface is rapidly heated to transfer them to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from

35 to 260 amu with a complete scan cycle time (including scan overhead) of 2 sec or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 10.2.6 (or construction of a linear or second order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 Micro syringes - 10, 100 µL.

6.4.4 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers -- 15-mL bottles with Teflon lined screw caps.

7. REAGENTS AND STANDARDS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 (or equivalent) by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic acid -- ACS reagent grade, granular.

7.2.6 Sodium thiosulfate -- ACS reagent grade, granular.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with Teflon lined screw caps. Methanol solutions of acrylonitrile, methyl iodide, and methyl acrylate are stable for only one week at 4°C. Methanol solutions prepared from other liquid analytes are stable for at least 4 weeks when stored at 4°C.

Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at $< 0^{\circ}C$; at room temperature, they must be discarded after 1 day.

7.4 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern in methanol or other suitable solvent. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.3.4 also apply to primary dilution standard solutions.

7.5 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.5.1 A solution containing the internal standard and the surrogate compounds is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2- dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each (any appropriate concentration is acceptable). A 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each. A 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each. Additional internal standards and surrogate analytes are optional. Additional surrogate compounds should be similar in physical and chemical characteristics to the analytes of concern.

7.6 PREPARATION OF LABORATORY REAGENT BLANK (LRB) -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject an appropriate volume of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.7 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard (Sect. 7.8). This is a calibration standard that is treated as a sample.

7.8 PREPARATION OF CALIBRATION STANDARDS

7.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration of 2-10 times the method detection limit (Tables 4, 5, and 7) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the method. Every CAL solution contains the internal standard and the surrogate compounds at the same concentration (5 µg/L suggested for a 5-mL sample; 1 µg/L for a 25-mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of acidified (pH 2) reagent water in a volumetric flask. Also add an appropriate volume of internal standard and surrogate compound solution from Sect. 7.5.1. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hr unless transferred to a sample bottle and sealed immediately. Alternately, aqueous calibration standards may be prepared in a gas tight, 5 mL or 25 mL syringe. **NOTE:** If unacidified samples are being analyzed for THMs only, calibration standards should be prepared without acid.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION AND DECHLORINATION

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking water, are suspected to contain residual chlorine, add about 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling. If analytes that are gases at room temperature (such as vinyl chloride), or analytes in Table 7 are not to be determined, sodium thiosulfate is recommended to reduce the residual chlorine. Three milligrams of sodium thiosulfate should be added for each 40 mL of water sample.
NOTE: If the residual chlorine is likely to be present > 5 mg/L, a determination of the amount of the chlorine may be necessary. Diethyl-p-phenylenediamine (DPD) test kits are commercially available to determine residual chlorine in the field. Add an additional 25 mg of ascorbic acid or 3 mg of sodium thiosulfate per each 5 mg/L of residual chlorine.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples containing the desired dechlorinating agent from the flowing stream.

8.1.3 When sampling from an open body of water, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area. Fill duplicate sample bottles containing the desired dechlorinating agent with sample from the larger container.

8.1.4 Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2 SAMPLE PRESERVATION

8.2.1 Adjust the pH of all samples to < 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min. Exceptions to the acidification requirement are detailed in Sections 8.2.2 and 8.2.3. **NOTE:** Do not mix the ascorbic acid or sodium thiosulfate with the HCl in the sample bottle prior to sampling.

8.2.2 **When sampling for THM analysis only**, acidification may be omitted if sodium thiosulfate is used to dechlorinate the sample. This exception to acidification does not apply if ascorbic acid is used for dechlorination.

8.2.3 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 24 hr of collection time if they are to be analyzed for any compounds other than THMs.

8.2.4 The samples must be chilled to about 4°C when collected and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.2 SAMPLE STORAGE

8.2.1 Store samples at ≤ 4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS (FRB)

8.3.1 Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks as for the field samples.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. A MDL for each analyte must also be determined. Each laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, reagent water, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 2-5 μg/L depending upon the calibration range of the instrumentation.

9.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. It is recommended that a QCS from a source different than the calibration standards be used for this set of LFBs, since it will serve as a check to verify the accuracy of the standards used to generate the calibration curve. This is particularly useful if the laboratory is using the method for the first time, and has no historical data base for standards. Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. Also add the appropriate amounts of internal standard and surrogates. If it is expected that field samples will contain a dechlorinating agent and HCl, then add these to the LFBs in the same amounts proscribed in Sect. 8.1.1. If only THMs are to be determined and field samples do not contain HCl, then do not acidify LFBs. Analyze each replicate according to the procedures described in Section 11.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 Some analytes, particularly early eluting gases and late eluting higher molecular weight compounds, will be measured with less accuracy and precision than other analytes. However, the accuracy and precision for all analytes must fall within the limits expressed below. If these criteria are not met for an analyte of interest, take remedial action and repeat the measurements for that analyte until satisfactory performance is achieved. For each analyte, the mean accuracy must be 80-120% (i.e. an accuracy of ± 20%). The precision of the recovery (accuracy) for each analyte must be less than twenty percent (<20%). These criteria are different than the ± 30% response factor criteria specified in Sect. 10.3.5. The criteria differ, because the measurements in Sect. 9.3.3 as part of the initial demonstration of capability are meant to be more stringent than the continuing calibration measurements in Sect. 10.3.5.

9.3.4 To determine the MDL, analyze a minimum of 7 LFBs prepared at a low concentration. MDLs in Table 5 were calculated from samples fortified from 0.1-0.5 µg/L, which can be used as a guide, or use calibration data to estimate a concentration for each analyte that will yield a peak with a 3-5 signal to noise response. Analyze the 7 replicates as described in Sect.11, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation in Sect. 13.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting surrogate recoveries is an especially valuable activity because surrogates are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates (Table 1) in all samples, continuing calibration checks, and blanks. These should remain reasonably constant over time. An abrupt change may indicate a matrix effect or an instrument problem. If a cryogenic interface is utilized, it may indicate an inefficient transfer from the trap to the column. These samples must be reanalyzed or a laboratory fortified duplicate sample analyzed to test for matrix effect. A more gradual drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected.

9.5 LABORATORY REAGENT BLANKS (LRB) -- With each batch of samples processed as a group within a work shift, analyze a LRB to determine the background system contamination.

9.6 Assessing Laboratory Performance. Use the procedures and criteria in Sects. 10.3.4 and 10.3.5 to evaluate the accuracy of the measurement of the laboratory fortified blank (LFB), which must be analyzed with each batch of samples that is processed as a group within a work shift. If more than 20 samples are in a work shift batch, analyze one LFB per 20 samples. Prepare the LFB with the concentration of each analyte that was used in the Sect. 9.3.3 analysis. If the acceptable accuracy for this measurement (±30%) is not achieved, the problem must be solved before additional samples may be reliably analyzed. Acceptance criteria for the IS and surrogate given in Sect.10.3.4 also applies to this LFB.

Since the calibration check sample in Sect. 10.3.5 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as a calibration check in Sect. 10.3.5. Add the results of the LFB analysis to the control charts to document data quality.

9.7 If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination.

9.8 At least quarterly, replicate LFB data should be evaluated to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, or ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required unless the criteria in Section 9.4 are not met. If matrix effects are observed or suspected to be causing low recoveries, analyze a laboratory fortified matrix sample for that matrix. The sample results should be flagged and the LFM results should be reported with them.

9.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. **NOTE:** Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.6, may be used here as a calibration check sample.

10.2 INITIAL CALIBRATION

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 10.2.2.

10.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 3, the MS must be returned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

10.2.3 Purge a medium CAL solution, (e.g., 10-20 μg/L) using the procedure given in Sect. 11.

10.2.4 Performance criteria for calibration standards. Examine the stored GC/MS data with the data system software. Figures 3 and 4 shown acceptable total ion chromatograms.

10.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if there is poor resolution between peaks, the wrong column has been selected or remedial action is probably necessary (Sect.10.3.6).

10.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 10.3.6.

10.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

10.2.6 Calculate a response factor (RF) for each analyte and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.5), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion of the internal standard.

Q_x = quantity of analyte purged in nanograms or concentration units.
Q_{is} = quantity of internal standard purged in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from analyses of CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance Sect. 10.3.6). Surrogate compounds are present at the same concentration on every sample, calibration standard, and all types of blanks.

10.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a linear or second order regression calibration curve, by plotting A/A_{is} vs. Q_x.

10.3 CONTINUING CALIBRATION CHECK -- Verify the MS tune and initial calibration at the beginning of each 12-hr work shift during which analyses are performed using the following procedure. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards.

10.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 3), the MS must be returned and adjusted to meet all criteria before proceeding with the continuing calibration check.

10.3.2 Purge a CAL solution and analyze with the same conditions used during the initial calibration. Selection of the concentration level of the calibration check standard should be varied so that the calibration is verified at more than one point over the course of several days.

10.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte of concern and surrogate compound from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear or second order regression is used, the concentration measured using the calibration curve must be within 30% of the true value of the concentration in the calibration solution. If these conditions do not exist, remedial action must be taken which may require recalibration. All data from field samples obtained after the last successful calibration check standard, should be considered suspect. After remedial action has been taken, duplicate samples should be analyzed if they are available.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner. This applies only if the injection liner is an integral part of the system.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a slight change in retention times. Analyst may need to redefine retention windows.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10.3.6.9 Replace the trap, especially when only a few compounds fail the criteria in Sect. 10.3.5 while the majority are determined successfully. Also check for gas leaks in the purge and trap unit as well as the rest of the analytical system.

10.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

10.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

10.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with one of the following equations:

$$5 \text{ mL samples, } S = 0.51\,(C)(V)$$
$$25 \text{ mL samples, } S = 0.102\,(C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in mg/L (v/v);
V = Volume of standard injected in mL.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING

11.1.1 This method is designed for a 25-mL or 5-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the helium purge gas flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0-mL (or 5-mL). To all samples, blanks, and calibration standards, add 5-µL (or an appropriate volume) of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

11.1.4 Standards and samples must be analyzed in exactly the same manner. Room temperature must be reasonably constant, and changes in excess of 10°F will adversely affect the accuracy and precision of the method.

11.2 SAMPLE DESORPTION

11.2.1 Non-cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode and preheat the trap to 180°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at a flow rate suitable for the column being used (optimum desorb flow rate is 15 mL/min) for about 4 min, begin the GC temperature program, and start data acquisition.

11.2.2 Cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is a -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/min for about 5 min. At the end of the 5 min desorption cycle, rapidly heat the cryogenic trap to 250°C, and simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.3 While the trapped components are being introduced into the gas chromatograph (or cryogenic interface), empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave syringe valve open to allow the purge gas to vent through the sample introduction needle.

11.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of 2 sec or less. If water, methanol, or carbon dioxide cause a background problem, start at 47 or 48 m/z. If ketones are to be determined, data must be acquired starting at m/z 43. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Suggested temperature programs are provided below. Alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide bore column 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to within the capacity of the separator, or about 15 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of desorption, then programmed to 160°C at 6°C/min, and held until all components have eluted.

11.3.2 Multi-ramp temperature program for wide bore column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced to 10°C and held for 6 min from the beginning of desorption, then heated to 70°C at 10°/min, heated to 120°C at 5°/min, heated to 180° at 8°/min, and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow bore column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced to 10°C and held for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°/min for 10 min, then 15°/min for 5 min to 145°C, and held until all components have eluted.

11.3.4 Multi-ramp temperature program for wide bore column 4 with the open split interface. Adjust the helium carrier gas flow rate to about 7.0 mL/min. The column temperature is - 10°C and held for 6 min. from beginning of desorption, then heated to 100°C at 10°C/min, heated to 200°C at 5°C/min and held at 200°C for 8 min or until all compounds of interest had eluted.

11.4 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recon-dition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. Maintain the moisture control module, if utilized, at 90°C to remove residual water. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. If the response for any analyte exceeds the linear range of the calibration established in Section 10, obtain and dilute a duplicate a duplicate sample. Do not extrapolate beyond the calibration range.

12.1.1 Calculate analyte and surrogate concentrations, using the multi-point calibration established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample.

A_x = integrated abundance of the quantitation ion of the analyte in the sample.

A_{is} = integrated abundance of the quantitation ion

of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in mL.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear or second order regression curve established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1- 99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at concentrations between 0.1 and 5 µg/L. Results were obtained using the four columns specified (Sect. 6.3.2.1) and the open split or jet separator (Sect. 6.3.3.1), or the cryogenic interface (Sect. 6.3.3.2). These data are shown in Tables 4-8.

13.2 With these data, method detection limits were calculated using the formula (3):

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. POLLUTION PREVENTION

14.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

15. WASTE MANAGEMENT

15.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174,176
1,2-Dichlorobenzene-d4	150	152	115,150
Target Analytes			
Acetone	58	43	58
Acrylonitrile	53	52	53
Allyl chloride	76	76	49
Benzene	78	78	77
Bromobenzene	156	156	77,158
Bromochloromethane	128	128	49,130
Bromodichloromethane	162	83	85,127
Bromoform	250	173	175,252
Bromomethane	94	94	96
2-Butanone	72	43	57,72
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Carbon disulfide	76	76	--
Carbon tetrachloride	152	117	119
Chloroacetonitrile	75	48	75
Chlorobenzene	112	112	77,114
1-Chlorobutane	92	56	49
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155,157
1,2-Dibromoethane	186	107	109,188
Dibromomethane	172	93	95,174
1,2-Dichlorobenzene	146	146	111,148
1,3-Dichlorobenzene	146	146	111,148
1,4-Dichlorobenzene	146	146	111,148

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
trans-1,4-Dichloro-2-butene	124	53	88,75
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65,83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61,63
cis-1,2-Dichloroethene	96	96	61,98
trans-1,2-Dichloroethene	96	96	61,98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97
1,1-Dichloropropene	110	75	110,77
1,1-Dichloropropanone	126	43	83
cis-1,3-dichloropropene	110	75	110
trans-1,3-dichloropropene	110	75	110
Diethyl ether	74	59	45,73
Ethylbenzene	106	91	106
Ethyl methacrylate	114	69	99
Hexachlorobutadiene	258	225	260
Hexachloroethane	234	117	119,201
2-Hexanone	100	43	58
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134,91
Methacrylonitrile	67	67	52
Methyl acrylate	86	55	85
Methylene chloride	84	84	86,49
Methyl iodide	142	142	127
Methylmethacrylate	100	69	99
4-Methyl-2-pentanone	100	43	58,85
Methyl-t-butyl ether	88	73	57
Naphthalene	128	128	--
Nitrobenzene	123	51	77
2-Nitropropane	89	46	--
Pentachloroethane	200	117	119,167
Propionitrile	55	54	--
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133,119
1,1,2,2-Tetrachloroethane	166	83	131,85
Tetrachloroethene	164	166	168,129
Tetrahydrofuran	72	71	72,42
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99,61
1,1,2-Trichloroethane	132	83	97,85

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Trichloroethene	130	95	130,I32
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

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[a] Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SETS OF CONDITIONS[a]

		Retention	Time	(min:sec)	
Compound	Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
Internal standard					
Fluorobenzene	8:49	6:27	14:06	8:03	22:00
Surrogates					
4-Bromofluorobenzene	18:38	15:43	23:38		31:21
1,2-Dichlorobenzene-d4	22:16	19:08	27:25		35:51
Target Analytes					
Acetone					16:14
Acrylonitrile					17:49
Allyl chloride					16:58
Benzene	8:14	5:40	13:30	7:25	21:32
Bromobenzene	18:57	15:52	24:00	16:25	31:52
Bromochloromethane	6:44	4:23	12:22	5:38	20:20
Bromodichloromethane	10:35	8:29	15:48	9:20	23:36
Bromoform	17:56	14:53	22:46	15:42	30:32
Bromomethane	2:01	0:58	4:48	1:17	12:26
2-Butanone					19:41
n-Butylbenzene	22:13	19:29	27:32	17:57	35:41
sec-Butylbenzene	20:47	18:05	26:08	17:28	34:04
tert-Butylbenzene	20:17	17:34	25:36	17:19	33:26
Carbon Disulfide					16:30
Carbon Tetrachloride	7:37	5:16	13:10	7:25	21:11
Chloroacetonitrile					23:51
Chlorobenzene	15:46	13:01	20:40	14:20	28:26
1-Chlorobutane					21:00
Chloroethane	2:05	1:01		1:27	
Chloroform	6:24	4:48	12:36	5:33	20:27
Chloromethane	1:38	0:44	3:24	0:58	9:11
2-Chlorotoluene	19:20	16:25	24:32	16:44	32:21
4-Chlorotoluene	19:30	16:43	24:46	16:49	32:38
Cyanogen chloride (8)				1:03	
Dibromochloromethane	14:23	11:51	19:12	12:48	26:57
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02	38:20
1,2-Dibromoethane	14:44	11:50	19:24	13:36	27:19
Dibromomethane	10:39	7:56	15:26	9:05	23:22
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47	35:55
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28	34:31
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38	34:45
t-1,4-Dichloro-2-butene					31:44
Dichlorodifluoromethane	1:33	0:42	3:08	0:53	7:16
1,1-Dichloroethane	4:51	2:56	10:48	4:02	18:46

TABLE 2. (continued)

		Retention	Time	(min:sec)	
Compound	Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
1,2-Dichloroethane	8:24	5:50	13:38	7:00	21:31
1,1-Dichloroethene	2:53	1:34	7:50	2:20	16:01
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04	19:53
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32	17:54
1,2-Dichloropropane	10:05	7:40	15:12	8:56	23:08
1,3-Dichloropropane	14:02	11:19	18:42	12:29	26:23
2,2-Dichloropropane	6:01	3:48	11:52	5:19	19:54
1,1-Dichloropropanone					24:52
1,1-Dichloropropene	7:49	5:17	13:06	7:10	21:08
cis-1,3-dichloropropene	11.58		16:42		24:24
trans-1,3-dichloropropene	13.46		17:54		25:33
Diethyl ether					15:31
Ethylbenzene	15:59	13:23	21:00	14:44	28:37
Ethyl Methacrylate					25:35
Hexachlorobutadiene	26:59	23:41	32:04	19:14	42:03
Hexachloroethane					36:45
Hexanone					26:23
Isopropylbenzene	18:04	15:28	23:18	16:25	30:52
4-Isopropyltoluene	21:12	18:31	26:30	17:38	34:27
Methacrylonitrile					20:15
Methylacrylate					20:02
Methylene Chloride	3:36	2:04	9:16	2:40	17:18
Methyl Iodide					16:21
Methylmethacrylate					23:08
4-Methyl-2-pentanone					24:38
Methyl-t-butyl ether					17:56
Naphthalene	27:10	23:31	32:12	19:04	42:29
Nitrobenzene					39:02
2-Nitropropane					23:58
Pentachloroethane					33:33
Propionitrile					19:58
n-Propylbenzene	19:04	16:25	24:20	16:49	32:00
Styrene	17:19	14:36	22:24	15:47	29:57
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44	28:35
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47	31:35
Tetrachloroethene	13:44	11:09	18:36	13:12	26:27
Tetrahydrofuran					20:26
Toluene	12:26	10:00	17:24	11:31	25:13
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14	43:31
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50	41:26
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46	20:51
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59	25:59
Trichloroethene	9:35	7:16	14:48	9:01	22:42
Trichlorofluoromethane	2:16	1:11	6:12	1:46	14:18
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16	31:47
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19	33:33

TABLE 2. (continued)

Compound	Col. 1[b]	Retention Col. 2[b]	Time Col. 2[c]	(min:sec) Col. 3[d]	Col. 4[e]
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59	32:26
Vinyl chloride	1:43	0:47	3:56	1:02	10:22
o-Xylene	17:07	14:31	22:16	15:47	29:56
m-Xylene	16:10	13:41	21:22	15:18	28:53
p-Xylene	16:07	13:41	21:18	15:18	28:53

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[a] Columns 1-4 are those given in Sect. 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (columns 1-2, and 4) or from the beginning of thermal release from the cryogenic interface (column 3).

[b] GC conditions given in Sect. 11.3.1.

[c] GC conditions given in Sect. 11.3.2.

[d] GC conditions given in Sect. 11.3.3.

[e] GC conditions given in Sect. 11.3.4.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon Tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-Chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2-Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Methylene Chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl Chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a] Data obtained by using Column 1 with a jet separator interface and a quadrupole mass spectrometer (Section 11.3.1) with analytes divided among three solutions.

[b] Replicate samples at the lowest concentration listed in Column 2 of this table were analyzed. These results were used to calculate MDLs.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW-BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Benzene	0.1	99	6.2	0.03
Bromobenzene	0.5	97	7.4	0.11
Bromochloromethane	0.5	97	5.8	0.07
Bromodichloromethane	0.1	100	4.6	0.03
Bromoform	0.1	99	5.4	0.20
Bromomethane	0.1	99	7.1	0.06
n-Butylbenzene	0.5	94	6.0	0.03
sec-Butylbenzene	0.5	90	7.1	0.12
tert-Butylbenzene	0.5	90	2.5	0.33
Carbon Tetrachloride	0.1	92	6.8	0.08
Chlorobenzene	0.1	91	5.8	0.03
Chloroethane	0.1	100	5.8	0.02
Chloroform	0.1	95	3.2	0.02
Chloromethane	0.1	99	4.7	0.05
2-Chlorotoluene	0.1	99	4.6	0.05
4-Chlorotoluene	0.1	96	7.0	0.05
Cyanogen Chloride[b]		92	10.6	0.30
Dibromochloromethane	0.1	99	5.6	0.07
1,2-Dibromo-3-Chloropropane	0.1	92	10.0	0.05
1,2-Dibromoethane	0.1	97	5.6	0.02
Dibromomethane	0.1	93	6.9	0.03
1,2-Dichlorobenzene	0.1	97	3.5	0.05
1,3-Dichlorobenzene	0.1	99	6.0	0.05
1,4-Dichlorobenzene	0.1	93	5.7	0.04
Dichlorodifluoromethane	0.1	99	8.8	0.11
1,1-Dichloroethane	0.1	98	6.2	0.03
1,2-Dichloroethane	0.1	100	6.3	0.02
1,1-Dichloroethene	0.1	95	9.0	0.05
cis-1,2-Dichloroethene	0.1	100	3.7	0.06
trans-1,2-Dichloroethene	0.1	98	7.2	0.03
1,2-Dichloropropane	0.1	96	6.0	0.02
1,3-Dichloropropane	0.1	99	5.8	0.04
2,2-Dichloropropane	0.1	99	4.9	0.05
1,1-Dichloropropene	0.1	98	7.4	0.02
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW-BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (μg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (μg/L)
Isopropylbenzene	0.5	98	6.4	0.10
4-Isopropyltoluene	0.5	87	13.0	0.26
Methylene Chloride	0.5	97	13.0	0.09
Naphthalene	0.1	98	7.2	0.04
n-Propylbenzene	0.1	99	6.6	0.06
Styrene	0.1	96	19.0	0.06
1,1,1,2-Tetrachloroethane	0.1	100	4.7	0.04
1,1,2,2-Tetrachloroethane	0.1	100	12.0	0.20
Tetrachloroethene	0.1	96	5.0	0.05
Toluene	0.1	100	5.9	0.08
1,2,3-Trichlorobenzene	0.1	98	8.9	0.04
1,2,4-Trichlorobenzene	0.1	91	16.0	0.20
1,1,1-Trichloroethane	0.1	100	4.0	0.04
1,1,2-Trichloroethane	0.1	98	4.9	0.03
Trichloroethene	0.1	96	2.0	0.02
Trichlorofluoromethane	0.1	97	4.6	0.07
1,2,3-Trichloropropane	0.1	96	6.5	0.03
1,2,4-Trimethylbenzene	0.1	96	6.5	0.04
1,3,5-Trimethylbenzene	0.1	99	4.2	0.02
Vinyl Chloride	0.1	96	0.2	0.04
o-Xylene	0.1	94	7.5	0.06
m-Xylene	0.1	94	4.6	0.03
p-Xylene	0.1	97	6.1	0.06

[a] Data obtained by using Column 3 with a cryogenic interface and a quadrupole mass spectrometer (Section 11.3.3).

[b] Reference 8.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 μg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 μg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	–	–	–	–
Surrogates					
4-Bromofluorobenze	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d$_4$	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon Tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	[d]	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-Chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	[d]	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,2-Dichloropropene[c]					
trans-1,2-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene Chloride	27	[e]		[e]	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl Chloride	36	104	3.5	115	14.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 μg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 μg/L Conc.)	RSD (%)
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	[f]		[f]	
p-Xylene	61	98	2.3	103	1.4

[a] Data obtained using Column 2 with the open split interface and an ion trap mass spectrometer (Section 11.3.2) with all method analytes in the same reagent water solution.

[b] Designation in Figures 1 and 2.

[c] Not measured; authentic standards were not available.

[d] Not found at 0.2 μg/L.

[e] Not measured; methylene chloride was in the laboratory reagent blank.

[f] m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 4[a]

Compound	True Conc. (µg/L)	Mean Conc. Detected (µg/L)	Rel. Std. Dev. (%)	Method Detect. Limit (µg/L)
Acetone	1.0	1.6	5.7	0.28
Acrylonitrile	1.0	0.81	8.7	0.22
Allyl Chloride	1.0	0.90	4.7	0.13
2-Butanone	2.0	2.7	5.6	0.48
Carbon Disulfide	0.20	0.19	15	0.093
Chloroacetonitrile	1.0	0.83	4.7	0.12
1-Chlorobutane	1.0	0.87	6.6	0.18
trans-Dichloro-2-Butene	1.0	1.3	8.7	0.36
1,1-Dichloropropanone	5.0	4.2	7.7	1.0
cis-1,3-Dichloropropene	0.20	0.20	3.1	0.020
trans-1,3-Dichloropropene	0.10	0.11	14	0.048
Diethyl Ether	1.0	0.92	9.5	0.28
Ethyl Methacrylate	0.20	0.23	3.9	0.028
Hexachloroethane	0.20	0.18	10	0.057
2-Hexanone	1.0	1.1	12	0.39
Methacrylonitrile	1.0	0.92	4.2	0.12
Methylacrylate	1.0	1.2	12	0.45
Methyl Iodide	0.20	0.19	3.1	0.019
Methylmethacrylate	1.0	1.0	13	0.43
4-Methyl-2-Pentanone	0.40	0.56	9.7	0.17
Methyl-tert-Butylether	0.40	0.52	5.6	0.090
Nitrobenzene	2.0	2.1	18	1.2
2-Nitrobenzene	1.0	0.83	6.2	0.16
Pentachloroethane	0.20	0.23	20	0.14
Propionitrile	1.0	0.87	5.3	0.14
Tetrahydrofuran	5.0	3.9	13	1.6

[a] Data obtained using Column 4 with the open split interface and an ion trap mass spectrometer.

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L[a]

	REAGENT WATER			RAW WATER			TAP WATER		
Compound	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Acetone	19	12%	95%	21	3.7%	105%	22	8.2%	110%
Acrylonitrile	20	4.7%	100%	22	3.4%	110%	21	1.3%	105%
Allyl Chloride	20	5.1%	100%	20	2.8%	100%	19	3.5%	95%
2-Butanone	17	11%	85%	19	7.3%	95%	17	5.6%	85%
Carbon Disulfide	19	6.4%	95%	18	2.5%	90%	18	3.0%	90%
Chloroacetonitrile	20	4.1%	100%	23	4.7%	115%	23	1.3%	115%
1-Chlorobutane	18	6.4%	90%	19	2.2%	95%	17	2.2%	85%
t-1,2-Dichloro-2-Butene	19	4.1%	95%	22	2.9%	110%	21	0.90%	105%
1,1-Dichloropropanone	20	5.6%	100%	22	6.4%	110%	21	7.7%	105%
Diethyl Ether	18	6.7%	90%	22	3.4%	110%	22	2.6%	110%
Ethyl Methacrylate	20	3.7%	100%	23	2.6%	115%	22	1.8%	110%
Hexachloroethane	20	6.1%	100%	21	2.5%	105%	21	2.0%	105%
2-Hexanone	19	6.3%	95%	21	3.8%	105%	21	4.0%	105%
Methacrylonitrile	20	3.4%	100%	23	2.9%	115%	22	2.0%	110%
Methylacrylate	20	3.7%	100%	22	3.1%	110%	21	2.1%	105%

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L[a]

	Reagent Water			Raw Water			Tap Water		
Compound	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Methyl Iodide	20	4.4%	100%	19	3.8%	95%	19	3.0%	95%
Methylmethacrylate	20	3.7%	100%	23	3.3%	115%	23	2.7%	115%
4-Methyl-2-Pentanone	19	8.7%	95%	21	5.5%	105%	22	7.2%	110%
Methyl-tert-Butylether	19	3.5%	95%	22	2.5%	110%	22	3.6%	110%
Nitrobenzene	20	5.4%	100%	22	4.8%	110%	21	2.4%	105%
2-Nitropropane	20	6.1%	100%	23	5.1%	115%	22	3.2%	110%
Pentachloroethane	19	5.2%	95%	21	2.6%	105%	22	1.7%	110%
Propionitrile	20	4.5%	100%	23	3.9%	115%	23	2.4%	115%
Tetrahydrofuran	20	2.8%	100%	24	3.2%	120%	21	2.9%	105%

[a] Data obtained using Column 4 with the open-split interface and an ion trap mass spectrometer with all Table 8 analyses in the same reagent water solution (1).

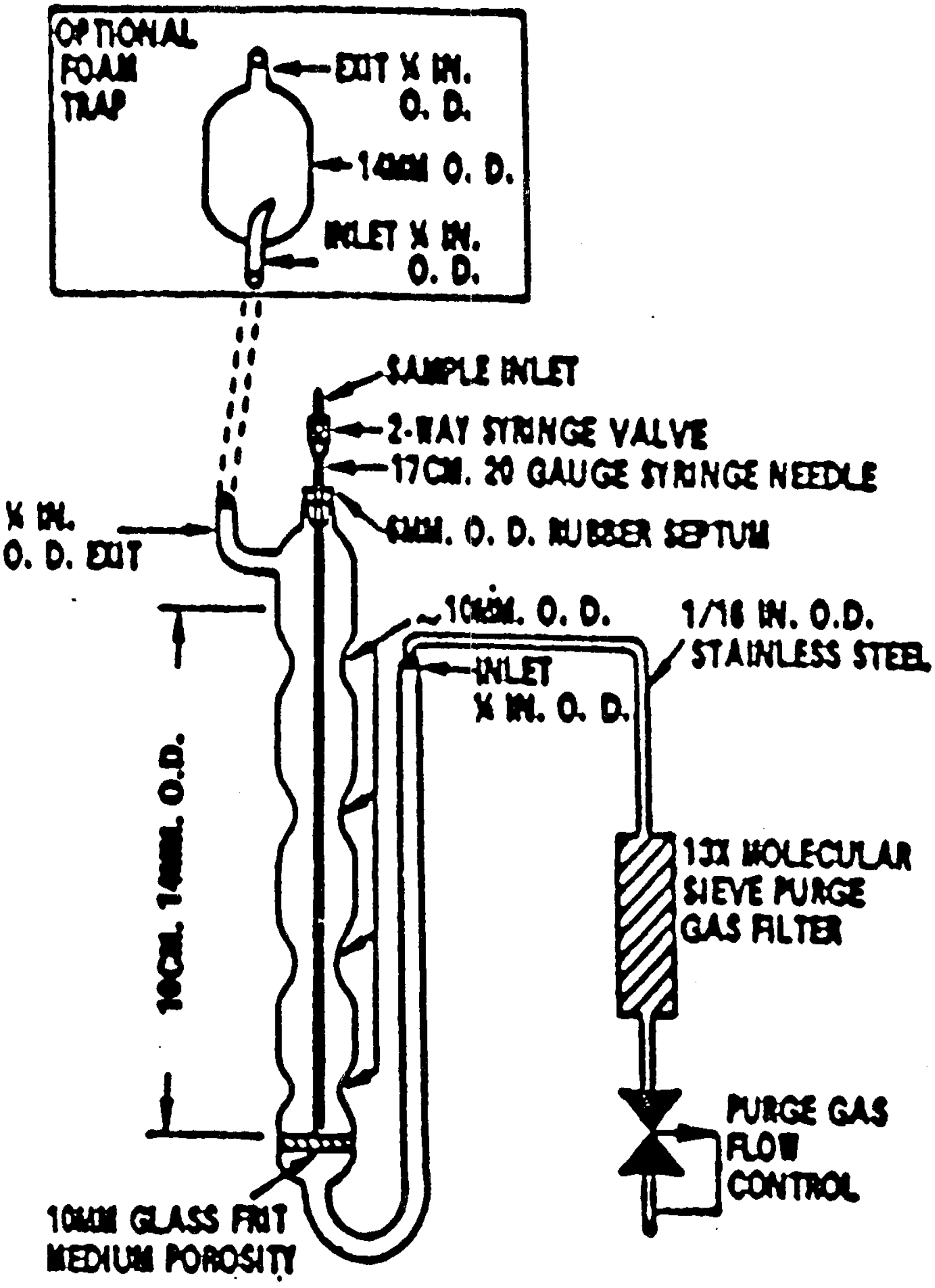


FIGURE 1. PURGING DEVICE

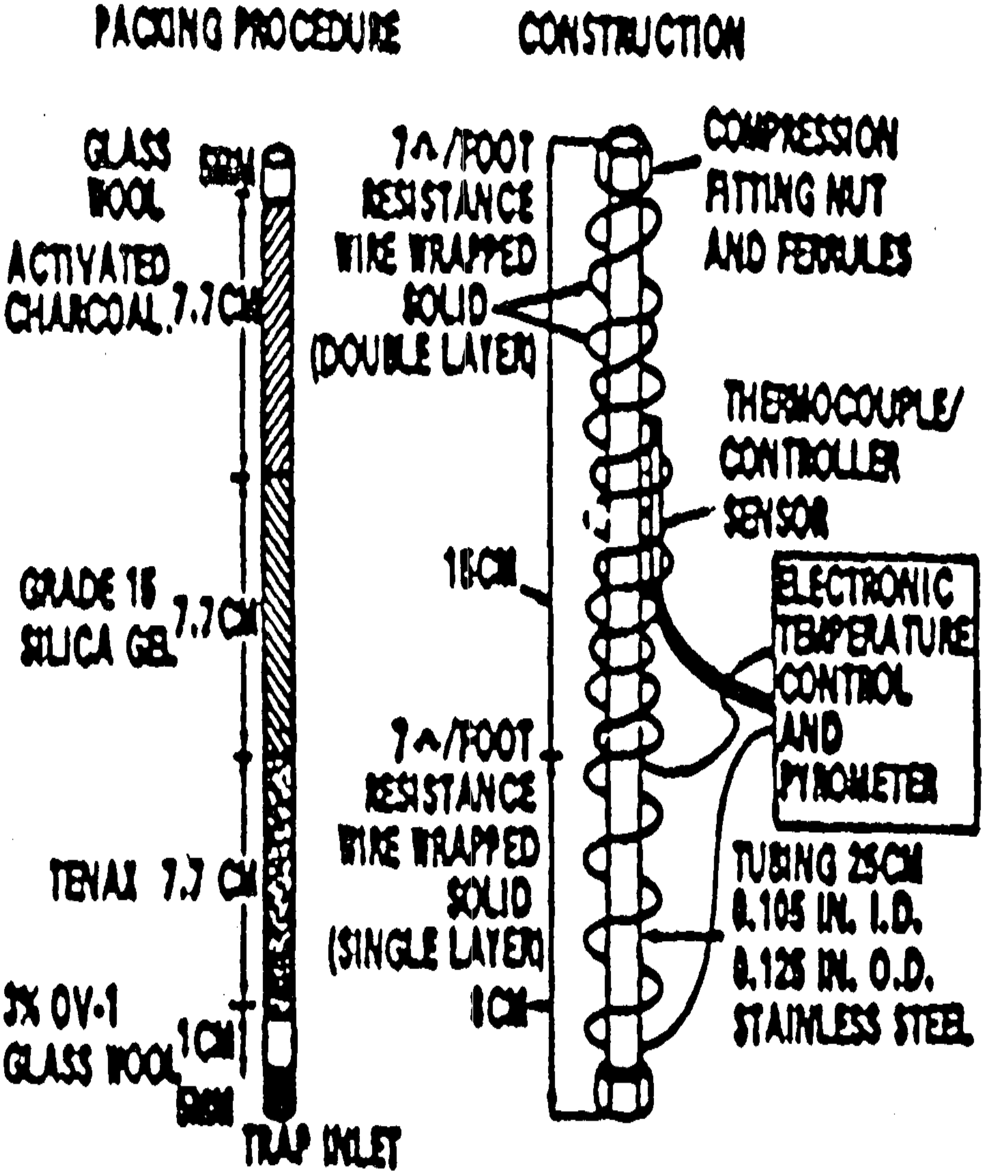


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

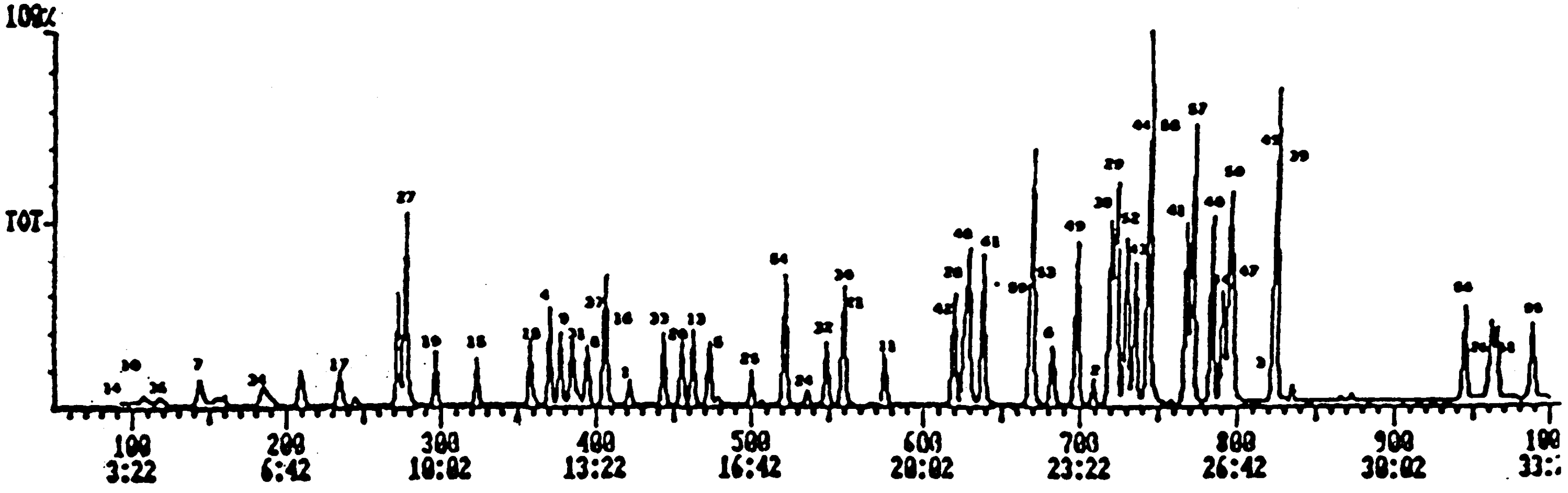
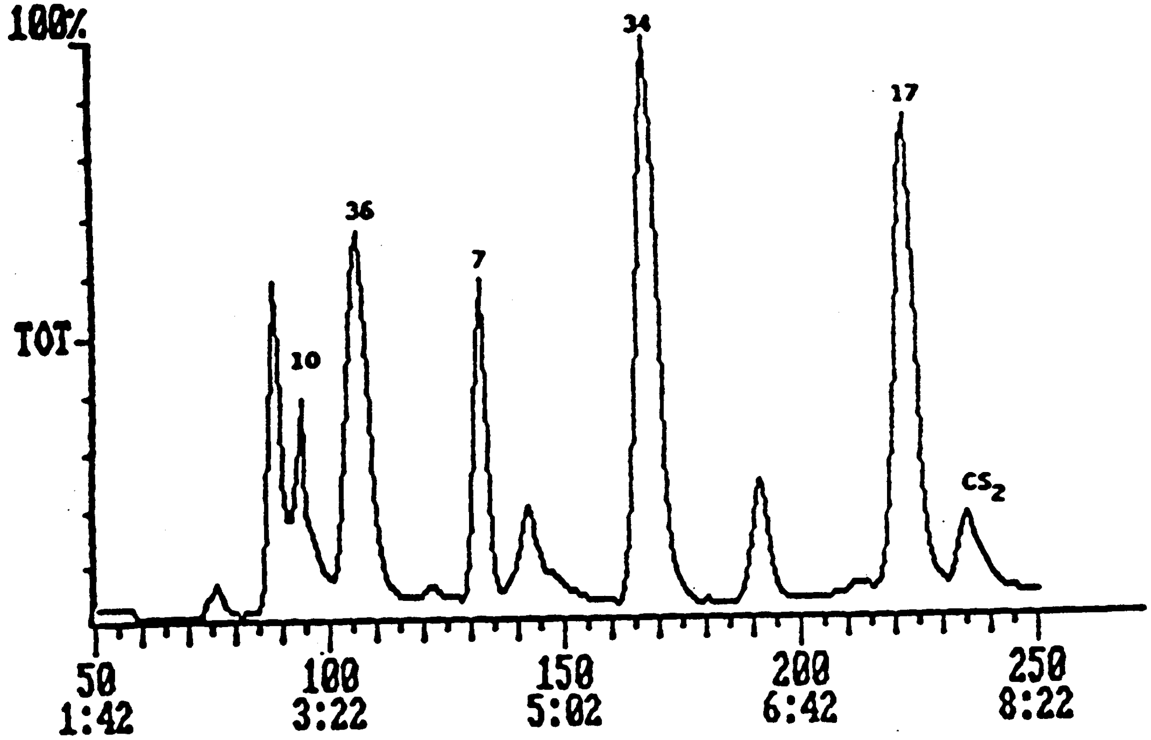


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 2.0

J.W. Eichelberger, T.D. Behymer, W.L. Budde - Method 525,
Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde - Method 525.1
Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker
Method 525.2 Revision 1.0 (February, 1994)

J.W. Munch - Method 525.2, Revision 2.0 (1995)

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatog-raphy. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for most of the following compounds:

Analyte	MW[1]	Chemical Abstract Services Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	317	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components		
alpha-Chlordane	406	5103-71-9
gamma-Chlordane	406	5103-74-2
trans-Nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6

Analyte	MW[1]	Chemical Abstract Services Registry Number
Chlorpyrifos	349	2921-88-2
2-Chlorobiphenyl	188	2051-60-7
Chrysene	228	218-01-9
Cyanazine	240	21725-46-2
Cycloate	215	1134-23-2
Dacthal (DCPA)	330	1861-32-1
4,4'-DDD	318	72-54-8
4,4'-DDE	316	72-55-9
4,4'-DDT	352	50-29-3
Diazinon[2]	304	333-41-5
Dibenz[a,h]anthracene	278	53-70-3
Di-n-Butylphthalate	278	84-74-2
2,3-Dichlorobiphenyl	222	16605-91-7
Dichlorvos	220	62-73-7
Dieldrin	378	60-57-1
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate	370	103-23-1
Di(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
2,4-Dinitrotoluene	182	121-14-2
2,6-Dinitrotoluene	182	606-20-2
Diphenamid	239	957-51-7
Disulfoton[2]	274	298-04-4
Disulfoton Sulfoxide[2]	290	2497-07-6
Disulfoton Sulfone	306	2497-06-5
Endosulfan I	404	959-98-8
Endosulfan II	404	33213-65-9
Endosulfan Sulfate	420	1031-07-8
Endrin	378	72-20-8
Endrin Aldehyde	378	7421-93-4
EPTC	189	759-94-4
Ethoprop	242	13194-48-4
Etridiazole	246	2593-15-9
Fenamiphos[2]	303	22224-92-6
Fenarimol	330	60168-88-9
Fluorene	166	86-73-7
Fluridone	328	59756-60-4
Heptachlor	370	76-44-8
Heptachlor Epoxide	386	1024-57-3
2,2', 3,3', 4,4', 6-Heptachloro-biphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2', 4,4', 5,6'-Hexachloro-biphenyl	358	60145-22-4

Analyte	MW[1]	Chemical Abstract Services Registry Number
Hexachlorocyclohexane, alpha	288	319-84-6
Hexachlorocyclohexane, beta	288	319-85-7
Hexachlorocyclohexane, delta	288	319-86-8
Hexachlorocyclopentadiene	270	77-47-4
Hexazinone	252	51235-04-2
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Isophorone	138	78-59-1
Lindane	288	58-89-9
Merphos[2]	298	150-50-5
Methoxychlor	344	72-43-5
Methyl Paraoxon	247	950-35-6
Metolachlor	283	51218-45-2
Metribuzin	214	21087-64-9
Mevinphos	224	7786-34-7
MGK 264	275	113-48-4
Molinate	187	2212-67-1
Napropamide	271	15299-99-7
Norflurazon	303	27314-13-2
2,2', 3,3', 4,5', 6,6'-Octachloro-biphenyl	426	40186-71-8
Pebulate	203	1114-71-2
2,2', 3', 4,6'-Pentachlorobiphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
cis-Permethrin	390	54774-45-7
trans-Permethrin	390	51877-74-8
Prometon	225	1610-18-0
Prometryn	241	7287-19-6
Pronamide	255	23950-58-5
Propachlor	211	1918-16-7
Propazine	229	139-40-2
Pyrene	202	129-00-0
Simazine	201	122-34-9
Simetryn	213	1014-70-6
Stirofos	364	22248-79-9
Tebuthiuron	228	34014-18-1
Terbacil	216	5902-51-2
Terbufos2	288	13071-79-9
Terbutryn	241	886-50-0
2,2', 4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene		8001-35-2
Triademefon	293	43121-43-3
2,4,5-Trichlorobiphenyl	256	15862-07-4
Tricyclazole	189	41814-78-2

Analyte	MW[1]	Chemical Abstract Services Registry Number
Trifluralin	335	1582-09-8
Vernolate	203	1929-77-7
Aroclor 1016		12674-11-2
Aroclor 1221		11104-28-2
Aroclor 1232		11141-16-5
Aroclor 1242		53469-21-9
Aroclor 1248		12672-29-6
Aroclor 1254		11097-69-1
Aroclor 1260		11096-82-5

[1] Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

[2] Only qualitative identification of these analytes is possible because of their instability in aqueous matrices. Merphos, carboxin, disulfoton, and disulfoton sulfoxide showed instability within 1 h of fortification. Diazinon, fenamiphos, and terbufos showed significant losses within seven days under the sample storage conditions specified in this method.

Attempting to determine all of the above analytes in all samples is not practical and not necessary in most cases. If all the analytes must be determined, multiple calibration mixtures will be required.

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero[1]. The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. MDLs for all method analytes are listed in Tables 3 through 6. The concentration calibration range demonstrated in this method is 0.1-10 µg/L for most analytes.

2.0 SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples.

The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and liquid- solid extraction devices. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited[2-4].

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 Sample Containers -- 1 L or 1 qt amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are very sensitive to light and are oxidized or decomposed upon exposure.

6.3 Volumetric Flasks -- Various sizes.

6.4 Laboratory or Aspirator Vacuum System -- Sufficient capacity to maintain a minimum vacuum of approximately 13 cm (5 in.) of mercury for cartridges. A greater vacuum (66 cm [26 in.] of mercury) may be used with disks.

6.5 Micro Syringes -- Various sizes.

6.6 Vials -- Various sizes of amber vials with Teflon-lined screw caps.

6.7 Drying Column -- The drying tube should contain about 5-7 g of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc. as long as no sodium sulfate passes through the column into the extract.

6.8 Analytical Balance -- Capable of weighing 0.0001 g accurately.

6.9 Fused Silica Capillary Gas Chromatography Column -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision (Section 10.0) can be used. Medium polar, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. A 30 m X 0.25 mm id fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5.MS) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.10 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

6.10.1 The GC must be capable of temperature programming and be equipped for splitless/split injection. On-column capillary injection is acceptable if all the quality control specifications in Section 9.0 and Section 10.0 are met. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.

6.10.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity (see Section 10.0 for calibration requirements).

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45-450 amu with a complete scan cycle time (including scan overhead) of 1.0 second or less. (Scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when an injection of approximately 5 ng of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance. The scan time should be set so that all analytes have a minimum of five scans across the chromatographic peak.

6.10.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Section 10.2.6 (or construction of a linear regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.0.

6.11 Standard Filter Apparatus, All Glass or Teflon Lined -- These should be used to carry out disk extractions when no automatic system or manifold is utilized.

6.12 A manifold system or an automatic or robotic commercially available sample preparation system designed for either cartridges or disks may be utilized in this method if all quality control requirements discussed in Section 9.0 are met.

7.0 REAGENTS AND STANDARDS

7.1 Helium Carrier Gas -- As contaminant free as possible.

7.2 Liquid-Solid Extraction (LSE) Cartridges -- Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into the ethyl acetate and methylene chloride eluant. The cartridges are packed with about 1 g of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into the eluting solvent. One liter of water should pass through the cartridge in about two hours with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. Section 9.0 provides criteria for acceptable LSE cartridges which are available from several commercial suppliers.

The extraction disks contain octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Other disk sizes are acceptable and larger disks may be used for special problems or when sample compositing is carried out. As with cartridges, the disks should not contain any organic compounds, either from the matrix or the bonded silica, which will leach into the ethyl acetate and methylene chloride eluant. One L of reagent water should pass through the disks in five to 20 minutes using a vacuum of about 66 cm (26 in.) of mercury. Section 9.0 provides criteria for acceptable LSE disks which are available commercially.

7.3 Solvents

7.3.1 Methylene Chloride, Ethyl Acetate, Acetone, Toluene, and Methanol -- High purity pesticide quality or equivalent.

7.3.2 Reagent Water -- Water in which an interference is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with Teflon-lined septa and screw caps.

7.4 Hydrochloric Acid -- 6N.

7.5 Sodium Sulfate, Anhydrous -- (Soxhlet extracted with methylene chloride for a minimum of four hours or heated to 400°C for two hours in a muffle furnace.)

7.6 Stock Standard Solutions (SSS) -- Individual solutions of surrogates, internal standards, and analytes, or mixtures of analytes, may be purchased from commercial suppliers or prepared from pure materials. To prepare, add 10 mg (weighed on an analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol, ethyl acetate, or acetone in a 2 mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the analytical standard is available only in quantities smaller than 10 mg, reduce the volume of solvent accordingly. Some polycyclic aromatic hydrocarbons are not soluble in methanol, ethyl acetate, or acetone, and their stock standard solutions are prepared in toluene. Methylene chloride should be avoided as a solvent for standards because its high vapor pressure leads to rapid evaporation and concentration changes. Methanol, ethyl acetate, and acetone are not as volatile as methylene chloride, but their solutions must also be handled with care to avoid evaporation. If compound purity is confirmed by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 µg/µL). Store the amber vials at 4°C or less.

7.7 Primary Dilution Standard Solution (PDS) -- The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple analytes. Mixtures of these analytes to be used as primary dilution standards may be purchased from commercial suppliers. Do not put every method analyte in a single primary dilution standard because chromatographic separation will be extremely difficult, if not impossible. Two or three primary dilution standards would be more appropriate. The recommended solvent for these standards is acetone or ethyl acetate. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 10 ng/µL. Store the primary dilution standard solution in an amber vial at 4°C or less, and check frequently for signs of degradation or evaporation, especially just before preparing calibration solutions.

7.8 Fortification Solution of Internal Standards and Surrogates -- Prepare an internal standard solution of acenaphthene-D_{10}, phenanthrene-D_{10}, and chrysene-D_{12}, in methanol, ethyl acetate, or acetone at a concentration of 500 µg/mL of each. This solution is used in the preparation of the calibration solutions. Dilute a portion of this solution by 10 to a concentration of 50 µg/mL and use this solution to fortify the actual water samples (see Section 11.1.3 and Section 11.2.3). Similarly, prepare both surrogate compound solutions (500 µg/mL for calibration, 50 µg/mL for fortification). Surrogate compounds used in developing this method are 1,3-dimethyl-2-nitrobenzene, perylene-D_{12}, and triphenylphosphate. Other surrogates, for example pyrene-D_{10} may be used in this solution as needed (a 100 µL aliquot of this 50 µg/mL solution added to 1 L of water gives a concentration of 5 µg/L of each internal standard or surrogate). Store these solutions in an amber vial at 4°C or less. These two solutions may be combined or made as a single solution.

7.9 GC/MS Performance Check Solution -- Prepare a solution in methylene chloride of the following compounds at 5 ng/µL of each: DFTPP and endrin, and 4,4'-DDT. Store this solution in an amber vial at 4°C or less. DFTPP is less stable in acetone or ethyl acetate than it is in methylene chloride.

7.10 Calibration Solutions (CAL1 through CAL6) -- Prepare a series of six concentration calibration solutions in ethyl acetate which contain analytes of interest (except pentachlorophenol, toxaphene, and the Aroclor compounds) at suggested concentrations of 10, 5, 2, 1, 0.5, and 0.1 ng/µL, with a constant concentration of 5 ng/µL of each internal standard and surrogate in each CAL solution. It should be noted that CAL1 through CAL6 are prepared by combining appropriate aliquots of a primary dilution standard solution (Section 7.7) and the fortification solution (500 µg/mL) of internal standards and surrogates (Section 7.8). All calibration solutions should contain at least 80% ethyl acetate to avoid gas chromatographic problems. IF ALL METHOD ANALYTES ARE TO BE DETERMINED, TWO OR THREE SETS OF CALIBRATION SOLUTIONS WILL LIKELY BE REQUIRED. Pentachlorophenol is included in this solution at a concentration four times the other analytes. Toxaphene CAL solutions should be prepared as separate solutions at concentrations of 250, 200, 100, 50, 25, and 10 ng/µL. Aroclor CAL solutions should be prepared individually at concentrations of 25, 10, 5, 2.5, 1.0, 0.5, and 0.2 ng/µL. Store these solutions in amber vials in a dark cool place. Check these solutions regularly for signs of degradation, for example, the appearance of anthraquinone from the oxidation of anthracene.

7.11 Reducing Agent, Sodium Sulfite, Anhydrous -- Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.

7.12 Fortification Solution for Recovery Standard -- Prepare a solution of terphenyl-D_{14} at a concentration of 500 µg/mL in methylene chloride or ethyl acetate. These solutions are also commercially available. An aliquot of this solution should be added to each extract to check on the recovery of the internal standards in the extraction process.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection -- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about two minutes). Adjust the flow to about 500 mL/min. and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers if possible.

8.2 Sample Dechlorination and Preservation -- All samples should be iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of 40-50 mg of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved) to each water sample. It is very important that the sample be dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in water. The sample pH is adjusted to <2 with 6 N hydrochloric acid. This is the same pH used in the extraction, and is required to support the recovery of acidic compounds like pentachlorophenol.

8.2.1 If cyanizine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described above.

8.2.2 Atraton and prometon are not efficiently extracted from water at pH 2 due to what appears to be their ionization in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no acid should be added. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

8.3 Holding Time -- Results of the time/storage study of all method analytes showed that all but six compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described in Section 8.2. Therefore, samples must be extracted within 14 days. If the following analytes are to be determined, the samples cannot be held for 14 days but must be extracted immediately after collection and preservation: carboxin, diazinon, disulfoton, disulfoton sulfoxide, fenamiphos, and terbufos. Sample extracts may be stored at 4°C for up to 30 days after sample extraction.

8.4 Field Blanks

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal, and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with the filled sample bottles.

8.4.2 When sodium sulfite and hydrochloric acid are added to samples, use the same procedure to add the same amounts to the FRB.

9.0 QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. A MDL should be determined for each analyte of interest. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial Demonstration of Low Disk or Cartridge System Background -- Before any samples are analyzed, or any time a new supply of cartridges or disks is received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it must be demonstrated that the particle size and packing of the LSE cartridges or the preparation of the disks are acceptable. Consistent flow rate with all samples is an indication of acceptable particle size distribution, packing, and proper preparation.

9.2.1 A source of potential contamination is the liquid-solid extraction (LSE) cartridge or disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes[5]. Although disks are generally made of an inert matrix, they may still contain phthalate material. Generally, phthalate esters can be leached from the cartridges into ethyl acetate and methylene chloride and produce a variable background in the water sample. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limits.

9.2.3 One L of water should pass through a cartridge in about two hours with a partial vacuum of about 13 cm (5 in.) of mercury. Using full aspirator or pump vacuum, approximately five to 20 minutes will normally be required to pass one liter of drinking water through a disk. The extraction time should not vary unreasonably among LSE cartridges or disks.

9.3 Initial Demonstration of Laboratory Accuracy and Precision -- Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a suggested concentration in the range of 2-5 µg/L. This concentration should be approximately in the middle of the calibration range, and will be dependent on the sensitivity of the instrumentation used.

9.3.1 Prepare each replicate by adding sodium sulfite and HCl according to Section 8.2, then adding an appropriate aliquot of the primary dilution standard solution, or certified quality control sample, to reagent water. Analyze each replicate according to the procedures described in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be $<30\%$. If these criteria are not met, locate the source of the problem, and repeat with freshly prepared LFBs.

9.3.4 Analyze seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.5 µg/L. Calculate the MDL of each analyte using the procedure described in Section 13.1.2[1]. It is recommended that these analyses be performed over a period of three or four days to produce more realistic method detection limits.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Section 10.3). In laboratory fortified blanks or samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in laboratory fortified blanks and samples. The addition of 10 µL of the recovery standard, terphenyl-D_{14} (500 µg/mL), to the extract is recommended to be used to monitor the recovery of the internal standards in laboratory fortified blanks and samples. Internal standard recovery should be in excess of 70%.

9.5 With each batch of samples processed as a group within a 12-hour work shift, analyze a laboratory reagent blank to determine the background system contamination. Any time a new batch of LSE cartridges or disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Section 9.2.

9.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in Section 9.3. If more than 20 samples are included in a batch, analyze a LFB for every 20 samples. Use the procedures described in Section 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Add the results to the on-going control charts to document data quality.

Note: If the LFB for each batch of samples contains the individual PCB congeners listed in Section 1.0, then a LFB for each Aroclor is not required. At least one LFB containing toxaphene should be extracted for each 24 hour period during which extractions are performed. Toxaphene should be fortified in a separate LFB from other method analytes.

If individual PCB congeners are not part of the LFB, then it is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) LFB be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days.

9.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. Over time, LFM data should be documented for all routine sample sources for the laboratory. A laboratory fortified sample matrix should be analyzed for every 20 samples processed in the same batch. If the recovery data for a LFM does not meet the criteria in Section 9.3.3., and LFBs show the laboratory to be in control , then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.8 With each set of samples, a FRB should be analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.

9.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Section 9.3.3), check the entire analytical procedure to locate and correct the problem source.

9.10 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required each day or at the beginning of each period in which analyses are performed not to exceed 12 hours. Additional periodic calibration checks are good laboratory practice. It is recommended that an additional calibration check be performed at the end of each period of continuous instrument operation, so that all field sample analyses are bracketed by a calibration check standard.

10.2 Initial Calibration

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.2.2.

10.2.2 Inject into the GC/MS system a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin and 4,4'-DDT. If desired, the endrin and DDT degradation checks may be performed simultaneously with the DFTPP check or in a separate injection. Acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak for each compound (Section 10.2.3.1 and Section 10.2.3.2). If the DFTPP mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum or an average spectrum across the GC peak may be used to evaluate the performance of the system. Locate any degradation products of endrin (endrin ketone [EK] and endrin aldehyde [EA]) and 4,4'-DDT (4,4'-DDE and 4,4'-DDD) at their appropriate retention times and quantitation ions (Table 2). Endrin ketone can be located at ≈1.1 to 1.2 times the endrin retention time with prominent m/z 67 and 317 ions in the mass spectrum. If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with the calibration. Calculate percent breakdown using peak areas based on total ion current (TIC) as follows:

% 4,4'-DDT breakdown =

$$\frac{\sum \text{ TIC area of DDT degradation peaks (DDE+DDD)}}{\sum \text{ TIC area of total DDT peaks (DDT+DDE+DDD)}} \text{ x } 100$$

% endrin breakdown =

$$\frac{\sum \text{ TIC area of endrin degradation peaks (EA+EK)}}{\sum \text{ TIC area of total endrin peaks (endrin+EA+EK)}} \text{ x } 100$$

10.2.3 Inject a 1 µL aliquot of a medium concentration calibration solution, for example 0.5-2 µg/L, and acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.0 second or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak. Calibration standards for toxaphene and Aroclors must be injected individually.

10.2.3.1 The following are suggested multi-ramp temperature program GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 45°C and hold in splitless mode for one minute. Heat rapidly to 130°C. At three minutes start the temperature program: 130-180°C at 12°/min.; 180-240°C at 7°/min.; 240-320°C at 12°/min. Start data acquisition at four minutes.

10.2.3.2 Single ramp linear temperature program suggested GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 40°C and hold in splitless mode for one minute. Heat rapidly to 160°C. At three minutes start the temperature program: 160-320°C at 6°/min.; hold at 320°C for two minutes. Start data acquisition at three minutes.

10.2.4 Performance Criteria for the Calibration Standards -- Examine the stored GC/MS data with the data system software.

10.2.4.1 GC Performance -- Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance. See Section 10.3.6.

10.2.4.2 MS Sensitivity -- The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Section 10.3.6.

10.2.5 If all performance criteria are met, inject a 1 µL aliquot of each of the other CAL solutions using the same GC/MS conditions. Calibration standards of toxaphene and Aroclors must be injected individually.

10.2.5.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. In this case, the analyst should prepare additional CAL solutions at slightly higher concentrations to obtain at least five calibration points that bracket the expected analyte concentration range.

10.2.6 Calculate a response factor (RF) for each analyte of interest and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 2 contains suggested internal standards for each analyte and surrogate, and quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Section 6.10.4), and many other software programs. The RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

Note: To calibrate for multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.

Option 1 - Calculate an average response factor or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using two to three of the suggested quantitation ions in Table 2.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms. Use an appropriate quantitation ion for each peak.

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion internal standard
Q_x = quantity of analyte injected in ng or concentration units
Q_{is} = quantity of internal standard injected in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Section 10.3.6.

10.2.7 As an alternative to calculating mean response factors, use the GC/MS data system software or other available software to generate a linear regression calibration by plotting A_x/A_{is} vs. Q_x.

10.3 Continuing Calibration Check -- Verify the MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed using the following procedure.

10.3.1 Inject a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin, and 4,4'-DDT. Acquire a mass spectrum for DFTPP that includes data for m/z 45-450. Ensure that all criteria in Section 10.2.2 are met.

10.3.2 Inject a 1 µL aliquot of a calibration solution and analyze with the same conditions used during the initial calibration. It is recommended that the concentration of calibration solution be varied, so that the calibration can be verified at more than one point.

Note: If the continuing calibration check standard contains the PCB congeners listed in Section 1.0, calibration verification is not required for each Aroclor. Calibration verification of toxaphene should be performed at least once each 24 hour period.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not changed by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear regression is used, the calculated amount for each analyte must be ±30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. Any field sample extracts that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored.

10.3.5.1 Because of the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. If analytes that missed the calibration check are detected in samples, they may be quantified using a single point calibration. The single point standards should be prepared at concentrations that produce responses close (±20%) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action MUST be taken. If more than 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action MUST be taken.

10.3.6 Some Possible Remedial Actions -- Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 m) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

11.0 PROCEDURE

11.1 Cartridge Extraction

11.1.1 This procedure may be carried out in the manual mode or in the automated mode (Section 6.12) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. If the manual mode is used, a suggested setup of the extraction apparatus is shown in Figure 1A. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of approximately 13 cm (5 in.) of mercury is used during all operations with the apparatus. About two hours should be required to draw a liter of water through the cartridge.

11.1.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. From this point, do not allow the cartridge to go dry. Add 10 mL of reagent water to the cartridge, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.1.3 Pour the water sample into the 2 L separatory funnel with the stopcock closed, add 5 mL methanol, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol is added to the sample. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.) Add a 100 µL aliquot of the fortification solution (50 µg/mL) for internal standards and surrogates, and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.1.4 Periodically transfer a portion of the sample into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 minutes.

11.1.5 Transfer the 125 mL solvent reservoir and LSE cartridge (from Figure 1A) to the elution apparatus if used (Figure 1B). The same 125 mL solvent reservoir is used for both apparatus. Rinse the inside of the 2 L separatory funnel and the sample jar with 5 mL of ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form an immiscible layer with the eluate. Pass the eluate through the drying column (Section 6.7) which is packed with approximately 5-7 g of anhydrous sodium sulfate and collect in a second vial. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same vial. Concentrate the extract in a warm water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.2 Disk Extraction

11.2.1 This procedure was developed using the standard 47 mm diameter disks. Larger disks (90 mm diameter) may be used if sample compositing is being done or special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL, the conditioning solvent volume is 15 mL, and the elution solvent volume is two 15 mL aliquots.

11.2.1.1 Extractions using the disks may be carried out either in the manual or automatic mode (Section 6.12) using an automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. Insert the disk into the filter apparatus (Figure 2) or sample preparation unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAc) and methylene chloride (MeCl2) by adding the solvent to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining solvent through the disk.

Note: Soaking the disk may not be desirable when disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Section 11.2.1.2 to ensure adequate contact time between solvent and disk.

11.2.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.2.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.2.2 Add 5 mL MeOH per liter of water to the sample. Mix well. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.)

11.2.3 Add 100 µL of the internal standard and surrogate compound fortification solution (50 µg/mL) to the sample and shake or mix until the sample is homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.2.4 Add the water sample to the reservoir and apply full vacuum to begin the extraction. Particulate-free water may pass through the disk in as little as five minutes without reducing analyte recoveries. Extract the entire sample, draining as much water from the sample container as possible. Dry the disk by maintaining vacuum for about 10 minutes.

11.2.5 Remove the filtration top, but do not disassemble the reservoir and fritted base. If a suction flask is being used, empty the water from the flask, and insert a suitable collection tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.6 Add 5 mL of ethyl acetate to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the disk. A disposable pipet or syringe may be used to do this, rinsing the sides of the glass filtration reservoir in the process. Draw about half of the solvent through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining solvent through the disk.

Note: Soaking the disk may not be desirable if disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Section 11.2.7 to ensure adequate contact time between solvent and disk.

11.2.7 Repeat the above step (Section 11.2.6) with methylene chloride.

11.2.8 Using a syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:MeCl2. Draw the solvent through the disk and into the collector tube. Pour the combined eluates (Section 11.2.6 through Section 11.2.8) through the drying tube (Section 6.7) containing about 5-7 g of anhydrous sodium sulfate. Rinse the drying tube and sodium sulfate with two 3 mL portions of 1:1 EtAc:MeCl2 mixture. Collect all the extract and washings in a concentrator tube.

11.2.9 While gently heating the extract in a water bath or a heating block, concentrate to between 0.5 mL and 1 mL under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, since this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.3 Analyze a 1 µL aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Section 10.2.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.

11.5 Identification of Analytes -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within five seconds of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.5.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. See Section 10.2.4.1. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Benzo[b] and benzo[k]fluoranthene may be measured as an isomeric pair. MGK 264 is made up of two structural isomers. These are listed separately in the data tables.

11.5.4 Each multi-component analyte can be identified by the presence of its individual components in a characteristic pattern based on the relative amounts of each component present. Chromatograms of standard materials of multi-component analytes should be carefully evaluated, so that these patterns can be recognized by the analyst.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 2. If the response of any analyte exceeds the calibration rage established in Section 10.0, dilute the extract and reanalyze.

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Section 10.0. Do not use daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)\ (Q_{is})}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample

A_x = integrated abundance of the quantitation ion of the analyte in the sample

A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample

Q_{is} = total quantity (in micrograms) of internal standard added to the water sample

V = original water sample volume in liters

RF = mean response factor of analyte from the initial calibration. RF is a unitless value

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression established in Section 10.0. Do not use daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

12.2 To quantitate multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.

Option 1 - Calculate an average RF or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using two to three of the suggested quantitation ions in Table 2.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the Aroclor or toxaphene pattern. Option 2 was used to generate the data in Table 6.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data (Tables 3-6) for each listed analyte (except multi-component analytes) were obtained at a concentration of 0.5 µg/L and/or 5 µg/L in reagent water utilizing both the disk and the cartridge technology and two different GC/MS systems, an ion trap and a quadrupole mass spectrometer. Table 8 lists accuracy and precision data from replicate determinations of method analytes in tap water using liquid-solid cartridge extractions and the ion trap mass spectrometer. Any type of GC/MS system may be used to perform this method if it meets the requirement in Sect. 6.10 and the quality control criteria in Section 9.0. The multi-component analytes (i.e., toxaphene and Aroclors) are presented in Tables 5 and 6. The average recoveries in the tables represent six to eight replicate analyses done over a minimum of a two-day period.

13.1.2 With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where: $t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses

13.2 Problem Compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 minutes (Section 11.1.4 and Section 11.2.4). Drying times longer than 10 minutes should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Merphos is partially converted to DEF in aqueous matrices, and also when introduced into a hot gas chromatographic injection system. The efficiency of this conversion appears to be unpredictable and not reproducible. Therefore, merphos cannot be quantified and can only be identified by the presence of DEF in the sample.

13.2.3 Several of the nitrogen and/or phosphorus containing pesticides listed as method analytes are difficult to chromatograph and appear as broad, asymmetrical peaks. These analytes, whose peak shapes are typically poor, are listed in Table 7. The method performance for these analytes is strongly dependent on chromatographic efficiency and performance. Poor peak shapes will affect the linearity of the calibration curves and result in poor accuracy at low concentrations. Also listed in Table 7 are data generated at a mid-concentration level for these analytes. In most cases, the data at this concentration meet the quality control criteria requirements of the method.

13.2.4 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentration of the background in the blank is highly variable.

13.2.5 Atraton and prometon are not efficiently extracted from the water at pH 2 due to what appears to be their ionization occurring in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no HCl should be added at the time of collection. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

13.2.6 Carboxin, disulfoton, and disulfoton sulfoxide were found to be unstable in water and began to degrade almost immediately. These analytes may be identified by this method but not accurately measured.

13.2.7 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. In samples fortified with approximately 80 analytes at 5 µg/L each, metribuzin was recovered at about 50% efficiency. This suggests that metribuzin may break through the C-18 phase in highly contaminated samples resulting in low recoveries.

13.2.8 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described in Section 8.0.

14.0 POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particu-larly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the respons-ibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, see "The Waste Management Manual for Laboratory Personnel", also avail-able from the American Chemical Society at the address in Section 14.2.

16.0 REFERENCES

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4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Junk, G. A., M. J. Avery, J. J. Richard. "Interferences in Solid-Phase Extraction Using C-18 Bonded Porous Silica Cartridges", Anal. Chem. 1988, 60, 1347.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. ION ABUNDANCE CRITERIA FOR BIS(PERFLUORO-PHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYL-PHOSPHINE, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	Low-mass sensitivity
68	<2% of Mass 69	Low-mass resolution
70	<2% of Mass 69	Low-mass resolution
127	10-80% of the base peak	Low- to mid-mass sensitivity
197	<2% of Mass 198	Mid-mass resolution
198	Base peak or >50% of Mass 442	Mid-mass resolution and sensitivity
199	5-9% of Mass 198	Mid-mass resolution and isotope ratio
275	10-60% of the base peak	Mid- to high-mass sensitivity
365	>1% of the base peak	Baseline threshold
441	Present and < Mass 443	High-mass resolution
442	Base peak or >50% of Mass 198	High-mass resolution and sensitivity
443	15-24% of Mass 442	High-mass resolution and isotope ratio

[1] All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

	Retention Time (min:sec)		Quantitation	IS
Compound	A[a]	B[b]	Ion	Reference #
Internal Standards				
Acenaphthene-d10 (#1)	7:47	7:01	164	
Chrysene-d12 (#2)	21:33	18:09	240	
Phenanthrene-d10 (#3)	11:37	10:13	188	
Surrogates				
1,3-Dimethyl-2-Nitrobenzene	5:16	4:33	134	1
Perylene-d12	26:60	21:31	264	3
Triphenylphosphate	20:25	17:25	326/325	3
Target Analytes				
Acenaphthylene	7:30	6:46	152	1
Alachlor	12:59	11:24	160	2
Aldrin	14:24	12:31	66	2
Ametryn	13:11	11:35	227/170	2
Anthracene	11:50	10:24	178	2
Aroclor 1016		7:30-14:00	152/256/292	2
Aroclor 1221		6:38-11:25	152/222/256	2
Aroclor 1232		6:38-13:54	152/256/292	2
Aroclor 1242		6:38-15:00	152/256/292	2
Aroclor 1248		8:47-15:00	152/256/292	2
Aroclor 1254		11:00-18:00	220/326/360	2
Aroclor 1260		13:10-21:00	326/360/394	2
Atraton	10:31	9:25	196/169	1
Atrazine	10:49	9:38	200/215	1/2
Benz[a]anthracene	21:31	18:08	228	3
Benzo[b]fluoranthene	25:33	20:44	252	3
Benzo[k]fluoranthene	25:45	20:48	252	3
Benzo[g,h,i]perylene	31:16	24:18	276	3
Benzo[a]pyrene	25:24	21:25	252	3
Bromacil	13:46	12:03	205	2
Butachlor	16:25	14:16	176/160	2
Butylate	6:60	6:23	57/146	1
Butylbenzylphthalate	19:39	16:53	149	2/3
Carboxin	17:37	15:13	143	2
Chlordane, (alpha-Chlordane)	16:43	14:28	375/373	2/3

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec)		Quantitation Ion	IS Reference #
	A[a]	B[b]		
Chlordane, (gamma-Chlordane)	16:19	14:05	373	2/3
Chlordane, (trans-Nonachlor)	16:47	14:30	409	2/3
Chlorneb	7:47	7:05	191	1
Chlorobenzilate	18:22	15:52	139	2
2-Chlorobiphenyl	7:53	7:08	188	1
Chlorpropham	9:33	8:36	127	1
Chlorpyrifos	14:10	12:23	197/97	2
Chlorothalonil	11:38	10:15	266	2
Chrysene	21:39	18:13	228	3
Cyanazine	14:14	12:28	225/68	2
Cycloate	9:23	8:26	83/154	1
DCPA	14:20	12:30	301	2
4,4'-DDD	18:40	16:05	235/165	2
4,4'-DDE	17:20	14:59	246	2
4,4'-DDT	19:52	17:00	235/165	2
DEF	17:24	15:05	57/169	2
Diazinon	11:19	10:05	137/179	2
Dibenz[a,h]anthracene	30:32	23:47	278	3
Di-n-Butylphthalate	13:49	12:07	149	2
2,3-Dichlorobiphenyl	10:20	9:12	222/152	1
Dichlorvos	5:31	4:52	109	1
Dieldrin	17:35	15:09	79	2
Di(2-Ethylhexyl)adipate	20:11	17:19	129	2/3
Di(2-Ethylhexyl)phthalate	22:11	18:39	149	2/3
Diethylphthalate	8:68	7:53	149	1
Dimethylphthalate	7:13	6:34	163	1
2,4-Dinitrotoluene	8:08	7:22	165	1
2,6-Dinitrotoluene	7:19	6:40	165	1
Diphenamid	14:52	12:58	72/167	2
Disulfoton	11:43	10:22	88	2
Disulfoton Sulfone	16:28	14:17	213/153	2
Disulfoton Sulfoxide	6:09	5:31	97	1
Endosulfan I	16:44	14:26	195	2
Endosulfan II	18:35	15:59	195	2
Endosulfan Sulfate	19:47	16:54	272	2
Endrin	18:15	15:42	67/81	2
Endrin Aldehyde	19:02	16:20	67	2
EPTC	6:23	5:46	128	1
Ethoprop	9:19	8:23	158	1

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Etridiazole	7:14	6:37	211/183	1
Fenamiphos	16:48	14:34	303/154	2
Fenarimol	23:26	19:24	139	3
Fluorene	8:59	8:03	166	1
Fluridone	26:51	21:26	328	3
HCH, alpha	10:19	9:10	181	1
HCH, beta	10:57	9:41	181	2
HCH, delta	11:57	10:32	181	2
HCH, gamma (Lindane)	11:13	9:54	181	2
Heptachlor	13:19	11:37	100	2
Heptachlor epoxide	15:34	13:29	81	2
2,2',3,3',4,4',6-Heptachlorobiphenyl	21:23	18:04	394/396	3
Hexachlorobenzene	10:27	9:15	284	1
2,2',4,4',5,6'-Hexachlorobiphenyl	17:32	15:09	360	2
Hexachlorocyclopentadiene	5:16	5:38	237	1
Hexazinone	20:00	17:06	171	2
Indeno[1,2,3-cd]pyrene	30:26	23:43	276	3
Isophorone	4:54	4:10	82	1
Merphos	15:38	13:35	209/153	2
Methoxychlor	21:36	18:14	227	3
Methyl Paraoxon	11:57	10:22	109	2
Metolachlor	14:07	12:20	162	2
Metribuzin	12:46	11:13	198	2
Mevinphos	5:54	6:19	127	1
MGK 264 - Isomer a	15:18	13:00	164/66	2
MGK 264 - Isomer b	14:55	13:19	164	2
Molinate	8:19	7:30	126	1
Napropamide	16:53	14:37	72	2
Norflurazon	19:31	16:46	145	2
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	21:33	18:11	430/428	3
Pebulate	7:18	6:40	128	1
2,2',3',4,6-Pentachlorobiphenyl	15:37	13:33	326	2
Pentachlorophenol	11:01	9:45	266	2
Permethrin, cis	24:25	20:01	183	3
Permethrin, trans	24:39	20:10	183	3
Phenanthrene	11:41	10:16	178	2
Prometon	10:39	9:32	225/168	2

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Prometryn	13:15	11:39	241/184	2
Pronamide	11:19	10:02	173	2
Propachlor	9:00	8:07	120	1
Propazine	10:54	9:43	214/172	2
Pyrene	16:41	14:24	202	2
Simazine	10:41	9:33	201/186	2
Simetryn	13:04	11:29	213	2
Stirofos	16:20	14:11	109	2
Tebuthiuron	8:00	7:16	156	1
Terbacil	11:44	10:24	161	2
Terbufos	11:14	9:58	57	2
Terbutryn	13:39	11:58	226/185	2
2,2',4,4'-Tetrachlorobiphenyl	14:02	12:14	292	2
Toxaphene		13:00-21:00	159	2
Triademefon	14:30	12:40	57	2
2,4,5-Trichlorobiphenyl	12:44	10:53	256	2
Tricyclazole	17:15	14:51	189	2
Trifluralin	9:31	8:37	306	1
Vernolate	7:10	6:32	128	1

[a] Single-ramp linear temperature program conditions (Section 10.2.3.2).

[b] Multi-ramp linear temperature program conditions (Section 10.2.3.1).

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.7	3.9	94	
Perylene-d12	5.0	4.9	4.8	98	
Triphenylphosphate	5.0	5.5	6.3	110	
Target Analytes					
Acenaphthylene	0.50	0.45	8.2	91	0.11
Alachlor	0.50	0.47	12	93	0.16
Aldrin	0.50	0.40	9.3	80	0.11
Ametryn	0.50	0.44	6.9	88	0.092
Anthracene	0.50	0.53	4.3	106	0.068
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1448	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
Atraton[a]	0.50	0.35	15	70	0.16
Atrazine	0.50	0.54	4.8	109	0.078
Benz[a]anthracene	0.50	0.41	16	82	0.20
Benzo[b]fluoranthene	0.50	0.49	20	98	0.30
Benzo[k]fluoranthene	0.50	0.51	35	102	0.54
Benzo[g,h,i]perylene	0.50	0.72	2.2	144	0.047
Benzo[a]pyrene	0.50	0.58	1.9	116	0.032
Bromacil	0.50	0.54	6.4	108	0.10
Butachlor	0.50	0.62	4.1	124	0.076
Butylate	0.50	0.52	4.1	105	0.064
Butylbenzylphthalate	0.50	0.77	11	154	0.25
Carboxin	5.0	3.8	12	76	1.4
Chlordane (alpha-Chlordane)	0.50	0.36	11	72	0.12
Chlordane (gamma-Chlordane)	0.50	0.40	8.8	80	0.11
Chlordane (trans-Nonachlor)	0.50	0.43	17	87	0.22

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Chlorneb	0.50	0.51	5.7	102	0.088
Chlorobenzilate	5.0	6.5	6.9	130	1.3
2-Chlorobiphenyl	0.50	0.40	7.2	80	0.086
Chlorpropham	0.50	0.61	6.2	121	0.11
Chlorpyrifos	0.50	0.55	2.7	110	0.044
Chlorothalonil	0.50	0.57	6.9	113	0.12
Chrysene	0.50	0.39	7.0	78	0.082
Cyanazine	0.50	0.71	8.0	141	0.17
Cycloate	0.50	0.52	6.1	104	0.095
DCPA	0.50	0.55	5.8	109	0.094
4,4'-DDD	0.50	0.54	4.4	107	0.071
4,4'-DDE	0.50	0.40	6.3	80	0.075
4,4'-DDT	0.50	0.79	3.5	159	0.083
Diazinon	0.50	0.41	8.8	83	0.11
Dibenz[a,h]anthracene	0.50	0.53	0.5	106	0.010
Di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-Dichlorobiphenyl	0.50	0.40	11	80	0.14
Dichlorvos	0.50	0.55	9.1	110	0.15
Dieldrin	0.50	0.48	3.7	96	0.053
Di(2-ethylhexyl)adipate	0.50	0.42	7.1	84	0.090
Di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
Diethylphthalate	0.50	0.59	9.6	118	0.17
Dimethylphthalate	0.50	0.60	3.2	120	0.058
2,4-Dinitrotoluene	0.50	0.60	5.6	119	0.099
2,6-Dinitrotoluene	0.50	0.60	8.8	121	0.16
Diphenamid	0.50	0.54	2.5	107	0.041
Disulfoton	5.0	3.99	5.1	80	0.62
Disulfoton Sulfone	0.50	0.74	3.2	148	0.070
Disulfoton Sulfoxide	0.50	0.58	12	116	0.20
Endosulfan I	0.50	0.55	18	110	0.30
Endosulfan II	0.50	0.50	29	99	0.44
Endosulfan Sulfate	0.50	0.62	7.2	124	0.13
Endrin	0.50	0.54	18	108	0.29
Endrin Aldehyde	0.50	0.43	15	87	0.19

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
EPTC	0.50	0.50	7.2	100	0.11
Ethoprop	0.50	0.62	6.1	123	0.11
Etridiazole	0.50	0.69	7.6	139	0.16
Fenamiphos	5.0	5.2	6.1	103	0.95
Fenarimol	5.0	6.3	6.5	126	1.2
Fluorene	0.50	0.46	4.2	93	0.059
Fluridone	5.0	5.1	3.6	102	0.55
HCH, alpha	0.50	0.51	13	102	0.20
HCH, beta	0.50	0.51	20	102	0.31
HCH, delta	0.50	0.56	13	112	0.21
HCH, gamma (Lindane)	0.50	0.63	8.0	126	0.15
Heptachlor	0.50	0.41	12	83	0.15
Heptachlor Epoxide	0.50	0.35	5.5	70	0.058
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.35	10	71	0.11
Hexachlorobenzene	0.50	0.39	11	78	0.13
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.37	9.6	73	0.11
Hexachlorocyclopentadiene	0.50	0.43	5.6	86	0.072
Hexazinone	0.50	0.70	5.0	140	0.11
Indeno[1,2,3-cd]pyrene	0.50	0.69	2.7	139	0.057
Isophorone	0.50	0.44	3.2	88	0.042
Methoxychlor	0.50	0.62	4.2	123	0.077
Methyl Paraoxon	0.50	0.57	10	115	0.17
Metolachlor	0.50	0.37	8.0	75	0.090
Metribuzin	0.50	0.49	11	97	0.16
Mevinphos	0.50	0.57	12	114	0.20
MGK 264 - Isomer a	0.33	0.39	3.4	116	0.040
MGK 264 - Isomer b	0.17	0.16	6.4	96	0.030
Molinate	0.50	0.53	5.5	105	0.087
Napropamide	0.50	0.58	3.5	116	0.060
Norflurazon	0.50	0.63	7.1	126	0.13
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.50	0.50	8.7	101	0.13
Pebulate	0.50	0.49	5.4	98	0.080
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.30	16	61	0.15

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Pentachlorophenol	ND	ND	ND	ND	ND
Permethrin, cis	0.25	0.30	3.7	121	0.034
Permethrin, trans	0.75	0.82	2.7	109	0.067
Phenathrene	0.50	0.46	4.3	92	0.059
Prometon[a]	0.50	0.30	42	60	0.38
Prometryn	0.50	0.46	5.6	92	0.078
Pronamide	0.50	0.54	5.9	108	0.095
Propachlor	0.50	0.49	7.5	98	0.11
Propazine	0.50	0.54	7.1	108	0.12
Pyrene	0.50	0.38	5.7	77	0.066
Simazine	0.50	0.55	9.1	109	0.15
Simetryn	0.50	0.52	8.2	105	0.13
Stirofos	0.50	0.75	5.8	149	0.13
Tebuthiuron	5.0	6.8	14	136	2.8
Terbacil	5.0	4.9	14	97	2.1
Terbufos	0.50	0.53	6.1	106	0.096
Terbutryn	0.50	0.47	7.6	95	0.11
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.36	4.1	71	0.044
Toxaphene	ND	ND	ND	ND	ND
Triademefon	0.50	0.57	20	113	0.33
2,4,5-Trichlorobiphenyl	0.50	0.38	6.7	75	0.075
Tricyclazole	5.0	4.6	19	92	2.6
Trifluralin	0.50	0.63	5.1	127	0.096
Vernolate	0.50	0.51	5.5	102	0.084

ND = Not determined.

[a] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.6	2.6	93	
Perylene-d12	5.0	4.8	1.6	95	
Triphenylphosphate	5.0	5.0	2.5	101	
Target Analytes					
Acenaphthylene	0.50	0.47	8.4	94	0.12
Alachlor	0.50	0.50	5.8	100	0.087
Aldrin	0.50	0.39	13	78	0.16
Ametryn	0.50	0.38	28	76	0.32
Anthracene	0.50	0.49	13	98	0.18
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
Atraton[a]	0.50	0.07	139	19	0.29
Atrazine	0.50	0.60	3.7	119	0.065
Benz[a]anthracene	0.50	0.38	6.1	76	0.070
Benzo[b]fluoranthene	0.50	0.61	2.5	121	0.046
Benzo[k]fluoranthene	0.50	0.61	27	122	0.50
Benzo[g,h,i]perylene	0.50	0.69	1.4	138	0.029
Benzo[a]pyrene	0.50	0.58	6.1	116	0.11
Bromacil	0.50	0.49	23	99	0.34
Butachlor	0.50	0.63	2.1	127	0.039
Butylate	0.50	0.50	4.9	99	0.073
Butylbenzylphthalate	0.50	0.78	5.5	156	0.13
Carboxin	5.0	2.7	12	54	0.98
Chlordane (alpha-Chlordane)	0.50	0.37	5.5	74	0.061
Chlordane (gamma-Chlordane)	0.50	0.40	4.2	80	0.050
Chlordane (trans-Nonachlor)	0.50	0.45	7.8	90	0.11
Chlorneb	0.50	0.51	7.3	100	0.11
Chlorobenzilate	5.0	7.9	8.4	156	2.0

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2-Chlorobiphenyl	0.50	0.42	1.9	84	0.023
Chlorpropham	0.50	0.68	5.4	134	0.11
Chlorpyrifos	0.50	0.61	6.5	119	0.12
Chlorothalonil	0.50	0.59	6.5	116	0.11
Chrysene	0.50	0.35	3.6	71	0.038
Cyanazine	0.50	0.68	15	136	0.31
Cycloate	0.50	0.53	4.9	106	0.077
DCPA	0.50	0.55	4.5	110	0.073
4,4'-DDD	0.50	0.67	14	137	0.28
4,4'-DDE	0.50	0.48	4.9	96	0.070
4,4'-DDT	0.50	0.93	3.2	187	0.090
Diazinon	0.50	0.56	6.8	109	0.11
Dibenz[a,h]anthracene	0.50	0.61	15	122	0.28
Di-n-Butylphthalate	ND	ND	ND	ND	ND
2,3-Dichlorobiphenyl	0.50	0.46	8.1	93	0.11
Dichlorvos	0.50	0.54	5.6	108	0.092
Dieldrin	0.50	0.52	7.8	104	0.12
Di-(2-ethylhexyl)adipate	ND	ND	ND	ND	ND
Di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
Diethylphthalate	0.50	0.66	10	132	0.20
Dimethylphthalate	0.50	0.57	8.3	114	0.14
2,4-Dinitrotoluene	0.50	0.54	5.7	109	0.093
2,6-Dinitrotoluene	0.50	0.48	4.9	96	0.071
Diphenamid	0.50	0.60	3.8	118	0.067
Disulfoton	5.0	4.8	9.4	96	1.3
Disulfoton Sulfone	0.50	0.82	2.8	164	0.070
Disulfoton Sulfoxide	0.50	0.68	8.9	136	0.18
Endosulfan I	0.50	0.65	10	132	0.20
Endosulfan II	0.50	0.60	21	122	0.38
Endosulfan Sulfate	0.50	0.67	6.1	133	0.12
Endrin	0.50	0.58	18	116	0.31
Endrin Aldehyde	0.50	0.51	16	101	0.24
EPTC	0.50	0.50	3.8	100	0.056
Ethoprop	0.50	0.69	2.3	138	0.048
Etridiazole	0.50	0.74	4.0	149	0.090

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (μg/L)	Mean Observed Conc. (μg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (μg/L)
Fenamiphos	5.0	6.3	8.8	124	1.6
Fenarimol	5.0	7.5	5.5	150	1.2
Fluorene	0.50	0.47	8.1	94	0.11
Fluridone	5.0	5.7	4.5	114	0.77
HCH, alpha	0.50	0.54	12	107	0.20
HCH, beta	0.50	0.57	17	112	0.28
HCH, delta	0.50	0.61	8.2	120	0.15
HCH, gamma (Lindane)	0.50	0.62	6.6	124	0.12
Heptachlor	0.50	0.40	12	80	0.14
Heptachlor Epoxide	0.50	0.36	8.7	71	0.093
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.36	13	71	0.14
Hexachlorobenzene	0.50	0.47	8.3	95	0.12
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.41	11	83	0.13
Hexachlorocyclopentadiene	0.50	0.42	12	84	0.16
Hexazinone	0.50	0.85	5.6	169	0.14
Indeno[1,2,3-cd]pyrene	0.50	0.69	2.4	138	0.050
Isophorone	0.50	0.41	4.2	83	0.052
Methoxychlor	0.50	0.58	1.9	117	0.033
Methyl Paraoxon	0.50	0.62	14	122	0.25
Metolachlor	0.50	0.38	7.5	75	0.084
Metribuzin	0.50	0.54	3.9	107	0.062
Mevinphos	0.50	0.72	3.7	143	0.079
MGK 264 - Isomer a	0.33	0.40	8.8	119	0.10
MGK 264 - Isomer b	0.17	0.17	5.9	103	0.030
Molinate	0.50	0.53	3.2	105	0.050
Napropamide	0.50	0.64	5.9	126	0.11
Norflurazon	0.50	0.70	4.2	141	0.089
2,2',3,3',4,5',6,6'-Octachloro-biphenyl	0.50	0.51	4.2	102	0.064
Pebulate	0.50	0.48	5.8	96	0.084
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.35	4.2	70	0.044
Pentachlorophenol	2.0	1.9	16	95	.89
Permethrin,cis	0.25	0.32	3.3	126	0.031
Permethrin,trans	0.75	0.89	1.9	118	0.051

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	**True Conc. (µg/L)**	**Mean Observed Conc. (µg/L)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**MDL (µg/L)**
Phenathrene	0.50	0.48	5.0	95	0.071
Prometon[a]	0.50	0.21	66	45	0.44
Prometryn	0.50	0.46	24	93	0.33
Pronamide	0.50	0.58	7.1	113	0.12
Propachlor	0.50	0.49	5.4	98	0.079
Propazine	0.50	0.59	5.0	117	0.088
Pyrene	0.50	0.40	3.2	79	0.038
Simazine	0.50	0.60	10	120	0.18
Simetryn	0.50	0.41	15	83	0.19
Stirofos	0.50	0.84	3.2	168	0.081
Tebuthiuron	5.0	9.3	8.6	187	2.4
Terbacil	5.0	5.0	11	100	1.7
Terbufos	0.50	0.62	4.2	123	0.077
Terbutryn	0.50	0.46	23	94	0.32
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.40	7.4	79	0.088
Toxaphene	ND	ND	ND	ND	ND
Triademefon	0.50	0.73	7.2	145	0.16
2,4,5-Trichlorobiphenyl	0.50	0.44	5.3	89	0.071
Tricyclazole	5.0	6.8	12	137	2.4
Trifluralin	0.50	0.62	2.6	124	0.048
Vernolate	0.50	0.51	3.4	100	0.051

ND = Not determined.

[a] Data from samples extracted at ph 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.9	8.4	98	
Perylene-d12	5.0	4.3	18	86	
Triphenylphosphate	5.0	4.8	13	96	
Target Analytes					
Acenaphthylene	0.50	0.50	8.8	100	0.13
Alachlor	0.50	0.58	4.0	115	0.069
Aldrin	0.50	0.42	3.5	85	0.045
Ametryn	0.50	0.46	3.3	91	0.045
Anthracene	0.50	0.42	3.8	84	0.048
Aroclor 1016	1.0	1.1	4.4	113	0.15
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
Aroclor 1254[a]	1.0	1.1	17	110	0.56
Aroclor 1260	1.0	0.96	9.3	96	0.27
Atraton[c]	0.50	0.35	11	70	0.12
Atrazine	0.50	0.55	5.0	109	0.081
Benz[a]anthracene	0.50	0.43	7.3	85	0.093
Benzo[b]fluoranthene	0.50	0.44	16	88	0.21
Benzo[k]fluoranthene	0.50	0.34	22	68	0.23
Benzo[g,h,i]perylene	0.50	0.38	31	76	0.35
Benzo[a]pyrene	0.50	0.36	21	73	0.23
Bromacil	0.50	0.45	9.1	90	0.12
Butachlor	0.50	0.67	12	133	0.24
Butylate	0.50	0.52	5.2	104	0.082
Butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
Carboxin	0.50	0.58	22	117	0.38
Chlordane, (alpha-Chlordane)	0.50	0.47	12	95	0.17
Chlordane, (gamma-Chlordane)	0.50	0.50	10	99	0.16
Chlordane, (trans-Nonachlor)	0.50	0.48	11	96	0.16

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	**True Conc. (µg/L)**	**Mean Observed Conc. (µg/L)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**MDL (µg/L)**
Chlorneb	0.50	0.51	8.1	103	0.13
Chlorobenzilate	0.50	0.61	9.7	123	0.17
2-Chlorobiphenyl	0.50	0.47	4.8	94	0.068
Chlorpropham	0.50	0.55	8.1	109	0.13
Chlorpyrifos	0.50	0.50	2.4	99	0.035
Chlorothalonil	0.50	0.62	5.3	123	0.098
Chrysene	0.50	0.50	9.2	99	0.14
Cyanazine	0.50	0.49	13	97	0.19
Cycloate	0.50	0.52	7.6	103	0.12
DCPA	0.50	0.55	7.2	109	0.12
4,4'-DDD	0.50	0.52	3.6	103	0.055
4,4'-DDE	0.50	0.41	5.8	81	0.070
4,4'-DDT	0.50	0.54	2.4	108	0.039
Diazinon	0.50	0.37	2.7	75	0.030
Dibenz[a,h]anthracene	0.50	0.37	29	74	0.32
Di-n-Butylphthalate[b]	5.0	6.2	4.6	124	0.89
2,3-Dichlorobiphenyl	0.50	0.45	5.8	90	0.079
Dichlorvos	0.50	0.53	8.0	106	0.13
Dieldrin	0.50	0.50	10	100	0.15
Di(2-Ethylhexyl)adipate	0.50	0.59	18	117	0.31
Di(2-Ethylhexyl)phthalate[b]	5.0	6.5	6.6	130	1.3
Diethylphthalate	0.50	0.63	15	126	0.28
Dimethylphthalate	0.50	0.51	9.5	102	0.14
2,4-Dinitrotoluene	0.50	0.45	18	91	0.24
2,6-Dinitrotoluene	0.50	0.40	17	80	0.20
Diphenamid	0.50	0.55	6.5	111	0.11
Disulfoton	0.50	0.62	9.8	124	0.18
Disulfoton Sulfone	0.50	0.64	3.5	128	0.068
Disulfoton Sulfoxide	0.50	0.57	8.6	114	0.15
Endosulfan I	0.50	0.60	6.1	121	0.11
Endosulfan II	0.50	0.64	3.9	128	0.074
Endosulfan Sulfate	0.50	0.58	5.4	116	0.093
Endrin	0.50	0.62	18	124	0.34
Endrin Aldehyde	0.50	0.58	8.7	116	0.15
EPTC	0.50	0.53	7.7	105	0.12

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Ethoprop	0.50	0.62	10	124	0.19
Etridiazole	0.50	0.61	6.5	122	0.12
Fenamiphos	0.50	0.67	12	133	0.24
Fenarimol	0.50	0.74	11	148	0.25
Fluorene	0.50	0.49	9.0	98	0.13
Fluridone	5.0	5.2	2.5	105	0.39
HCH, alpha	0.50	0.55	6.8	109	0.11
HCH, beta	0.50	0.54	5.3	107	0.085
HCH, delta	0.50	0.52	3.1	105	0.049
HCH, gamma (Lindane)	0.50	0.53	5.3	105	0.084
Heptachlor	0.50	0.50	4.1	100	0.061
Heptachlor Epoxide	0.50	0.54	8.2	108	0.13
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.45	11	90	0.15
Hexachlorobenzene	0.50	0.41	6.0	82	0.074
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.40	15	80	0.18
Hexachlorocyclopentadiene	0.50	0.34	13	68	0.13
Hexazinone	0.50	0.80	5.6	159	0.14
Indeno[1,2,3-cd]pyrene	0.50	0.36	28	71	0.30
Isophorone	0.50	0.54	7.9	107	0.13
Methoxychlor	0.50	0.58	7.7	115	0.13
Methyl Paraoxon	0.50	0.85	3.7	170	0.094
Metolachlor	0.50	0.58	4.8	117	0.085
Metribuzin	0.50	0.54	14	108	0.22
Mevinphos	0.50	0.47	12	95	0.17
MGK 264 - Isomer a	0.33	0.38	9.5	113	0.11
MGK 264 - Isomer b	0.16	0.18	5.4	105	0.029
Molinate	0.50	0.55	5.2	111	0.086
Napropamide	0.50	0.63	10	127	0.20
Norflurazon	0.50	0.82	3.8	165	0.093
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.50	0.49	19	99	0.28
Pebulate	0.50	0.56	6.1	112	0.10

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	**True Conc. (µg/L)**	**Mean Observed Conc. (µg/L)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**MDL (µg/L)**
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.43	8.7	86	0.11
Pentachlorophenol	2.0	2.4	10	119	0.72
Permethrin,cis	0.25	0.45	3.2	179	0.043
Permethrin,trans	0.75	1.1	2.2	153	0.074
Phenanthrene	0.50	0.48	4.8	96	0.069
Prometon[c]	0.50	0.24	27	48	0.20
Prometryn	0.50	0.46	3.0	92	0.041
Pronamide	0.50	0.56	5.3	113	0.089
Propachlor	0.50	0.56	8.6	112	0.14
Propazine	0.50	0.52	4.3	103	0.066
Pyrene	0.50	0.47	11	95	0.16
Simazine	0.50	0.48	8.8	96	0.13
Simetryn	0.50	0.48	2.9	96	0.042
Stirofos	0.50	0.80	3.9	160	0.093
Tebuthiuron	0.50	0.67	7.4	134	0.15
Terbacil	0.50	0.59	12	119	0.22
Terbufos	0.50	0.46	11	92	0.15
Terbutryn	0.50	0.48	2.6	97	0.038
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.40	6.4	81	0.077
Toxaphene	10	11	4.9	118	1.7
Triademefon	0.50	0.73	6.4	146	0.14
2,4,5-Trichlorobiphenyl	0.50	0.44	3.3	88	0.043
Tricyclazole	0.50	0.63	16	127	0.31
Trifluralin	0.50	0.62	13	124	0.24
Vernolate	0.50	0.50	9.3	101	0.14

[a] Seven replicates.

[b] Seven replicates in fortified tap water.

[c] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	10	98	
perylene-d12	5.0	4.9	4.5	98	
triphenylphosphate	5.0	5.9	8.1	117	
Target Analytes					
Acenaphthylene	0.50	0.51	4.5	102	0.068
Alachlor	0.50	0.54	6.6	108	0.11
Aldrin	0.50	0.45	6.3	90	0.085
Ametryn	0.50	0.41	23	82	0.29
Anthracene	0.50	0.39	15	79	0.18
Aroclor 1016	0.20	0.25	4.7	123	0.040
Aroclor 1221	0.20	0.26	6.1	130	0.054
Aroclor 1232	0.20	0.24	4.7	121	0.042
Aroclor 1242	0.20	0.26	4.9	129	0.043
Aroclor 1248	0.20	0.24	4.1	118	0.038
Aroclor 1254	0.20	0.22	3.7	110	0.028
Aroclor 1260[a]	0.20	0.21	2.2	108	0.018
Atraton[d]	0.50	0.10	46	21	0.14
Atrazine	0.50	0.56	4.6	111	0.076
Benz[a]anthracene	0.50	0.44	7.4	88	0.098
Benzo[b]fluoranthene	0.50	0.50	9.1	100	0.14
Benzo[k]fluoranthene	0.50	0.46	2.2	91	0.031
Benzo[g,h,i]perylene	0.50	0.47	7.9	95	0.11
Benzo[a]pyrene	0.50	0.44	12	89	0.16
Bromacil	0.50	0.49	4.4	99	0.066
Butachlor	0.50	0.66	5.1	132	0.10
Butylate	0.50	0.50	5.4	100	0.082
Butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
Carboxin	0.50	0.40	38.1	79	0.45
Chlordane, (alpha-Chlordane)	0.50	0.50	4.3	101	0.065
Chlordane, (gamma-Chlordane)	0.50	0.51	7.2	102	0.11
Chlordane, (trans-Nonachlor)	0.50	0.52	6.2	104	0.097
Chlorneb	0.50	0.54	6.3	108	0.10

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Chlorobenzilate	0.50	0.59	9.7	117	0.17
2-Chlorobiphenyl	0.50	0.50	4.7	100	0.070
Chlorpropham	0.50	0.55	4.7	111	0.079
Chlorpyrifos	0.50	0.54	11	109	0.18
Chlorothalonil	0.50	0.59	4.4	119	0.079
Chrysene	0.50	0.48	6.1	96	0.088
Cyanazine	0.50	0.52	8.3	105	0.13
Cycloate	0.50	0.51	4.1	102	0.063
DCPA	0.50	0.53	3.2	105	0.051
4,4'-DDD	0.50	0.63	16	127	0.31
4,4'-DDE	0.50	0.48	3.7	96	0.054
4,4'-DDT	0.50	0.58	7.2	117	0.13
Diazinon	0.50	0.50	4.5	101	0.068
Dibenz[a,h]anthracene	0.50	0.47	9.9	94	0.14
Di-n-Butylphthalate[b]	5.0	5.7	3.3	115	0.59
2,3-Dichlorobiphenyl	0.50	0.50	2.6	100	0.039
Dichlorvos	0.50	0.50	8.7	99	0.13
Dieldrin	0.50	0.53	7.0	106	0.11
Di(2-Ethylhexyl)adipate[b]	5.0	5.4	7.5	107	1.3
Di(2-Ethylhexyl)phthalate[b]	5.0	5.7	2.6	114	0.46
Diethylphthalate	0.50	0.68	5.0	137	0.10
Dimethylphthalate	0.50	0.51	5.0	102	0.077
2,4-Dinitrotoluene	0.50	0.30	8.1	59	0.072
2,6-Dinitrotoluene	0.50	0.28	6.4	56	0.054
Diphenamid	0.50	0.56	6.4	112	0.11
Disulfoton	0.50	0.70	5.3	139	0.11
Disulfoton Sulfone	0.50	0.64	5.9	128	0.11
Disulfoton Sulfoxide	0.50	0.60	3.8	119	0.068
Endosulfan I	0.50	0.61	4.9	122	0.089
Endosulfan II	0.50	0.66	6.1	131	0.12
Endosulfan Sulfate	0.50	0.57	9.0	115	0.16
Endrin	0.50	0.68	7.9	137	0.16
Endrin Aldehyde	0.50	0.57	2.8	114	0.048
EPTC	0.50	0.48	5.2	97	0.076
Ethoprop	0.50	0.61	7.5	122	0.14

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (μg/L)	Mean Observed Conc. (μg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (μg/L)
Etridiazole	0.50	0.54	4.2	108	0.067
Fenamiphos	0.50	0.67	10	133	0.20
Fenarimol	0.50	0.59	5.8	118	0.10
Fluorene	0.50	0.53	3.4	106	0.054
Fluridone	5.0	5.2	2.3	104	0.16
HCH, alpha	0.50	0.55	5.0	110	0.083
HCH, beta	0.50	0.54	4.1	109	0.068
HCH, delta	0.50	0.53	3.6	106	0.058
HCH, gamma (Lindane)	0.50	0.50	3.2	100	0.047
Heptachlor	0.50	0.49	4.0	98	0.059
Heptachlor Epoxide	0.50	0.50	3.2	100	0.048
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.46	7.3	92	0.10
Hexachlorobenzene	0.50	0.49	3.4	97	0.049
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.50	5.3	99	0.079
Hexachlorocyclopentadiene	0.50	0.37	9.3	73	0.10
Hexazinone	0.50	0.75	4.2	150	0.094
Indeno[1,2,3-cd]pyrene	0.50	0.48	7.3	96	0.10
Isophorone	0.50	0.51	4.3	102	0.066
Methoxychlor	0.50	0.52	6.7	104	0.10
Methyl Paraoxon	0.50	0.75	4.5	151	0.10
Metolachlor	0.50	0.57	3.2	114	0.054
Metribuzin	0.50	0.53	5.7	107	0.090
Mevinphos	0.50	0.56	6.2	112	0.10
MGK 264 - Isomer a	0.33	0.38	6.7	113	0.076
MGK 264 - Isomer b	0.16	0.18	5.3	110	0.029
Molinate	0.50	0.53	3.8	105	0.060
Napropamide	0.50	0.58	7.9	116	0.14
Norflurazon	0.50	0.71	4.3	142	0.091
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.50	0.47	5.3	94	0.076
Pebulate	0.50	0.56	7.1	112	0.11
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.49	4.0	97	0.059
Pentachlorophenol	2.0	2.2	15	111	1.0
Permethrin,cis	0.25	0.37	3.1	149	0.035

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Permethrin,trans	0.75	0.84	1.6	112	0.039
Phenanthrene	0.50	0.49	6.3	97	0.092
Prometon[d]	0.50	0.16	63	32	0.30
Prometryn	0.50	0.46	23	91	0.32
Pronamide	0.50	0.56	3.9	111	0.064
Propachlor	0.50	0.58	5.7	115	0.098
Propazine	0.50	0.53	4.7	106	0.074
Pyrene	0.50	0.52	5.2	104	0.080
Simazine	0.50	0.54	2.8	107	0.045
Simetryn	0.50	0.36	20	71	0.22
Stirofos	0.50	0.72	3.7	144	0.080
Tebuthiuron	0.50	0.67	7.9	133	0.16
Terbacil	0.50	0.64	12	129	0.23
Terbufos	0.50	0.57	6.8	113	0.11
Terbutryn	0.50	0.46	24	93	0.34
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.46	7.4	91	0.10
Toxaphene[c]	10	12	2.7	122	1.0
Triademefon	0.50	0.71	7.3	142	0.16
2,4,5-Trichlorobiphenyl	0.50	0.48	4.5	97	0.066
Tricyclazole	0.50	0.65	14	130	0.27
Trifluralin	0.50	0.59	7.8	117	0.14
Vernolate	0.50	0.50	3.2	99	0.047

[a] Six replicates.

[b] Seven replicates in fortified tap water.

[c] Seven replicates.

[d] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 7. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS AT 5 µg/L IN REAGENT WATER OF POORLY CHROMATOGRAPHED NITROGEN AND PHOSPHOROUS CONTAINING PESTICIDES

	Ion Trap Mass Spectrometer				**Quadrupole Mass Spectrometer**			
	Cartridge		**Disk**		**Cartridge**		**Disk**	
Compound	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**	**Relative Standard Deviation (%)**	**Mean Method Accuracy (% of True Conc.)**
Fenamiphos	7.7	99	4.5	108	6.1	103	8.8	124
Fenarimol	2.0	104	10	110	6.5	126	5.5	150
Fluridone	2.5	105	2.3	104	3.6	102	4.5	114
Hexazinone	4.2	106	9.7	116	5.3	104	8.3	127
Norflurazon	4.1	111	9.6	119	3.2	98	11.1	113
Stirofos	8.2	114	12	124	4.1	110	11.1	125
Tebuthiuron	9.5	119	5.3	145	13	136	8.6	182
Triademeton	7.8	113	10	128	3.7	100	9.8	118
Tricyclazole	16	81	9.5	99	19	92	12	137

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
Acenaphthylene	5.0	5.2	5.3	104
Alachlor	5.0	5.5	6.9	110
Aldrin	5.0	4.4	14	88
Ametryn	5.0	4.2	3.4	83
Anthracene	5.0	4.3	5.2	87
Aroclor 1016	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND
Atraton[a]	5.0	2.2	28	43
Atrazine	5.0	5.6	6.2	111
Benz[a]anthracene	5.0	4.9	8.8	97
Benzo[b]fluoranthene	5.0	5.7	7.5	114
Benzo[k]fluoranthene	5.0	5.7	2.9	113
Benzo[g,h,i]perylene	5.0	5.6	7.1	113
Benzo[a]pyrene	5.0	6.1	4.6	121
Bromacil	5.0	3.5	5.1	69
Butachlor	5.0	5.4	7.5	109
Butylate	5.0	5.1	4.5	102
Butylbenzylphthalate	5.0	7.2	8.3	144
Carboxin	5.0	1.0	23	20
Chlordane, (alpha-Chlordane)	5.0	5.2	8.9	104
Chlordane, (gamma-Chlordane)	5.0	5.1	8.0	102
Chlordane, (trans-Nonachlor)	5.0	5.6	7.4	111
Chlorneb	5.0	5.2	3.0	105
Chlorobenzilate	5.0	5.7	4.4	114
2-Cchlorobiphenyl	5.0	5.8	5.4	115
Chlorpropham	5.0	6.3	4.9	127
Chlorpyrifos	5.0	5.3	7.2	107
Chlorthalonil	5.0	5.4	9.9	108
Chrysene	5.0	5.5	3.9	110
Cyanazine	5.0	6.1	13	122
Cycloate	5.0	5.6	1.5	112
DCPA	5.0	5.4	5.0	107
4,4'-DDD	5.0	5.3	6.5	105

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
4,4'-DDE	5.0	5.2	6.6	104
4,4'-DDT	5.0	5.6	9.6	111
Diazinon	5.0	4.9	8.7	98
Dibenz[a,h]anthracene	5.0	5.9	7.5	118
Di-n-Butylphthalate	5.0	6.2	4.6	124
2,3-Dichlorobiphenyl	5.0	5.3	7.4	106
Dichlorvos	5.0	2.8	7.3	56
Dieldrin	5.0	5.3	7.2	105
Di(2-Ethylhexyl)adipate	5.0	6.7	10	134
Di(2-Ethylhexyl)phthalate	5.0	6.5	6.6	130
Diethylphthalate	5.0	6.4	7.4	127
Dimethylphthalate	5.0	5.8	7.1	116
2,4-Dinitrotoluene	5.0	4.2	8.7	84
2,6-Dinitrotoluene	5.0	4.1	8.5	82
Diphenamid	5.0	5.2	7.7	104
Disulfoton	5.0	2.5	33	50
Disulfoton Sulfone	5.0	5.5	7.4	110
Disulfoton Sulfoxide	5.0	9.4	11	188
Endosulfan I	5.0	5.5	11	109
Endosulfan II	5.0	5.3	9.6	106
Endosulfan Sulfate	5.0	5.3	7.8	106
Endrin	5.0	6.1	3.9	121
Endrin Aldehyde	5.0	5.1	9.1	102
EPTC	5.0	5.1	2.1	102
Ethoprop	5.0	6.3	4.2	125
Etridiazole	5.0	5.8	7.5	117
Fenamiphos	5.0	5.9	22	119
Fenarimol	5.0	7.1	3.3	141
Fluorene	5.0	5.7	5.2	114
Fluridone	5.0	6.2	9.0	125
HCH, alpha	5.0	5.9	2.6	118
HCH, beta	5.0	5.3	8.4	106
HCH, delta	5.0	5.3	5.2	106
HCH, gamma (Lindane)	5.0	5.3	6.9	107
Heptachlor	5.0	4.7	8.7	93
Heptachlor Epoxide	5.0	5.2	7.7	105
2,2',3,3',4,4',6-Heptachlorobiphenyl	5.0	5.1	6.9	103
Hexachlorobenzene	5.0	4.6	7.4	93

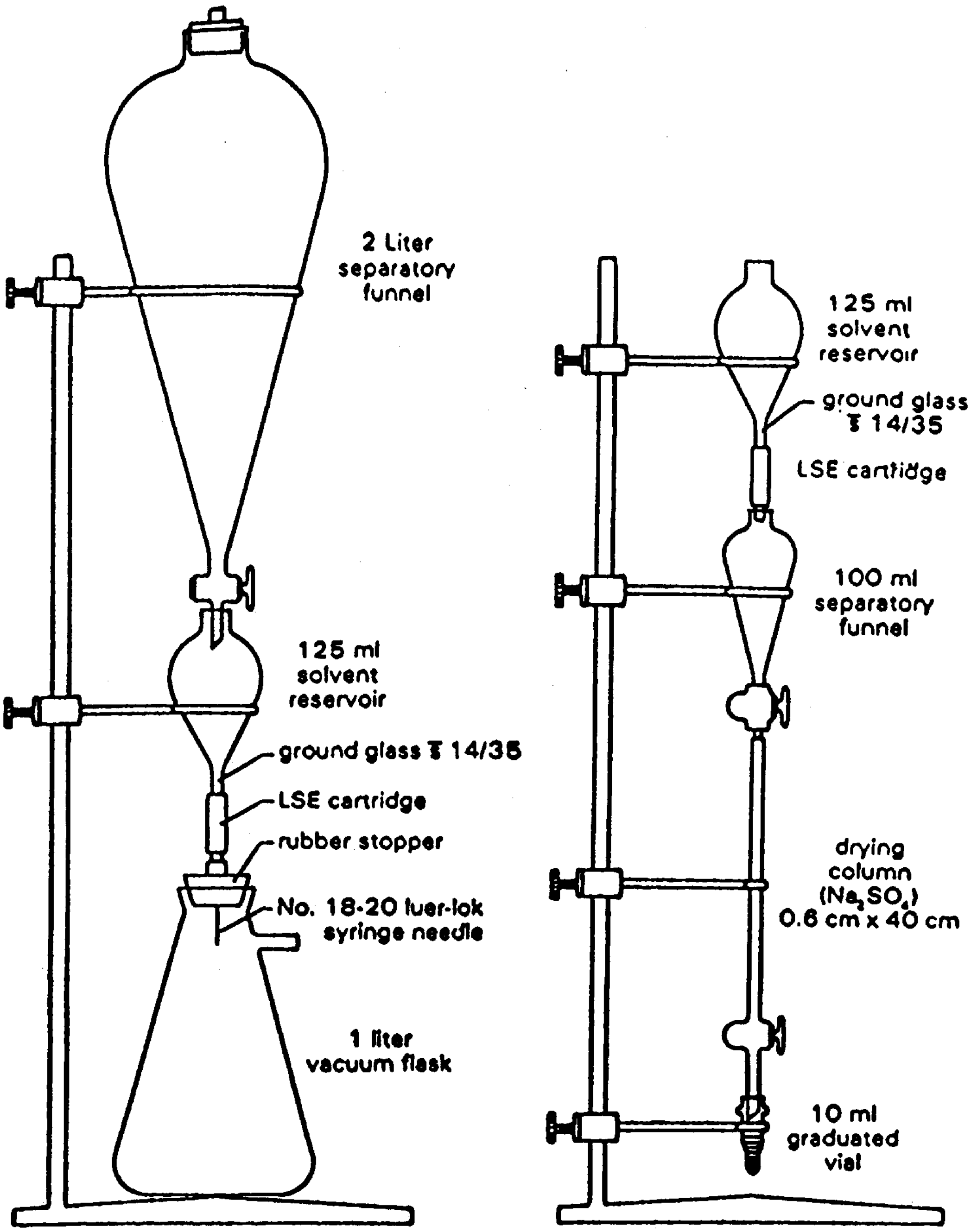
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
2,2',4,4',5,6'-Hexachlorobiphenyl	5.0	5.6	8.1	112
Hexachlorocyclopentadiene	5.0	6.0	4.8	120
Hexazinone	5.0	6.9	6.3	138
Indeno[1,2,3-cd]pyrene	5.0	6.8	7.7	135
Isophorone	5.0	4.9	12	99
Methoxychlor	5.0	5.6	4.9	112
Methyl Paraoxon	5.0	5.6	11	111
Metolachlor	5.0	5.6	7.7	111
Metribuzin	5.0	2.1	5.8	42
Mevinphos	5.0	3.3	1.6	67
MGK 264 - Isomer a	3.3	3.6	6.2	107
MGK 264 - Isomer b	1.7	1.8	7.6	110
Molinate	5.0	5.5	1.5	110
Napropamide	5.0	5.3	8.9	106
Norflurazon	5.0	6.7	7.2	135
2,2',3,3',4,5',6,6'-Octaclorobiphenyl	5.0	4.9	6.9	97
Pebulate	5.0	5.3	3.1	106
2,2',3',4,6-Pentachlorobiphenyl	5.0	5.3	8.1	107
Pentachlorophenol	20.	33	4.9	162
Permethrin, cis	5.0	3.3	3.5	130
Permethrin, trans	5.0	8.5	2.2	113
Phenanthrene	5.0	5.5	4.0	109
Prometona[a]	5.0	2.0	25	40
Prometryn	5.0	4.5	4.3	89
Pronamide	5.0	5.7	5.3	115
Propachlor	5.0	6.2	4.0	124
Propazine	5.0	5.6	4.9	113
Pyrene	5.0	5.2	6.7	104
Simazine	5.0	6.0	9.0	120
Simetryn	5.0	3.9	7.0	78
Stirofos	5.0	6.1	12	121
Tebuthiuron	5.0	6.5	9.7	130
Terbacil	5.0	4.0	5.5	79
Terbufos	5.0	4.5	8.4	90
Terbutryn	5.0	4.3	6.5	86
2,2',4,4'-Tetrachlorobiphenyl	5.0	5.3	4.3	106
Toxaphene	ND	ND	ND	ND
Triademefon	5.0	6.0	12	121

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

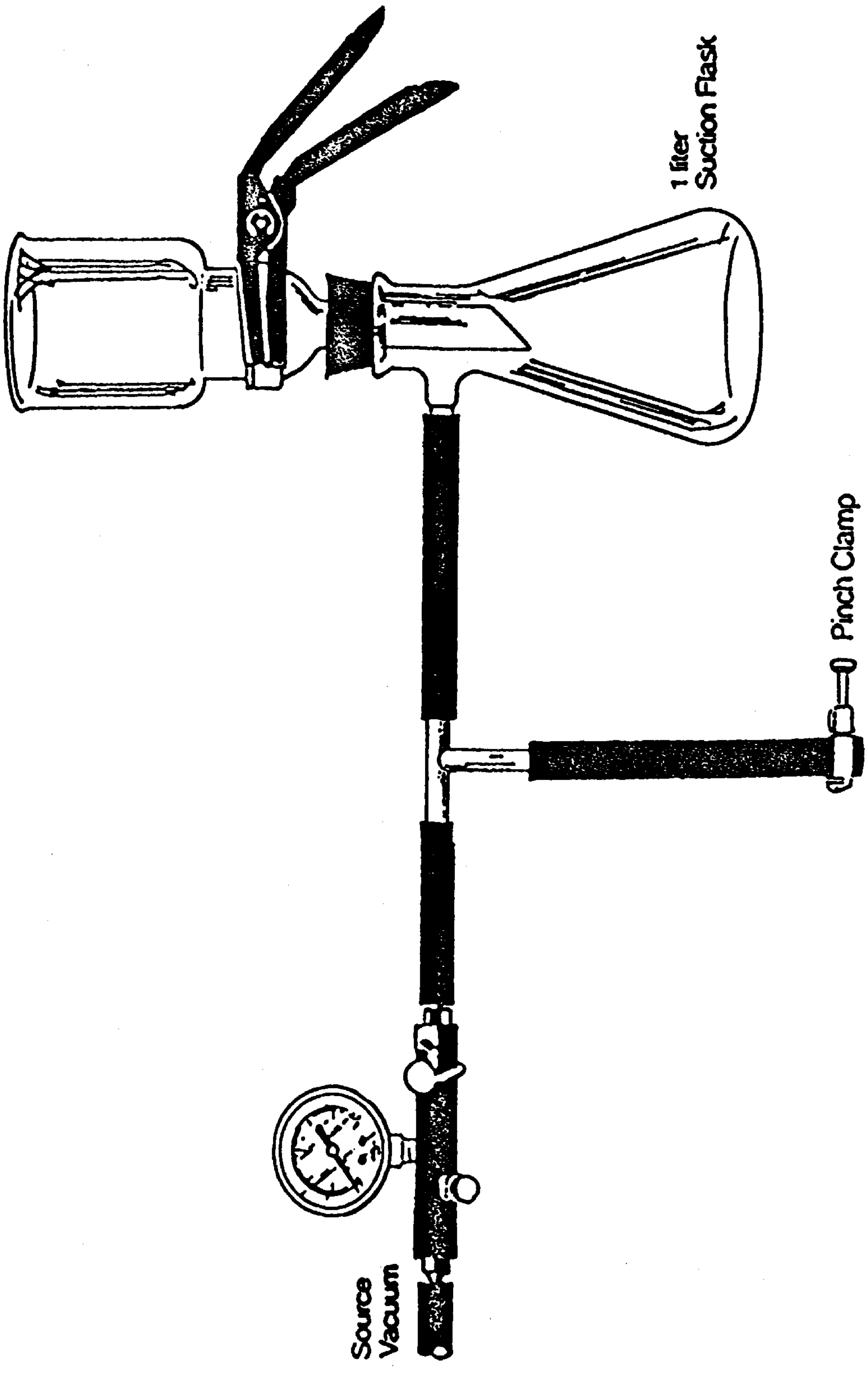
Compound	True Conc.	Mean	% RSD	% REC
2,4,5-Trichlorobiphenyl	5.0	5.2	5.1	103
Tricyclazole	5.0	4.8	5.2	96
Trifluralin	5.0	5.9	7.8	119
Vernolate	5.0	5.4	3.3	108

[a] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.



A. Extraction apparatus **B. Elution apparatus**

FIGURE 1. CARTRIDGE EXTRACTION APPARATUS


1 liter
Suction Flask
Pinch Clamp
Vacuum
Source

United States
Environmental Protection
Agency

METHOD 533: DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER BY ISOTOPE DILUTION ANION EXCHANGE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

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Disclaimer

This analytical method may support a variety of monitoring applications, which include the analysis of multiple short-chain per- and polyfluoroalkyl substances (PFAS) that cannot be measured by Method 537.1. This publication meets an agency commitment identified within the 2019 EPA PFAS Action Plan. Publication of the method, in and of itself, does not establish a requirement, although the use of this method may be specified by the EPA or a state through independent actions. Terms such as "must" or "required," as used in this document, refer to procedures that are to be followed to conform with the method. References to specific brands and catalog numbers are included only as examples and do not imply endorsement of the products. Such reference does not preclude the use of equivalent products from other vendors or suppliers.

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1 Scope and Application

This is a solid phase extraction (SPE) liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for the determination of select per- and polyfluoroalkyl substances (PFAS) in drinking water. Method 533 requires the use of MS/MS in Multiple Reaction Monitoring (MRM) mode to enhance selectivity. Accuracy and precision data have been generated in reagent water and drinking water for the compounds included in the Analyte List.

This method is intended for use by analysts skilled in the performance of solid phase extractions, the operation of LC-MS/MS instrumentation, and the interpretation of the associated data.

Analyte List

Analyte[a]	Abbreviation	CASRN
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acd	9Cl-PF3ONS	756426-58-1
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA	919005-14-4
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluoroheptanoic acid	PFHpA	375-85-9
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Perfluorononanoic acid	PFNA	375-95-1
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluoroundecanoic acid	PFUnA	2058-94-8

[a] Some PFAS are commercially available as ammonium, sodium, and potassium salts. This method measures all forms of the analytes as anions while the identity of the counterion is inconsequential. Analytes may be purchased as acids or as any of the corresponding salts.

1.1 Detection of PFAS Isomers

Both branched and linear PFAS isomers may be found in the environment. This method includes procedures for summing the contribution of multiple isomers to the final reported concentration. In those cases where standard materials containing multiple isomers are commercially available, laboratories should obtain such standards for the method analytes.

1.2 Lowest Concentration Minimum Reporting Limits

The lowest concentration minimum reporting level (LCMRL) is the lowest concentration for which the future recovery is predicted to fall between 50 and 150% with high confidence (99%). Single-laboratory LCMRLs determined for the method analytes during method development are reported in **Table 7**. It should be noted that most of the LCMRL values determined during the second laboratory evaluation were lower than the values listed in **Table 7**. The values that a laboratory can obtain are dependent on the design and capability of the instrumentation used. The procedure used to determine the LCMRL is described elsewhere.[1,2] Laboratories using this method are not required to determine LCMRLs, but they must demonstrate that they are able to meet the minimum reporting level (MRL) (Sect. 3.15) for each analyte per the procedure described in Section 9.1.4.

1.3 Method Flexibility

The laboratory may select LC columns, LC conditions, and MS conditions different from those used to develop the method. At a minimum, the isotope dilution standards and the isotope performance standards specified in the method must be used, if available. The laboratory may select the aqueous sample volume within the range of 100–250 mL that meets their objectives. During method development, 250 mL aqueous samples were extracted using a 500 mg solid phase extraction (SPE) sorbent bed volume. The ratio of sorbent mass to aqueous sample volume may not be decreased. If a laboratory uses 100 mL aqueous samples, the sorbent mass must be at least 200 mg. Changes may not be made to sample preservation, the quality control (QC) requirements, or the extraction procedure. The chromatographic separation should minimize the number of compounds eluting within a retention window to obtain a sufficient number of scans across each peak. Instrumental sensitivity (or signal-to-noise) will decrease if too many compounds are permitted to elute within a retention time window. Method modifications should be considered only to improve method performance. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the Initial Demonstration of Capability (IDC, Sect. 9.1), verify that all QC acceptance criteria in this method (Sect. 9.2) are met, and verify method performance in a representative sample matrix (Sect. 9.3.2).

2 Method Summary

A 100–250 mL sample is fortified with isotopically labeled analogues of the method analytes that function as isotope dilution standards. The sample is passed through an SPE cartridge containing polystyrene divinylbenzene with a positively charged diamino ligand to extract the method analytes and isotope dilution analogues. The cartridge is rinsed with sequential washes of aqueous ammonium acetate followed by methanol, then the compounds are eluted from the solid phase sorbent with methanol containing ammonium hydroxide. The extract is concentrated to dryness with nitrogen in a heated water bath. The extract volume is adjusted to 1.0 mL with 20% water in methanol (v/v), and three isotopically labeled isotope performance standards are added. Extracts are analyzed by LC-MS/MS in the MRM detection mode. The concentration of each analyte is calculated using the isotope dilution technique. For QC purposes, the percent recoveries of the isotope dilution analogues are calculated using the integrated peak areas of isotope performance standards, which are added to the final extract and function as traditional internal standards, exclusively applied to the isotope dilution analogues.

3 Definitions

3.1 Analysis Batch

A set of samples that are analyzed on the same instrument during a 24-hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) standards. Additional CCCs may be required depending on the length of the Analysis Batch and the number of field samples.

3.2 Calibration Standard

A solution of the method analytes, isotope dilution analogues, and isotope performance standards prepared from the Primary Dilution Standards and stock standards. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.3 Continuing Calibration Check (CCC)

A calibration standard that is analyzed periodically to verify the accuracy of the existing calibration.

3.4 Extraction Batch

A set of up to 20 field samples (not including QC samples) extracted together using the same lot of solid phase extraction devices, solvents, and fortifying solutions.

3.5 Field Duplicates (FD)

Separate samples collected at the same time and sampling location, shipped and stored under identical conditions. Method precision, including the contribution from sample collection procedures, is estimated from the analysis of Field Duplicates. Field Duplicates are used to prepare Laboratory Fortified Sample Matrix and Laboratory Fortified Sample Matrix Duplicate QC samples. For the purposes of this method, Field Duplicates are collected to support potential repeat analyses (if the original field sample is lost or if there are QC failures associated with the analysis of the original field sample).

3.6 Field Reagent Blank (FRB)

An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are introduced into the sample from shipping, storage, and the field environment.

3.7 Isotope Dilution Analogues

Isotopically labeled analogues of the method analytes that are added to the sample prior to extraction in a known amount. Note: Not all target PFAS currently have an isotopically labelled analogue. In these cases, an alternate isotopically labelled analogue is used as recommended in **Table 5**.

3.8 Isotope Dilution Technique

An analytical technique for measuring analyte concentration using the ratio of the peak area of the native analyte to that of an isotopically labeled analogue, added to the original sample in a known amount and carried through the entire analytical procedure.

3.9 Isotope Performance Standards

Quality control compounds that are added to all standard solutions and extracts in a known amount and used to measure the relative response of the isotopically labelled analogues that are components of the same solution. For this method, the isotope performance standards are three isotopically labeled analogues of the method analytes. The isotope performance standards are indicators of instrument performance and are used to calculate the recovery of the isotope dilution analogues through the extraction procedure. In this method, the isotope performance standards are not used in the calculation of the recovery of the native analytes.

3.10 Laboratory Fortified Blank (LFB)

An aliquot of reagent water to which known quantities of the method analytes and isotope dilution analogues are added. The results of the LFB verify method performance in the absence of sample matrix.

3.11 Laboratory Fortified Sample Matrix (LFSM)

An aliquot of a field sample to which known quantities of the method analytes and isotope dilution analogues are added. The purpose of the LSFM is to determine whether the sample matrix contributes bias to the analytical results. Separate field samples are required for preparing fortified matrix so that sampling error is included in the accuracy estimate.

3.12 Laboratory Fortified Sample Matrix Duplicate (LFSMD)

A Field Duplicate of the sample used to prepare the LFSM that is fortified and analyzed identically to the LFSM. The LFSMD is used instead of the Field Duplicate to assess method precision when the method analytes are rarely found at concentrations greater than the MRL.

3.13 Laboratory Reagent Blank (LRB)

An aliquot of reagent water fortified with the isotope dilution analogues and processed identically to a field sample. An LRB is included in each Extraction Batch to determine if the method analytes or other interferences are introduced from the laboratory environment, the reagents, glassware, or extraction apparatus.

3.14 Lowest Concentration Minimum Reporting Level (LCMRL)

The single-laboratory LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%.[1,2]

3.15 Minimum Reporting Level (MRL)

The minimum concentration that may be reported by a laboratory as a quantified value for a method analyte. For each method analyte, the concentration of the lowest calibration standard must be at or below the MRL and the laboratory must demonstrate its ability to meet the MRL per the criteria defined in Section 9.1.4.

3.16 Precursor Ion

The gas-phase species corresponding to the method analyte that is produced in the electrospray ionization interface. During tandem mass spectrometry, or MS/MS, the precursor ion is mass selected and fragmented by collision-activated dissociation to produce distinctive product ions of smaller mass to charge (*m/z*) ratio. For this method, the precursor ion is usually the deprotonated molecule ($[M - H]^-$) of the method analyte, except for HFPO-DA. For this analyte, the precursor ion is formed by decarboxylation of HFPO-DA.

3.17 Primary Dilution Standard (PDS)

A solution that contains method analytes (or QC analytes) prepared from stock standards. PDS solutions are used to fortify QC samples and diluted to prepare calibration standards.

3.18 Product Ion

One of the fragment ions that is produced in MS/MS by collision-activated dissociation of the precursor ion.

3.19 Quality Control Standard (QCS)

A calibration standard prepared independently from the primary calibration solutions. For this method, the QCS is a repeat of the entire dilution scheme starting with the same stock materials (neat compounds or purchased stock solutions) used to prepare the primary calibration solutions. Independent sources and separate lots of the starting materials are not required, provided the laboratory has obtained the purest form of the starting materials commercially available. The purpose of the QCS is to verify the integrity of the primary calibration standards.

3.20 Quantitative Standard

A quantitative standard of assayed concentration and purity traceable to a Certificate of Analysis.

3.21 Stock Standard Solution

A concentrated standard that is prepared in the laboratory using assayed reference materials or that is purchased from a commercial source with a Certificate of Analysis.

3.22 Technical-Grade Standard

As defined for this method, a technical-grade standard includes a mixture of the branched and linear isomers of a method analyte. For the purposes of this method, technical-grade standards are used to identify retention times of branched and linear isomers of method analytes.

4 Interferences

4.1 Labware, Reagents and Equipment

Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts or elevated baselines in the chromatograms. The analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, deactivated syringes, SPE sample transfer lines, etc.[3] Laboratories must demonstrate that these items are not contributing to interference by analyzing LRBs as described in Section 9.2.1.

4.2 Sample Contact with Glass

Aqueous samples should not come in contact with any glass containers or pipettes as PFAS analytes can potentially adsorb to glass surfaces. Standards dissolved in organic solvent may be purchased in glass ampoules. These standards in organic solvent are acceptable and subsequent transfers may be performed using glass syringes and pipets. Following extraction, the eluate must be collected in a polypropylene tube prior to concentration to dryness. Concentration to dryness in glass tubes may cause poor recovery.

4.3 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and fulvic material may be co-extracted during SPE and high levels may cause enhancement or suppression in the electrospray ionization source.[4] Inorganic salts may cause low recoveries during the anion-exchange SPE procedure.

4.3.1 Co-extracted Organic Material

Under the LC conditions used during method development, matrix effects due to co-extracted organic material enhanced the ionization of 4:2 FTS appreciably. Total organic carbon (TOC) is a good indicator of humic content of the sample.

4.3.2 Inorganic Salts

The authors confirmed acceptable method performance for matrix ion concentrations up to 250 mg/L chloride, 250 mg/L sulfate, and 340 mg/L hardness measured as $CaCO_3$. Acceptable performance was defined as recovery of the isotope dilution analogues between 50–200%.

4.3.3 Ammonium Acetate

Relatively large quantities of ammonium acetate are used as a preservative. The potential exists for trace-level organic contaminants in this reagent. Interferences from this source should be monitored by analysis of LRBs, particularly when new lots of this reagent are acquired.

4.3.4 SPE Cartridges

Solid phase extraction cartridges may be a source of interferences. The analysis of LRBs provides important information regarding the presence or absence of such interferences. Each brand and lot of SPE devices must be monitored to ensure that contamination does not preclude analyte identification and quantitation. SPE cartridges should be sealed while in storage to prevent ambient contamination of the SPE sorbent.

4.4 Bias Caused by Isotopically Labeled Standards

During method development, no isotopically labeled standard solution yielded any signal that gave the same mass and retention time as any native analyte. However, due to isotopic impurity, the $^{13}C_3$-PFBA isotope performance standard contained a small amount of $^{13}C_4$-PFBA, slightly contributing to the signal of the isotope dilution analogue. Further, due to natural abundance of ^{34}S, the native telomer sulfonates produced a small contribution to the $^{13}C_2$ labeled telomer sulfonate isotope dilution analogues. The effects on quantitation are insignificant. However, these cases are described below in Sections 4.4.2 and 4.4.3 to alert the user that these situations could occur.

4.4.1 Method Analytes

At the concentrations used to collect method performance data, the authors could not detect any contribution from the isotope dilution analogues or isotope performance standards to the corresponding native analyte response. However, the user should evaluate each source of isotopically labeled analogues and isotope performance standards to verify that they do not contain any native analyte at concentrations greater than 1/3 of the MRL.

4.4.2 Isotopic purity of $^{13}C_3$-PFBA

In this method, $^{13}C_3$-PFBA is used as an isotope performance standard and $^{13}C_4$-PFBA is used as an isotope dilution analogue. Both share the same product ion, *m/z* 172. Ten nanograms per liter of $^{13}C_4$-PFBA is added to the sample prior to extraction (10 ng/mL extract concentration assuming 100% recovery), and 10 ng/mL of $^{13}C_3$-PFBA is added to the final extract. Because the natural abundance of ^{13}C is 1.1%, there is a 1.1% contribution to the $^{13}C_4$-PFBA area from the lone, unlabeled ^{12}C atom in $^{13}C_3$-PFBA. The authors confirmed this contribution empirically. Users of this method may consider this bias to the area of the PFBA isotope dilution analogue insignificant.

4.4.3 Isotopic purity of $^{13}C_4$-PFBA

A trace amount of $^{13}C_3$-PFBA was detected in the $^{13}C_4$-PFBA. The contribution was no greater than 1%. The contribution of the isotope performance standard to the isotope dilution analogue is insignificant.

4.4.4 Telomer Sulfonates

Each of the three telomer sulfonates in the analyte list (4:2FTS, 6:2FTS, and 8:2FTS) are referenced to their $^{13}C_2$ isotope dilution analogue. The mass difference between the telomer sulfonates and the isotope dilution analogues is 2 mass units. The single sulfur atom in each of the unlabeled molecules has a naturally occurring M+2 isotope (^{34}S) at 4.25%. Thus, the precursor ions of the $^{13}C_2$ isotopically labeled analogues and the naturally occuring ^{34}S analogues present in the native analytes have the same nominal masses. The product ions of the telomer sulfonate isotope dilution analogues listed in **Table 6** would contain a small contribution from the ^{34}S analogue of the native telomer sulfonates. At the concentrations used in this study, the contribution of the ^{34}S analogue to the isotope dilution analogue was not greater than 2.7%. Alternate product ions may be used if there is sufficient abundance.

5 Safety

Each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of safety data sheets should be made available to all personnel involved in the chemical analysis.

6 Equipment and Supplies

References to specific brands and catalog numbers are included as examples only and do not imply endorsement of the products. Such reference does not preclude the use of equivalent products from other vendors or suppliers. Due to potential adsorption of analytes onto glass, polypropylene containers were used for sample preparation and extraction steps. Other plastic materials (e.g., polyethylene) that meet the QC requirements of Section 9 may be substituted.

6.1 Sample Containers

Polypropylene bottles with polypropylene screw caps (for example, 250 mL bottles, Fisher Scientific, Cat. No. 02-896-D or equivalent).

6.2 Polypropylene Vials

These vials are used to store stock standards and PDS solutions (4 mL, VWR Cat. No. 16066-960 or equivalent).

6.3 Centrifuge Tubes

Conical polypropylene centrifuge tubes (15 mL) with polypropylene screw caps for storing standard solutions and for collection of the eluate during the extraction procedure (Thomas Scientific Cat. No. 2602A10 or equivalent).

6.4 Autosampler Vials

Polypropylene autosampler vials (ThermoFisher, Cat. No. C4000-14) with polypropylene caps (ThermoFisher, Cat. No. C5000-50 or equivalent). Note: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, creating the potential for evaporation to occur after injection. Multiple injections from the same vial are not permissible unless the cap is replaced immediately after injection.

6.5 Micro Syringes

Suggested sizes include 10, 25, 50, 100, 250, 500 and 1000 µL.

6.6 Pipets

Polypropylene or glass pipets may be used for methanolic solutions.

6.7 Analytical Balance

Capable of weighing to the nearest 0.0001 g.

6.8 Solid Phase Extraction (SPE) Apparatus

6.8.1 SPE Cartridges

SPE cartridges containing weak anion exchange, mixed-mode polymeric sorbent (polymeric backbone and a diamino ligand), particle size approximately 33 µm. The SPE sorbent must have a pKa above 8 so that it remains positively charged during extraction. SPE cartridges containing 500 mg sorbent

(Phenomenex Cat. No. 8B-S038-HCH) were used during method development. Use of 200 mg cartridges is acceptable for the extraction of 100 mL samples.

6.8.2 Vacuum Extraction Manifold

Equipped with flow and vacuum control [Supelco Cat. No. 57030-U, UCT Cat. No. VMF016GL (the latter requires UCT Cat. No. VMF02116 control valves), or equivalent systems]. Automated devices designed for use with SPE cartridges may be used; however, all extraction and elution steps must be the same as in the manual procedure. Care must be taken with automated SPE systems to ensure that Teflon tubing and other PTFE components commonly used in these systems, do not contribute to unacceptable analyte concentrations in LRBs.

6.8.3 Sample Delivery System

Use of large volume sampling lines, constructed with polyethylene tubing, are recommended, but not mandatory. Large volume sample transfer lines, constructed with PTFE tubing, are commercially available for standard extraction manifolds (Supelco Cat. No. 57275 or equivalent). The PTFE tubing can be replaced with 1/8” o.d. x 1/16” i.d. polyethylene tubing [Freelin-Wade (McMinnville, Oregon) LLDPE or equivalent] cut to an appropriate length. This prevents potential contamination from PTFE transfer lines. Other types of non-PTFE tubing may be used provided it meets the LRB and LFB QC requirements. PTFE tubing may be used, but an LRB must be run on each individual transfer line and the QC requirements in Section 9.2.1 must be met. In the case of automated SPE, the removal of PTFE lines may not be feasible; therefore, acceptable performance for the LRB must be met for each port during the IDC (Sect 9.1.1). LRBs must be rotated among the ports during routine analyses thereafter. Plastic reservoirs are difficult to rinse during elution and their use may lead to lower recovery.

6.9 Extract Concentration System

Extracts are concentrated by evaporation with high-purity nitrogen using a water bath set no higher than 60 °C [N-Evap, Model 11155, Organomation Associates (Berlin, MA), Inc., or equivalent].

6.10 Laboratory Vacuum System

Sufficient capacity to maintain a vacuum of approximately 15 to 20 inches of mercury for extraction cartridges.

6.11 pH Meter

Used to verify the pH of the phosphate buffer and to measure the pH of the aqueous sample prior to anion exchange SPE.

6.12 LC-MS/MS System

6.12.1 LC System

The LC system must provide consistent sample injection volumes and be capable of performing binary linear gradients at a constant flow rate. On some LC systems, PFAS may build up in PTFE transfer lines when the system is idle for more than one day. To prevent long delays in purging high levels of PFAS from the LC solvent lines, it may be useful to replace PTFE tubing with PEEK™ tubing and the PTFE solvent frits with stainless steel frits. These modifications were not used on the LC system used for method development. However, a delay column, HLB Direct Connect 2.1 x 30 mm (Waters 186005231), was placed in the mobile phase flow path immediately before the injection valve. This direct connect column may have reduced the co-elution of PFAS originating from sources prior to the sample loop from the PFAS injected in the sample. It may not be possible to remove all PFAS background contamination.

6.12.2 Analytical Column

C18 liquid chromatography column (2 x 50 mm) packed with 3 µm C18 solid phase particles (Phenomenex Part Number 00B-4439-B0 or equivalent).

6.12.3 Electrospray Ionization Tandem Mass Spectrometer (ESI-MS/MS)

The mass spectrometer must be capable of electrospray ionization in the negative ion mode. The system must be capable of performing MS/MS to produce unique product ions for the method analytes within specified retention time segments. A minimum of 10 scans across the chromatographic peak is needed to ensure adequate precision. Some ESI-MS/MS instruments may not be suitable for PFAS analysis. See the procedures in Section 10.1.2.1 to ensure that the selected MS/MS platform is capable of monitoring all the required MS/MS transitions for the method analytes.

6.12.4 MS/MS Data System

An interfaced data system is required to acquire, store, and output MS data. The computer software must have the capability of processing stored data by recognizing a chromatographic peak within a given retention time window. The software must allow integration of the abundance of any specific ion between specified time or scan number limits. The software must be able to construct a linear regression or quadratic regression calibration curve and calculate analyte concentrations using the internal standard technique.

7 Reagents and Standards

Reagent grade or better chemicals must be used. Unless otherwise indicated, all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used if the reagent is demonstrated to be free of analytes and interferences and all requirements of the IDC are met when using these reagents.

7.1 Reagent Water

Purified water which does not contain any measurable quantities of any method analytes or interfering compounds greater than one-third of the MRL for each method analyte. It may be necessary to flush the water purification unit to rinse out any build-up of PFAS in the system prior to collection of reagent water.

7.2 Methanol

CH_3OH, CASRN 67-56-1, LC grade (Fisher Scientific, Cat. No. A456 or equivalent).

7.3 Ammonium Acetate

$NH_4C_2H_3O_2$, CASRN 631-61-8, HPLC grade, molecular weight equals 77.08 g/mole.

7.3.1 20 mM Ammonium Acetate

Chromatographic mobile phase. To prepare 1 L, add 1.54 g ammonium acetate to 1 L of reagent water. This solution is volatile and must be replaced at least once per week. More frequent replacement may be necessary if unexplained losses in sensitivity or retention time shifts are encountered.

7.3.2 1 g/L Ammonium Acetate

Used to rinse SPE cartridges after loading the aqueous sample and prior to the methanol rinse. Prepare in reagent water.

7.4 Concentrated Ammonium Hydroxide Reagent

NH_4OH, CASRN 1336-21-6, approximately 56.6% in water as ammonium hydroxide (w/w), approximately 28% in water as ammonia, approximately 14.5 N (Fisher Scientific, Cat. No. A669, Certified ACS Plus grade, or equivalent).

7.5 Solution of Ammonium Hydroxide in Methanol

Used for elution of SPE cartridges. Dilute 2 mL of concentrated ammonium hydroxide (56.6% w/w) in 100 mL methanol. This solution should be made fresh on the day of extraction.

7.6 Sodium Phosphate Dibasic (Na_2HPO_4)

Used for creating the aqueous buffer for conditioning the SPE cartridges. Dibasic sodium phosphate may be purchased in either the anhydrous or any hydrated form. The formula weight will vary based on degree of hydration.

7.7 Sodium Phosphate Monobasic (NaH_2PO_4)

Used for creating the aqueous buffer for conditioning the SPE cartridges. Monobasic sodium phosphate may be purchased in either the anhydrous or any hydrated form. The formula weight will vary based on degree of hydration.

7.8 0.1 M Phosphate Buffer pH 7.0

Mix 500 mL of 0.1 M dibasic sodium phosphate with approximately 275 mL of 0.1 M monobasic sodium phosphate. Verify that the solution pH is approximately 7.0.

7.9 Nitrogen

7.9.1 Nitrogen Nebulizer Gas

Nitrogen used as a nebulizer gas in the ESI interface and as collision gas in some MS/MS platforms should meet or exceed the instrument manufacturer’s specifications.

7.9.2 Nitrogen used for Concentrating Extracts

Ultra-high-purity-grade nitrogen should be used to concentrate sample extracts.

7.10 Argon

Used as collision gas in MS/MS instruments. Argon should meet or exceed instrument manufacturer’s specifications. Nitrogen may be used as the collision gas if recommended by the instrument manufacturer.

7.11 Sodium Hydroxide

May be purchased as pellets or as aqueous solution of known concentration. Added to methanolic solutions of PFAS to prevent esterification.

7.12 Acetic Acid (glacial)

May be necessary to adjust pH of aqueous samples. The pH of the aqueous sample containing 1 g/L ammonium acetate must be between 6 and 8.

7.13 Standard Solutions

7.13.1 Stability of Methanolic Solutions

Fluorinated carboxylic acids will esterify in anhydrous acidic methanol. To prevent esterification, standards must be stored under basic conditions. If base is not already present, this may be accomplished by the addition of sodium hydroxide (approximately 4 mole equivalents) when standards are diluted in methanol. When calculating molarity for solutions containing multiple PFAS, the molecular weight can be estimated as 250 atomic mass units (amu). It is necessary to include sodium hydroxide in solutions of both isotopically labeled and native analytes. The amount of sodium hydroxide needed may be calculated using the following equation:

$$\frac{Total\ PFAS\ mass\ (g) \times 160(\frac{g}{mol})}{250\ (\frac{g}{mol})} = Mass\ of\ NaOH\ Required\ (g)$$

7.13.2 Preparation of Standards

When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Sorption of PFAS analytes in methanol solution to glass surfaces after prolonged storage has not been evaluated. PFAS analyte and isotopically labeled analogues commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be stored in polypropylene containers.

Solution concentrations listed in this section were used to develop this method and are included as examples. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples. Laboratories should use standard QC practices to determine when standards need to be replaced. The analyte supplier's guidelines may be helpful when making this determination.

7.14 Storage Temperatures for Standards Solutions

Store stock standards at less than 4 °C unless the vendor recommends otherwise. The Primary Dilution Standards may be stored at any temperature, but cold storage is recommended to prevent solvent evaporation. During method development, the PDS was stored at –20 °C and no change in analyte concentrations was observed over a period of 6 months.

7.15 Isotope Performance Standards

This method requires three isotope performance standards listed in the table below. These isotopically labeled compounds were chosen during method development to include the analogues of three method analytes: two carboxylates with different chain lengths and a sulfonate.

Obtain the isotope performance standards as certified standard solutions, if available, or as the neat compounds. During method development, the isotope performance standards were obtained from Wellington Laboratories (Guelph, ON, Canada) as certified stocks in basic methanol. Note that Chemical Abstracts Registry Numbers are not currently available for these compounds. The concentrations of the stocks supplied by Wellington are listed in the table below.

Isotope Performance Standards	Abbreviation	Wellington Stock, µg/mL	PDS, ng/µL
Perfluoro-*n*-[2,3,4-$^{13}C_3$]butanoic acid	$^{13}C_3$-PFBA	50	1.0
Perfluoro-[1,2-$^{13}C_2$]octanoic acid	$^{13}C_2$-PFOA	50	1.0
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	$^{13}C_4$-PFOS	50[a]	3.0

[a] 47.8 µg/mL as the anion.

All the isotope performance standards listed in this section must be used, if available. Additional isotope performance standards may be used provided they are isotopically labeled analytes or labeled analytes with similar functional groups as the method analytes. Linear isomers are recommended to simplify peak integration. Method modification QC requirements must be met (Sect. 9.3) whenever additional isotope performance standards are used.

7.15.1 Isotope Performance Standard PDS

Prepare the isotope performance standard PDS in methanol and add sodium hydroxide if not already present to prevent esterification as described in Section 7.13.1. The PDS concentrations used to develop the method are listed in the table above (Sect. 7.15). During collection of method performance data, the final extracts were fortified with 10 µL of the PDS to yield a concentration of 10 ng/mL for $^{13}C_3$-PFBA and $^{13}C_2$-PFOA, and 30 ng/mL for $^{13}C_4$-PFOS (28.7 ng/mL as the anion).

7.16 Isotope Dilution Analogues

Obtain the isotopically labeled analogues listed in the table in this section as individual certified standard solutions or as certified standard mixes. All listed isotope dilution analogues must be used, if available. Linear isomers are recommended to simplify peak integration. During method development, the isotope dilution analogues were obtained from Wellington Laboratories (Guelph, ON, Canada) as certified stocks in basic methanol. These analogues were chosen during method development because they encompass most of the functional groups, as well as the molecular weight range of the method analytes. Note that Chemical Abstracts Registry Numbers are not currently available for these isotopically labeled analogues.

Isotope Dilution Standards	**Abbreviation**	**PDS, ng/µL[a]**
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4$-PFBA	0.50
Perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	$^{13}C_5$-PFPeA	0.50
Sodium perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	$^{13}C_3$-PFBS	0.50
Sodium 1*H*,1*H*,2*H*,2*H*-perfluoro-1-[1,2-$^{13}C_2$]hexane sulfonate	$^{13}C_2$-4:2FTS	2.0
Perfluoro-*n*-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	$^{13}C_5$-PFHxA	0.50
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-$^{13}C_3$-propanoic acid	$^{13}C_3$-HFPO-DA	0.50
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$]heptanoic acid	$^{13}C_4$-PFHpA	0.50
Sodium perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonate	$^{13}C_3$-PFHxS	0.50
Sodium 1*H*,1*H*,2*H*,2*H*-perfluoro-1-[1,2-13C_2]-octane sulfonate	$^{13}C_2$-6:2FTS	2.0
Perfluoro-*n*-[$^{13}C_8$]octanoic acid	$^{13}C_8$-PFOA	0.50
Perfluoro-*n*-[$^{13}C_9$]nonanoic acid	$^{13}C_9$-PFNA	0.50
Sodium perfluoro-[$^{13}C_8$]octanesulfonate	$^{13}C_8$-PFOS	0.50
Sodium 1*H*,1*H*,2*H*,2*H*-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate	$^{13}C_2$-8:2FTS	2.0
Perfluoro-*n*-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	$^{13}C_6$-PFDA	0.50
Perfluoro-*n*-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	$^{13}C_7$-PFUnA	0.50
Perfluoro-*n*-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2$-PFDoA	0.50

[a] Concentrations used during method development.

As additional isotopically labelled PFAS analogues become commercially available they may be integrated into the method provided they have similar functional groups as the method analytes or are isotopically labeled analogues of the method analytes. Method modification QC requirements must be met (Sect. 9.3) whenever new analogues are proposed.

7.16.1 Isotope Dilution Analogue PDS

Prepare the isotope dilution analogue PDS in methanol and add sodium hydroxide if not already present to prevent esterification as described in Section 7.13.1. The PDS concentrations used during method development are listed in the table above. Method performance data were collected using 20 µL of this PDS to yield concentrations of 40–160 ng/L in the 250 mL aqueous samples. Note that the concentrations of sulfonates in the isotope dilution analogue PDS is based on the weight of the salt. It is not necessary to account for difference in the formula weight of the salt compared to the free acid for sample quantitation.

7.17 Analyte Standard Materials

Analyte standards may be purchased as certified standard solutions or prepared from neat materials of assayed purity. If available, the method analytes should be purchased as technical-grade (as defined in Sect. 3.22) to ensure that linear and branched isomers are represented. Standards or neat materials that contain only the linear isomer can be substituted if technical-grade analytes are not available as quantitative standards.

During method development, analyte standards were obtained from AccuStandard, Inc. (New Haven, CT), Absolute Standards (Hamden, CT), Wellington Laboratories (Guelph, Ontario, Canada), Santa Cruz Biotechnology (Dallas, TX), and Synquest Laboratories, Inc. (Alachua, FL). Stock standards are made by dilution in methanol containing 4 mole equivalents of sodium hydroxide as described in Section 7.13.1

7.17.1 PFOA

A quantitative standard for PFOA is currently available only for the linear isomer; however, a technical-grade standard (Sect. 3.22) is available for PFOA that contains the linear and branched isomers (Wellington Labs, Cat. No. T-PFOA, or equivalent). This product or a similar technical-grade PFOA standard must be used to identify the retention times of the branched and linear PFOA isomers. However, the linear-only PFOA standard must be used for quantitation until a quantitative PFOA standard containing the branched and linear isomers becomes commercially available.

7.17.2 PFHxS and PFOS

Technical grade, quantitative PFHxS and PFOS standards containing branched and linear isomers must be used when available.

7.17.3 Correction for Analytes Obtained in the Salt Form

This method measures all forms of the analytes as anions while the identity of the counterion is inconsequential. Analytes may be commercially available as neat materials or as certified stock standards as their corresponding ammonium, sodium, or potassium salts. These salts are acceptable standards provided the measured mass, or concentration, is corrected for the salt content. The equation for this correction is provided below.

$$mass(acid\ form) = mass(salt\ form) \times \frac{MWacid}{MWsalt}$$

7.17.4 Analyte PDS

The analyte PDS is used to prepare the calibration standards and to fortify the LFBs, LFSMs and LFSMDs with the method analytes. Prepare the analyte PDS by combining and diluting the analyte stock standards in 100% methanol and add sodium hydroxide if not already present to prevent esterification as described in Section 7.13.1. Select nominal analyte concentrations for the PDS such that between 5 and 100 µL of the PDS is used to fortify samples and prepare standard solutions. More than one PDS concentration may be necessary to meet this requirement. During method development, the analyte PDS was prepared at an identical concentration for all analytes, 0.5 ng/µL. The user may modify the concentrations of the individual analytes based on the confirmed MRLs and the desired monitoring range. If the PDS is stored cold, warm the vials to room temperature and vortex prior to use.

7.17.5 Calibration Standards

Prepare a series of calibration standards of at least five levels by diluting the analyte PDS into methanol containing 20% reagent water. The lowest calibration standard must be at or below the MRL for each analyte. The calibration standards may also be used as Continuing Calibration Checks (CCCs). Using the PDS solutions, add a constant amount of the isotope performance standards and the isotope dilution analogues to each calibration standard. The concentration of the isotope dilution analogues should match the concentration of the analogues in sample extracts, assuming 100% recovery through the extraction process. During method development, the concentrations of the isotope dilution analogues were 40 ng/mL extract concentration (160 ng/L in the aqueous sample) for 4:2FTS, 6:2FTS and 8:2FTS, and 10 ng/mL (40 ng/L) for all others. The analyte calibration ranged from approximately 0.50 ng/mL to 25 ng/mL extract concentration.

8 Sample Collection, Preservation, and Storage

8.1 Sample Bottles

Samples must be collected in plastic bottles: polypropylene bottles fitted with polypropylene screw-caps, or polyethylene bottles with polypropylene screw caps. Discard sample bottles after a single use. The bottle volume should approximate the volume of the sample. Subsampling from a single bottle is not permitted except as described in Section 12.5.

8.2 Sample Preservation

Based on sample volume, add ammonium acetate to each sample bottle as a solid (prior to shipment to the field or immediately prior to sample collection) to achieve a 1g/L concentration of ammonium acetate. Ammonium acetate will sequester free chlorine to form chloramine.

8.3 Sample Collection

8.3.1 Precautions against Contamination

Workers must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. Users should seek to minimize accidental contamination of the samples.

8.3.2 Collection Procedure

Open the tap and allow the system to flush until the water temperature has stabilized. Collect samples from the flowing system. Samples do not need to be collected headspace free. After collecting the sample, cap the bottle and agitate by hand until the preservative is dissolved. Keep the sample sealed from time of collection until extraction.

8.4 Field Reagent Blanks (FRB)

Each sample set must include an FRB. A sample set is defined as samples collected from the same site and at the same time. The same lot of preservative must be used for the FRBs as for the field samples.

8.4.1 Analysis of Reagent Water used for FRBs

Reagent water used for the FRBs must be analyzed prior to shipment to ensure the water has minimal residual PFAS. Extract an LRB prepared with reagent water using the same lot of sample bottles destined for shipment to the sampling site and ensure that analyte concentrations are less than one-third the MRL, as described in Section 9.2.1. This will ensure that any significant contamination detected in the FRBs originated from exposure in the field.

8.4.2 Field Reagent Blank Procedure

In the laboratory, fill the FRB sample bottle with the analyzed reagent water (Sect. 8.4.1), then seal and ship to the sampling site with the sample bottles. For each FRB shipped, a second FRB sample bottle containing only preservative must also be shipped. At the sampling site, open the FRB bottle and pour the reagent water into the second sample bottle containing preservative; seal and label this bottle as the FRB with the date, time and location of the site.

8.5 Sample Shipment and Storage

Samples must be shipped on ice. Samples are valid if any ice remains in the cooler when it is received at the laboratory or bottles are received within 2 days of collection and below 10 ^{0}C. Once at the laboratory, samples must be stored at or below 6 °C until extraction. Samples must not be frozen.

8.6 Sample and Extract Holding Times

Analyze samples as soon as possible. Samples must be extracted within 28 days of collection. Extracts are generally stored at room temperature and must be analyzed within 28 days after extraction.

9 Quality Control

QC procedures include the IDC and ongoing QC requirements. This section describes each QC parameter, its required frequency, and the performance criteria that must be met in order to satisfy method objectives. The QC criteria discussed in the following sections are summarized in **Table 16** and **Table 17**. These QC requirements are considered the minimum for an acceptable QC program. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.1 Initial Demonstration of Capability

The IDC must be successfully performed prior to analyzing field samples. The IDC must be repeated if changes are made to analytical parameters not previously validated during the IDC. This may include, for example, changing the sample volume, selecting alternate quantitation ions, extending the calibration range, adding additional isotope performance standards, or adding additional isotope dilution analogues. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10. The same calibration range used during the IDC must be used for the analysis of field samples.

9.1.1 Demonstration of Low System Background

Analyze an LRB immediately after injecting the highest calibration standard in the selected calibration range. Confirm that the blank is free from contamination as defined in Section 9.2.1. If an automated extraction system is used, an LRB must be extracted on each port to fulfil this requirement.

9.1.2 Demonstration of Precision

Prepare, extract, and analyze seven replicate LFBs in a valid Extraction Batch (seven LFBs and an LRB). Fortify the LFBs near the midpoint of the initial calibration curve. The percent relative standard deviation (%RSD) of the concentrations of the replicate analyses must be less than 20% for all method analytes.

9.1.3 Demonstration of Accuracy

Using the same set of replicate data generated for Section 9.1.2, calculate the average percent recovery. The average recovery for each analyte must be within a range of 70–130%.

9.1.4 Minimum Reporting Level (MRL) Confirmation

Establish a target concentration for the MRL (Sect. 3.15) based on the intended use of the method. If there is a programmatic MRL requirement, the laboratory MRL must be set at or below this level. In doing so, one should consider that establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements.

Perform initial calibration following the procedures in Section 10.3. The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be at, or below, the MRL. Confirm the laboratory's ability to meet the MRL following the procedure outlined below.

9.1.4.1 Prepare and Analyze MRL Samples

Fortify, extract, and analyze seven replicate LFBs at, or below, the proposed MRL concentration.

9.1.4.2 Calculate MRL Statistics

Calculate the mean and standard deviation for each analyte in these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the following equation:

$$HR_{PIR} = 3.963S$$

Where,

S = the standard deviation and 3.963 is a constant value for seven replicates.[1]

Calculate the Upper and Lower Limits for the Prediction Interval of Results ($PIR = Mean \pm HR_{PIR}$) as shown below. These equations are only defined for seven replicate samples.

$$Upper\ PIR\ Limit = \frac{Mean + HR_{PIR}}{Fortified\ Concentration} \times 100$$

$$Lower\ PIR\ Limit = \frac{Mean - HR_{PIR}}{Fortified\ Concentration} \times 100$$

9.1.4.3 MRL Acceptance Criteria

The laboratory's ability to meet the MRL is confirmed if the *Upper PIR Limit* is less than, or equal to, 150%; and the *Lower PIR Limit* is greater than, or equal to, 50%. If these criteria are not met, the MRL has been set too low and must be confirmed again at a higher concentration.

9.1.5 Calibration Verification

Analyze a QCS (Sect. 9.2.9) to confirm the accuracy of the primary calibration standards.

9.2 Ongoing QC Requirements

This section describes the ongoing QC elements that must be included when processing and analyzing field samples.

9.2.1 Laboratory Reagent Blank (LRB)

Analyze an LRB with each Extraction Batch. Background concentrations of method analytes must be less than one-third the MRL. If method analytes are detected in the LRB at concentrations greater than or equal to this level, then all positive field sample results (i.e., results at or above the MRL) for those analytes are invalid for all samples in the Extraction Batch. Subtracting blank values from sample results is not permitted.

9.2.1.1 Estimating Background Concentrations

Although quantitative data below the MRL may not be accurate enough for data reporting, such data are useful in determining the magnitude of background interference. Therefore, the analyte concentrations in the LRB may be estimated by extrapolation when results are below the MRL.

9.2.1.2 Influence of Background on Selection of MRLs

Because background contamination can be a significant problem, some MRLs may be background limited.

9.2.1.3 Evaluation of Background when Analytes Exceed the Calibration Range

After analysis of a sample in which method analytes exceed the calibration range, one or more LRBs must be analyzed (to detect potential carryover) until the system meets the LRB acceptance criteria. If this occurs during an automated sequence, examine the results of samples analyzed following the sample that exceeded the calibration range. If the analytes that exceeded the calibration range in the previous sample are detected at, or above, the MRL, these samples are invalid. If the affected analytes do not exceed the MRL, these subsequent samples may be reported.

9.2.2 Continuing Calibration Check (CCC)

Analyze CCC standards at the beginning of each Analysis Batch, after every tenth field sample, and at the end of the Analysis Batch. See Section 10.4 for concentration requirements and acceptance criteria for CCCs.

9.2.3 Laboratory Fortified Blank

An LFB is required with each Extraction Batch. The concentration of the LFB must be rotated between low, medium, and high concentrations from batch to batch.

9.2.3.1 LFB Concentration Requirements

Fortify the low concentration LFB near the MRL. The high concentration LFB must be near the high end of the calibration range.

9.2.3.2 Evaluate Analyte Recovery

Results for analytes fortified at concentrations near or at the MRL (within a factor of two times the MRL concentration) must be within 50–150% of the true value. Results for analytes fortified at all other concentrations must be within 70–130% of the true value. If the LFB results do not meet these criteria, then all data for the problem analytes must be considered invalid for all samples in the Extraction Batch.

9.2.4 Isotope Performance Standard Areas

The analyst must monitor the peak areas of the isotope performance standards in all injections of the Analysis Batch. The isotope performance standard responses (as indicated by peak area) in any chromatographic run must be within 50–150% of the average area measured during the initial calibration. Random evaporation losses have been observed with the polypropylene caps causing high-biased isotope performance standard areas. If an isotope performance standard area for a sample does not meet these criteria, reanalyze the extract in a subsequent Analysis Batch. If the isotope performance standard area fails to meet the acceptance criteria in the repeat analysis, extraction of the sample must be repeated, provided the sample is still within holding time.

9.2.5 Isotope Dilution Analogue Recovery

Calculate the concentration of each isotope dilution analogue in field and QC samples using the average area in the initial calibration and the internal standard technique. Calculate the percent recovery (%R) for each analogue as follows:

$$\%R = \frac{A}{B} \times 100$$

Where,
A = measured concentration of the isotope dilution analogue, and
B = fortification concentration of the isotope dilution analogue.

The percent recovery for each analogue must be within a range of 50–200%.

9.2.5.1 Corrective Action for Failed Analogue Recovery

If an isotope dilution analogue fails to meet the recovery criterion, evaluate the area of the isotope performance standard to which the analogue is referenced and the recovery of the analogues in the CCCs. If necessary, recalibrate and service the LC-MS/MS system. Take corrective action, then analyze the failed extract in a subsequent Analysis Batch. If the repeat analysis meets the 50–200% recovery criterion, report only data for the reanalyzed extract. If the repeat analysis fails the recovery criterion after corrective action, extraction of the sample must be repeated provided a sample is available and still within the holding time.

9.2.6 Laboratory Fortified Sample Matrix (LFSM)

Within each Extraction Batch, analyze a minimum of one LFSM. The native concentrations of the analytes in the sample matrix must be determined in a separate field sample and subtracted from the measured values in the LFSM. If various sample matrices are analyzed regularly, for example, drinking water processed from ground water and surface water sources, collect performance data for each source.

9.2.6.1 Prepare the LFSM

Prepare the LFSM by fortifying a Field Duplicate with an appropriate amount of the analyte PDS (Sect. 7.17.4) and isotope dilution analogue PDS (Sect. 7.16.1). Generally, select a spiking concentration that is greater than or equal to the native concentration for the analytes. Selecting a duplicate aliquot of a sample that has already been analyzed aids in the selection of an appropriate spiking level. If this is not possible, use historical data when selecting a fortifying concentration.

9.2.6.2 Calculate the Percent Recovery

Calculate the percent recovery (%R) using the equation:

$$\%R = \frac{(A - B)}{C} \times 100$$

Where,
A = measured concentration in the fortified sample,
B = measured concentration in the unfortified sample, and
C = fortification concentration.

In order to obtain meaningful percent recovery results, correct the measured values in the LFSM and LFSMD for the native levels in the unfortified samples, even if the native values are less than the MRL.

9.2.6.3 Evaluate Analyte Recovery in the LFSM

Results for analytes fortified at concentrations near or at the MRL (within a factor of two times the MRL concentration) must be within 50–150% of the true value. Results for analytes fortified at all other concentrations must be within 70–130% of the true value. If the accuracy for any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and in the LFB, the recovery is judged matrix biased. Report the result for the corresponding analyte in the unfortified sample as “suspect–matrix”.

9.2.7 Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicate (FD)

Within each Extraction Batch, analyze a minimum of one Field Duplicate or one Laboratory Fortified Sample Matrix Duplicate. If the method analytes are not routinely observed in field samples, analyze an LFSMD rather than an FD.

9.2.7.1 Calculate the RPD for the LFSM and LFSMD

If an LFSMD is analyzed instead of a Field Duplicate, calculate the RPD using the equation:

$$RPD = \frac{|LFSMD - LFSM|}{(LFSMD + LFSM)/2} \times 100$$

9.2.7.2 Acceptance Criterion for the RPD of the LFSM and LFSMD

RPDs for duplicate LFSMs must be less than, or equal to, 30% for each analyte. Greater variability may be observed when the matrix is fortified at analyte concentrations near or at the MRL (within a factor of two times the MRL concentration). LFSMs at these concentrations must have RPDs that are less than or equal to 50%. If the RPD of an analyte falls outside the designated range, and the laboratory performance for the analyte is shown to be in control in the CCCs and in the LFB, the precision is judged matrix influenced. Report the result for the corresponding analyte in the unfortified sample as “suspect–matrix”.

9.2.7.3 Calculate the RPD for Field Duplicates

Calculate the relative percent difference (RPD) for duplicate measurements. (FD1 and FD2) using the equation:

$$RPD = \frac{|\mathrm{FD}_1 - \mathrm{FD}_2|}{(\mathrm{FD}_1 + \mathrm{FD}_2)/2} \times 100$$

9.2.7.4 Acceptance Criterion for Field Duplicates

RPDs for Field Duplicates must be less than, or equal to, 30% for each analyte. Greater variability may be observed when Field Duplicates have analyte concentrations that are near or at the MRL (within a factor of two times the MRL concentration). At these concentrations, Field Duplicates must have RPDs that are less than or equal to 50%. If the RPD of an analyte falls outside the designated range, and the laboratory performance for the analyte is shown to be in control in the CCC and in the LFB, the precision is judged matrix influenced. Report the result for the corresponding analyte in the unfortified sample as “suspect–matrix”

9.2.8 Field Reagent Blank (FRB)

The purpose of the FRB is to ensure that PFAS measured in the field samples were not inadvertently introduced into the sample during sample collection and handling. The FRB is processed, extracted, and analyzed in exactly the same manner as a field sample. Analysis of the FRB is required only if a field sample contains a method analyte or analytes at, or above, the MRL. If a method analyte found in the field sample is present in the FRB at a concentration greater than one-third of the MRL, then the results for that analyte are invalid for all samples associated with the failed FRB.

9.2.9 Calibration Verification using QCS

A QCS must be analyzed during the IDC, and then quarterly thereafter. For this method, the laboratory is not required to obtain standards from a source independent of the primary calibration standards. Instead, the laboratory should acquire the best available quantitative standards (Sect. 3.20) and use these to prepare both the primary calibration standards and the QCS. The QCS must be an independent dilution beginning with the common starting materials. Preparation by a second analyst is recommended. The acceptance criterion for the QCS is 70–130% of the true value. If the accuracy for any analyte fails the recovery criterion, prepare fresh standard dilutions and repeat the Calibration Verification.

9.3 Method Modification QC Requirements

The analyst is permitted to modify the chromatographic and MS/MS conditions. Examples of permissible method modifications include alternate LC columns, MRM transitions, and additional QC analytes proposed for use with the method. Any method modifications must be within the scope of the established method flexibility and must retain the basic chromatographic elements of this method (Sect. 2). The following are required after a method modification.

9.3.1 Repeat the IDC

Establish an acceptable initial calibration (Sect. 10.3) using the modified conditions. Repeat the procedures of the IDC (Sect. 9.1).

9.3.2 Document Performance in Representative Sample Matrices

The analyst is also required to evaluate and document method performance for the modifications in real matrices that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably in the IDC, which is conducted in reagent water, could fail ongoing method QC requirements in real matrices. This is particularly important for methods subject to matrix effects, such as LC-MS/MS-based methods. For example, a laboratory may routinely analyze finished drinking water from municipal treatment plants that process ground water, surface water, or a blend of surface and ground water. In this case, the method modification requirement could be accomplished by assessing precision (Sect. 9.1.2) and accuracy (Sect. 9.1.3) in finished drinking waters derived from a surface water with moderate to high total organic carbon (e.g., 2 mg/L or greater) and from a hard ground water (e.g., 250 mg/L as calcium carbonate ($CaCO_3$) equivalent, or greater).

10 Calibration and Standardization

Demonstration and documentation of acceptable MS calibration and initial analyte calibration are required before performing the IDC and prior to analyzing field samples. The initial calibration should be repeated each time a major instrument modification or maintenance is performed.

10.1 MS/MS Optimization

10.1.1 Mass Calibration

Calibrate the mass spectrometer with the calibration compounds and procedures specified by the manufacturer.

10.1.2 MS Parameters

During the development of this method, instrumental parameters were optimized for the precursor and product ions listed in **Table 6**. Product ions other than those listed may be selected; however, the analyst should avoid using ions with lower mass or common ions that may not provide sufficient discrimination between the analytes of interest and co-eluting interferences.

10.1.2.1 Requirement for Branched Isomers

There have been reports that not all product ions in the linear PFOS are produced in all branched PFOS isomers.[5] (This phenomenon may exist for many of the PFAS.) For this method, the *m/z* 80 product ion must be used for PFOS and PFHxS to minimize this problem and promote comparability between laboratories. Some MS/MS instruments, may not be able to scan a product ion with such a wide mass difference from the precursor ion. These instruments may not be used for this method if PFOS or PFHxS analysis is to be conducted.

10.1.2.2 Precursor Ion

Optimize the response of the precursor ion ($[M - H]^-$ or $[M - CO_2 - H]^-$) for each analyte following manufacturer's guidance. Analyte concentrations of 1.0 µg/mL were used for this step during method development. Vary the MS parameters (source voltages, source and desolvation temperatures, gas flows, etc.) until optimal analyte responses are determined. The electrospray parameters used during method development are listed in **Table 2**. The analytes may have different optimal parameters, requiring some compromise on the final operating conditions. See **Table 6** for ESI-MS conditions used to collect method performance data.

10.1.2.3 Product Ion

Optimize the product ion for each analyte following the manufacturer's guidance. Typically, the carboxylic acids have similar MS/MS conditions and the sulfonic acids have similar MS/MS conditions. See **Table 6** for MS/MS conditions used to collect method performance data.

10.2 Chromatographic Conditions

Establish LC operating parameters that optimize resolution and peak shape. Suggested LC conditions can be found in **Table 1**. Modifying the solvent composition of the standard or extract by increasing the aqueous content to better focus early eluting compounds on the column is not permitted. A decrease in methanol concentration could lead to lower or imprecise recovery of the more hydrophobic method analytes, while higher methanol concentration could lead to the precipitation of salts in some extracts. The peak shape of the early eluting compounds may be improved by increasing the volume of the injection loop or increasing the aqueous content of the initial mobile phase composition.

10.2.1 Minimizing PFAS Background

LC system components, as well as the mobile phase constituents, may contain many of the analytes in this method. Thus, these PFAS will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFAS peaks and to keep baseline levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, priming the mobile phase and flushing the column with at least 90% methanol before initiating a sequence may reduce background contamination.

10.2.2 Establishing Branched vs. Linear Isomer Profiles

Prepare and analyze the technical-grade standard of PFOA, discussed in Section 7.17.1, at a mid- to high-level concentration. Identify the retention times of the branched isomers of PFOA present in the technical-grade PFOA standard. When PFOA is chromatographed on a reversed-phase column, the branched isomers elute prior to the linear isomer. Repeat the procedure in this section for PFHxS and PFOS discussed in Section 7.17.2, and any other analytes for which technical-grade standards have been acquired. The branched isomer identification checks must be repeated any time chromatographic changes occur that alter analyte retention times.

10.2.3 Establish LC-MS/MS Retention Times and MRM Segments

Inject a mid- to high-level calibration standard under optimized LC-MS/MS conditions to obtain the retention times of each method analyte. Divide the chromatogram into segments that contain one or more chromatographic peaks. For maximum sensitivity, minimize the number of MRM transitions that are simultaneously monitored within each segment. Ensure that the retention time window used to collect data for each analyte is of sufficient width to detect earlier eluting branched isomers.
The retention times observed during collection of the method performance data are listed in **Table 3**, **Table 4**, and **Table 5**.

10.3 Initial Calibration

This method has three isotope performance standards that are used as reference compounds for the internal standard quantitation of the isotope dilution analogues. The suggested isotope performance standard reference for each isotope dilution analogue is listed in **Table 4**. The sixteen isotope dilution analogues are used as reference compounds to quantitate the native analyte concentrations. The suggested isotope dilution analogue references for the native analytes are listed in **Table 5**.

10.3.1 Calibration Standards

Prepare a set of at least five calibration standards as described in Section 7.17.5. The analyte concentrations in the lowest calibration standard must be at or below the MRL.

10.3.2 Calibration Curves of Native Analytes

Quantitate the native analytes using the internal standard calibration technique. The internal standard technique calculates concentration based on the ratio of the peak area of the native analyte to that of the isotope dilution analogue. Calibrate the LC-MS/MS and fit the calibration points with either a linear or quadratic regression. Weighting may be used. Forcing the calibration curve through the origin is mandatory for this method. Forcing zero allows for a better estimate of the background levels of method analytes. The MS/MS instrument used during method development was calibrated using weighted (1/x) quadratic regression with forced zero.

10.3.3 Calibration of Isotope Dilution Analogues

The isotope dilution analogues are quantified using the internal standard calibration technique. Because isotope dilution analogues are added at a single concentration level to the calibration standards, calibrate for each of these using an average response factor.

10.3.4 Calibration of Isotope Performance Standards

Because Isotope performance standards are added at a single concentration level to the calibration standards, calibrate for each of these using an average response factor.

10.3.5 Calibration Acceptance Criteria

Evaluate the initial calibration by calculating the concentration of each analyte as an unknown against its regression equation. For calibration levels that are less than or equal to the MRL, the result for each analyte should be within 50–150% of the true value. All other calibration points should be within 70–130% of their true value. If these criteria cannot be met, the analyst could have difficulty meeting ongoing QC criteria. In this case, corrective action is recommended such as reanalyzing the calibration standards, restricting the range of calibration, or performing instrument maintenance. If the cause for failure to meet the criteria is due to contamination or standard degradation, prepare fresh calibration standards and repeat the initial calibration.

10.4 Continuing Calibration

Analyze a CCC to verify the initial calibration at the beginning of each Analysis Batch, after every tenth field sample, and at the end of each Analysis Batch. The beginning CCC for each Analysis Batch must be at, or below, the MRL for each analyte. This CCC verifies instrument sensitivity prior to the analysis of samples. If standards have been prepared such that all low calibration levels are not in the same solution, it may be necessary to analyze two standards to meet this requirement. Alternatively, the nominal analyte concentrations in the analyte PDS may be customized to meet these criteria. Alternate subsequent CCCs between the mid and high calibration levels. Verify that the CCC meets the criteria in the following sections.

10.4.1 CCC Isotope Performance Standard Responses

The absolute area of the quantitation ion for each of the three isotope performance standards must be within 50–150% of the average area measured during the initial calibration. If these limits are exceeded, corrective action is necessary (Sect. 10.5).

10.4.2 CCC Isotope Dilution Analogue Recovery

Using the average response factor determined during the initial calibration and the internal standard calibration technique, calculate the percent recovery of each isotope dilution analogue in the CCC. The recovery for each analogue must be within a range of 70–130%. If these limits are exceeded, corrective action is necessary (Sect. 10.5).

10.4.3 CCC Analyte Responses

Calculate the concentration of each method analyte in the CCC. Each analyte fortified at a level less than or equal to the MRL must be within 50–150% of the true value. The concentration of the analytes in CCCs fortified at all other levels must be within 70–130%. If these limits are exceeded, then all data for the failed analytes must be considered invalid. Any field samples analyzed since the last acceptable CCC that are still within holding time must be reanalyzed after an acceptable calibration has been restored.

10.4.3.1 Exception for High Recovery

If the CCC fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a method analyte, and field sample extracts show no concentrations above the MRL for that analyte, non-detects may be reported without re-analysis.

10.5 Corrective Action

Failure to meet the CCC QC performance criteria requires corrective action. Following a minor remedial action, such as servicing the autosampler or flushing the column, check the calibration with a mid-level CCC and a CCC at the MRL, or recalibrate according to Section 10.3. If isotope performance standard and calibration failures persist, maintenance may be required, such as servicing the LC-MS/MS system or replacing the LC column. These latter measures constitute major maintenance and the analyst must return to the initial calibration step (Sect. 10.3).

11 Procedure

This procedure may be performed manually or in an automated mode using a robotic or automatic sample preparation device. The data published in this method (Sect. 17) demonstrate acceptable performance using manual extraction. The authors did not evaluate automated extraction systems. If an automated system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. Extraction and elution steps may not be changed or omitted to accommodate the use of an automated system. If an automated system is used, the LRBs should be rotated among the ports to ensure that all the valves and tubing meet the LRB requirements (Sect. 9.2.1).

11.1 Sample Bottle Rinse

Some of the PFAS adsorb to surfaces, including polypropylene. During the elution step of the procedure, sample bottles must be rinsed with the elution solvent whether extractions are performed manually or by automation.

11.2 Reuse of Extraction Cartridges

The SPE cartridges described in this section are designed for a single use. They may not be reconditioned for subsequent analyses.

11.3 Sample Preparation

11.3.1 Sample Volume

Determine sample volume. An indirect measurement may be done in one of two ways: by marking the level of the sample on the bottle or by weighing the sample and bottle to the nearest 1 gram. After extraction, proceed to Section 11.5 to complete the volume measurement. Some of the PFAS adsorb to surfaces, thus the sample may not be transferred to a graduated cylinder for volume measurement. The LRB, LFB and FRB must have the same volume as that of the field samples and may be prepared by measuring reagent water with a graduated cylinder.

11.3.2 Verifying Sample pH

Verify that the sample containing 1 g/L ammonium acetate has a pH between 6.0 and 8.0. Acetic acid may be added as needed to reduce the pH

11.3.3 Fortify QC Samples

Fortify LFBs, LFSMs, and LFSMDs, with an appropriate volume of Analyte PDS (Sect. 7.17.4). Cap and invert each sample several times to mix.

11.3.4 Addition of Isotope Dilution Analogues

Add an aliquot of the isotope dilution analogue PDS (Sect. 7.16.1) to each sample, then cap and invert to mix. During method development, a 20 µL aliquot of the PDS (0.50–2.0 ng/µL) was added to achieve a final concentration of 40 ng/L of the isotopically labeled carboxylates and perfluorinated sulfonates, and 160 ng/L of the telomer sulfonates.

11.4 Extraction Procedure

11.4.1 Cartridge Cleaning and Conditioning

Do not allow cartridge packing material to go dry during any of the conditioning steps. If the cartridge goes dry during the conditioning phase, the conditioning must be repeated. Rinse each cartridge with 10 mL of methanol. Next, rinse each cartridge with 10 mL of aqueous 0.1 M phosphate buffer (Sect. 7.8) without allowing the water to drop below the top edge of the packing. Close the valve and add 2–3 mL of phosphate buffer to the cartridge reservoir and fill the remaining volume with reagent water.

11.4.2 Cartridge Loading

Attach the sample transfer tubes (Sect. 6.8.3) and adjust the vacuum to approximately 5 inches Hg. Begin adding sample to the cartridge. Adjust the vacuum and control valves so that the approximate flow rate is 5 mL/min. Do not allow the cartridge to go dry before all the sample has passed through. Flow rates above 5 mL/min during loading may cause low analyte recovery.

11.4.3 Sample Bottle Rinse and Cartridge Drying

After the entire sample has passed through the cartridge, rinse the sample bottle with a 10 mL aliquot of 1 g/L ammonium acetate in reagent water. Draw the rinsate through the sample transfer tubes and the cartridges. Add 1 mL of methanol to the sample bottle and draw through the transfer tube and SPE cartridge. This step is designed to remove most of the water from the transfer line and cartridge resulting in the reduction of the salt and water present in the eluate. The methanol rinse may also reduce interferences by removing weakly retained organic material prior to elution. If plastic reservoirs are used instead of transfer lines, the reservoirs must be rinsed with the ammonium acetate solution and the 1 mL aliquot of methanol.

11.4.4 Cartridge Drying

Draw air or nitrogen through the cartridge for 5 min at high vacuum (15–20 in. Hg).

11.4.5 Sample Bottle and Cartridge Elution

After the drying step, release the vacuum on the extraction manifold and place a collection tube under each sample position. Rinse the sample bottles with 5 mL of the elution solvent, methanol with 2% ammonium hydroxide (v/v), then elute the analytes from the cartridges by pulling the elution solvent through the sample transfer tubes and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion. Repeat sample bottle rinse and cartridge elution with a second 5 mL aliquot of elution solvent. If plastic reservoirs are used instead of transfer lines, attempt to rinse the entire inner surface of the reservoir with the elution solvent.

11.4.6 Extract Concentration

Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (55–60 °C). Reconstitute the extract with 1.0 mL of 20% reagent water in methanol (v/v). Add the isotope performance standards to the extract and vortex.

11.4.7 Extract Transfer and Storage

Transfer the final extract to a polypropylene autosampler vial. Store extracts at room temperature. Recap vials as soon as possible after injection to prevent evaporation losses; the polypropylene caps do not reseal after puncture. Alternatively, extracts can be stored in the 15 mL collection tubes after extraction. A small aliquot can be removed for analysis if the autosampler vial and injection system accommodate small volumes.

11.5 Sample Volume Determination

Use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made prior to extraction. If using weight to determine the volume, weigh the empty bottle to the nearest 1 gram and subtract this value from the weight recorded prior to extraction. Assume a sample density of 1.0 g/mL. Record the sample volumes for use in the final calculations of analyte concentrations.

11.6 Sample Analysis

11.6.1 Establish LC-MS/MS Operating Conditions

Establish MS/MS operating conditions per the procedures in Section 10.1 and chromatographic conditions per Section 10.2. Establish a valid initial calibration following the procedures in Section 10.3 or confirm that the existing calibration is still valid by analyzing a low-level CCC. If establishing an initial calibration for the first time, complete the IDC prior to analyzing field samples. Analyze field and QC samples in a properly sequenced Analysis Batch as described in Section 11.7.

11.6.2 Verify Retention Time Windows

The analyst must ensure that each method analyte elutes entirely within the assigned window during each Analysis Batch. Make this observation by viewing the quantitation ion for each analyte in the CCCs analyzed during an Analysis Batch. If an analyte peak drifts out of the assigned window, then data for that analyte is invalid in all injections acquired since the last valid CCC. In addition, all peaks representing multiple isomers of an analyte must elute entirely within the same MRM window.

11.7 Analysis Batch Sequence

An Analysis Batch is a sequence of samples, analyzed within a 24-hour period, of no more than 20 field samples and includes all required QC samples (LRB, CCCs, the LFSM and LFSMD (or FD)). The required QC samples are not included in counting the maximum field sample total of 20. LC-MS/MS conditions for the Analysis Batch must be the same as those used during calibration.

11.7.1 Analyze Initial CCC

After a valid calibration is established, begin every Analysis Batch by analyzing an initial low-level CCC at or below the MRL. This initial CCC must be within 50–150% of the true value for each method analyte and must pass both the isotope performance standard area response criterion (Sect. 10.4.1) and the isotope dilution analogue recovery criterion (Sect. 10.4.2). The initial CCC confirms that the calibration is still valid. Failure to meet the QC criteria may indicate that recalibration is required prior to analyzing samples.

11.7.2 Analyze Field and QC Samples

After the initial CCC, continue the Analysis Batch by analyzing an LRB, followed by the field samples and QC samples. Analyze a mid- or high-level CCC after every ten field samples and at the end each Analysis Batch. Do not count QC samples (LRBs, FDs, LFSMs, LFSMDs) when calculating the required frequency of CCCs.

11.7.3 Analyze Final CCC

The last injection of the Analysis Batch must be a mid- or high-level CCC. The acquisition start time of the final CCC must be within 24 hours of the acquisition start time of the low-level CCC at the beginning of the Analysis Batch. More than one Analysis Batch within a 24-hour period is permitted. An Analysis Batch may contain field and QC samples from multiple extraction batches.

11.7.4 Initial Calibration Frequency

A full calibration curve is not required before starting a new Analysis Batch. A previous calibration can be confirmed by running an initial, low-level CCC followed by an LRB. If a new calibration curve is analyzed, an Analysis Batch run immediately thereafter must begin with a low-level CCC and an LRB.

12 Data Analysis and Calculations

Because environmental samples may contain both branched and linear isomers of the method analytes, but quantitative standards that contain branched isomers do not exist for all method analytes, integration and quantitation of the PFAS is dependent on the type of standard materials available.

12.1 Identify Peaks by Retention Times

At the conclusion of data acquisition, use the same software settings established during the calibration procedure to identify analyte peaks in the predetermined retention time windows. Confirm the identity of each analyte by comparison of its retention time with that of the corresponding analyte peak in an initial calibration standard or CCC. Proceed with quantitation based on the type of standard available for each method analyte.

12.1.1 Method Analytes without Technical-Grade Standards

If standards containing the branched and linear isomers cannot be purchased (i.e., only the linear isomer is available), only the linear isomer can be identified and quantitated in field samples and QC samples because the retention time of the branched isomers cannot be confirmed.

12.1.2 PFHxS, PFOS, and other Analytes with Technical-Grade Standards

During method development, multiple chromatographic peaks, representing branched and linear isomers, were observed for standards of PFHxS and PFOS using the LC conditions in **Table 1**. For PFHxS and PFOS, all the chromatographic peaks observed in the standard must be integrated and the areas summed. Chromatographic peaks in all field samples and QC samples must be integrated in the same way as the calibration standard for analytes with quantitative standards containing the branched and linear isomers.

12.1.3 PFOA

For PFOA, identify the branched and linear isomers by analyzing a technical-grade standard that includes both linear and branched isomers as directed in Section 10.2.2 and ensure that all isomers elute within the same acquisition segment. Quantitate field samples and fortified matrix samples by integrating the total response, accounting for peaks that are identified as linear and branched isomers. Quantitate based on the initial calibration with the quantitative PFOA standard containing just the linear isomer.

12.2 Calculate Analyte Concentrations

Calculate analyte concentrations using the multipoint calibration and the measured sample volume. Report only those values that fall between the MRL and the highest calibration standard.

12.3 Calculate Isotope Dilution Analogue Recovery

Calculate the concentration of each isotope dilution analogue using the multipoint calibration and the measured sample volume. Verify that the percent recovery is within 50–200% of the true value.

12.4 Significant Figures

Calculations must use all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

12.5 Exceeding the Calibration Range

The analyst must not extrapolate beyond the established calibration range. If an analyte result exceeds the range of the initial calibration curve, a field duplicate of the sample must be extracted, if available. Dilute an aliquot of the field duplicate with reagent water to a final volume equal to that used for the IDC. Add ammonium acetate to a final concentration of 1 g/L and process the diluted sample. Report all concentrations measured in the original sample that do not exceed the calibration range. Report concentrations of analytes that exceeded the calibration range in the in the original sample based on measurement in a diluted sample. Incorporate the dilution factor into final concentration calculations and the resulting data must be annotated as a dilution. This is the only circumstance when subsampling is permitted.

13 Method Performance

13.1 Precision, Accuracy, and LCMRL Results

Tables for these data are presented in Section 17. LCMRLs are presented in **Table 7**. Single-laboratory precision and accuracy data are presented for three water matrices: reagent water (**Table 8**), finished ground water (**Table 10**), and a drinking water matrix from a surface water source (**Table 12)**. The mean isotope dilution analogue recoveries measured in the replicate samples used in these studies are presented in **Table 9** for reagent water, **Table 11** for finished groundwater, and **Table 13** for the surface water matrix.

13.2 Analyte Stability Study

Chlorinated (finished) surface water samples were inoculated with microbial-rich water from an impacted surface source and fortified with 40 ng/L of the PFAS method analytes. These samples were stored as required in this method. The percent change from the initial analyzed concentration observed after 7, 14, 21, and 28 days is presented in Section 17, **Table 14**.

13.3 Extract Storage Stability

Extract storage stability studies were conducted on extracts obtained from the analyte stability study (Sect. 13.2). The percent change from the initial analyzed concentration observed after 14, 21, and 27 days storage is presented in Section 17, **Table 15**.

14 Pollution Prevention

For information about pollution prevention applicable to laboratory operations described in this method, consult: Less is Better, Guide to Minimizing Waste in Laboratories, a publication available from the American Chemical Society (accessed April 2019) at www.acs.org.

15 Waste Management

Laboratory waste management practices should be consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. In addition, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16 References

1. US EPA. *Statistical Protocol for the Determination of the Single-Laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of Laboratory Performance at or Below the Minimum Reporting Level (MRL)*; EPA 815-R-05-006; Office of Water: Cincinnati, OH, November 2004.
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3. Martin, J.W., et al. Analytical Challenges Hamper Perfluoroalkyl Research. *Environ. Sci. Technol*. 2004, Vol. 38, 248A–255A.
4. Cahill, J.D., et al. Determination of Pharmaceutical Compounds in Surface- and Ground-Water Samples by Solid-Phase Extraction and High-Performance Liquid Chromatography Electrospray Ionization Mass Spectrometry. *J. Chromatography A*, 2004, 1041, 171–180.
5. Langlois, I. and Oehme, M. Structural Identification of Isomers Present in Technical Perfluorooctane Sulfonate by Tandem Mass Spectrometry. *Rapid Communication Mass Spectrometry*. 2006, Vol. 20, 844–850.

17 Tables, Figures and Method Performance Data

Table 1. HPLC Method Conditions[a]

Time (min)	% 20 mM ammonium acetate	% Methanol
Initial	95.0	5.0
0.5	95.0	5.0
3.0	60.0	40.0
16.0	20.0	80.0
18.0	20.0	80.0
20.0	5.0	95.0
22.0	5.0	95.0
25.0	95.0	5.0
35.0	95.0	5.0

[a] Phenomenex Gemini® C18, 2 x 50 mm, 3.0 µm silica with TMS end-capping. Flow rate of 0.25 mL/min; run time 35 minutes; 10 µL injection into a 50 µL loop. The chromatogram in **Figure 1** was obtained under these conditions.

Table 2. ESI-MS Method Conditions

ESI Conditions for Waters (Milford, MA) Xevo TQD	
Polarity	Negative ion
Capillary needle voltage	-2.7 kV
Cone gas flow	40 L/hour
Nitrogen desolvation gas	800 L/hour
Desolvation gas temperature	300 °C

Table 3. Isotopically Labeled Isotope Performance Standards and Retention Times

Isotope Performance Standard	Peak # (Figure 1)	RT (min)
$^{13}C_3$-PFBA	1	4.14
$^{13}C_2$-PFOA	26	12.19
$^{13}C_4$-PFOS	32	13.73

Table 4. Isotope Dilution Analogues: RTs and Suggested Isotope Performance Standard References

Isotopically Labeled Analyte	Peak # (Fig. 1)	RT (min)	Suggested Isotope Performance Standard
$^{13}C_4$-PFBA	2	4.14	$^{13}C_3$-PFBA
$^{13}C_5$-PFPeA	5	6.13	$^{13}C_3$-PFBA
$^{13}C_3$-PFBS	7	6.62	$^{13}C_4$-PFOS
$^{13}C_2$-4:2FTS	12	8.12	$^{13}C_4$-PFOS
$^{13}C_5$-PFHxA	14	8.35	$^{13}C_2$-PFOA
$^{13}C_3$-HFPO-DA	17	9.06	$^{13}C_2$-PFOA
$^{13}C_4$-PFHpA	19	10.34	$^{13}C_2$-PFOA
$^{13}C_3$-PFHxS	21	10.61	$^{13}C_4$-PFOS
$^{13}C_2$-6:2FTS	24	12.05	$^{13}C_4$-PFOS
$^{13}C_8$-PFOA	27	12.19	$^{13}C_2$-PFOA
$^{13}C_9$-PFNA	30	13.70	$^{13}C_2$-PFOA
$^{13}C_8$-PFOS	33	13.73	$^{13}C_4$-PFOS
$^{13}C_2$-8:2FTS	36	14.94	$^{13}C_4$-PFOS
$^{13}C_6$-PFDA	38	15.00	$^{13}C_2$-PFOA
$^{13}C_7$-PFUnA	40	16.14	$^{13}C_2$-PFOA
$^{13}C_2$-PFDoA	43	17.13	$^{13}C_2$-PFOA

Table 5. Method Analytes, Retention Times and Suggested Isotope Dilution Analogue References

Analyte	Peak # (Figure 1)	RT (min)	Isotope Dilution Analogue
PFBA	3	4.15	$^{13}C_4$-PFBA
PFMPA	4	4.84	$^{13}C_4$-PFBA
PFPeA	6	6.13	$^{13}C_5$-PFPeA
PFBS	8	6.62	$^{13}C_3$-PFBS
PFMBA	9	6.81	$^{13}C_5$-PFPeA
PFEESA	10	7.53	$^{13}C_3$-PFBS
NFDHA	11	8.01	$^{13}C_5$-PFHxA
4:2FTS	13	8.12	$^{13}C_2$-4:2FTS
PFHxA	15	8.36	$^{13}C_5$-PFHxA
PFPeS	16	8.69	$^{13}C_3$-PFHxS
HFPO-DA	18	9.06	$^{13}C_3$-HFPO-DA
PFHpA	20	10.42	$^{13}C_4$-PFHpA
PFHxS	22	10.62	$^{13}C_3$-PFHxS
ADONA	23	10.73	$^{13}C_4$-PFHpA
6:2FTS	25	12.04	$^{13}C_2$-6:2FTS
PFOA	28	12.19	$^{13}C_8$-PFOA
PFHpS	29	12.28	$^{13}C_8$-PFOS
PFNA	31	13.70	$^{13}C_9$-PFNA
PFOS	34	13.74	$^{13}C_8$-PFOS
9Cl-PF3ONS	35	14.53	$^{13}C_8$-PFOS
8:2 FTS	37	14.94	$^{13}C_2$-8:2FTS
PFDA	39	15.00	$^{13}C_6$-PFDA
PFUnA	41	16.14	$^{13}C_7$-PFUnA
11Cl-PF3OUdS	42	16.70	$^{13}C_8$-PFOS
PFDoA	44	17.13	$^{13}C_2$-PFDoA

Table 6. MS/MS Method Conditions[a]

Segment[b]	**Analyte**	**Precursor Ion [c]** ***(m/z)***	**Product Ion[c,d]** **(*m/z*)**	**Cone Voltage (v)**	**Collision Energy[e] (v)**
1	PFBA	213	169	22	10
1	$^{13}C_3$-PFBA	216	172	22	10
1	$^{13}C_4$-PFBA	217	172	22	10
1	PFMPA	229	85	23	10
2	PFPeA	263	219	20	8
2	$^{13}C_5$-PFPeA	268	223	20	8
2	$^{13}C_3$-PFBS	302	80	45	30
2	PFBS	299	80	45	30
2	PFMBA	279	85	22	10
3	PFEESA	315	135	44	20
3	NFDHA	295	201	14	8
3	$^{13}C_2$-4:2FTS	329	309	40	18
3	4:2FTS	327	307	40	18
3	$^{13}C_5$-PFHxA	318	273	20	8
3	PFHxA	313	269	20	8
3	PFPeS	349	80	45	35
3	$^{13}C_3$-HFPO-DA	287[f]	169	15	5
3	HFPO-DA	285[f]	169	15	5
4	$^{13}C_4$-PFHpA	367	322	15	8
4	PFHpA	363	319	15	8
4	$^{13}C_3$-PFHxS[g]	402	80	45	40
4	PFHxS[h]	399	80	45	40
4	ADONA	377	251	15	10
5	$^{13}C_2$-6:2FTS	429	409	47	22
5	6:2FTS	427	407	47	22
5	$^{13}C_2$-PFOA	415	370	18	10
5	$^{13}C_8$-PFOA	421	376	18	10
5	PFOA	413	369	18	10
5	PFHpS	449	80	45	40
6	$^{13}C_9$-PFNA	472	427	17	10
6	PFNA	463	419	17	10
6	$^{13}C_4$-PFOS[g]	503	80	45	45
6	$^{13}C_8$-PFOS[g]	507	80	45	45
6	PFOS[h]	499	80	45	45
7	9Cl-PF3ONS	531	351	55	25
7	$^{13}C_2$-8:2FTS	529	509	53	28
7	8:2FTS	527	507	53	28
7	$^{13}C_6$-PFDA	519	474	22	10
7	PFDA	513	469	22	10

Segment[b]	Analyte	Precursor Ion [c] *(m/z)*	Product Ion[c,d] (*m/z*)	Cone Voltage (v)	Collision Energy[e] (v)
8	$^{13}C_7$-PFUnA	570	525	24	10
8	PFUnA	563	519	24	10
8	11Cl-PF3OUdS	631	451	60	30
8	$^{13}C_2$-PFDoA	615	570	22	10
8	PFDoA	613	569	22	10

[a] An LC-MS/MS chromatogram of the analytes obtained using these parameters is shown in **Figure 1**.

[b] Segments are time durations in which single or multiple scan events occur.

[c] Precursor and product ions listed in this table are nominal masses. During MS and MS/MS optimization, the analyst should determine precursor and product ion masses to one decimal place by locating the apex of the mass spectral peak (e.g., *m/z* 498.9→79.9 for PFOS). These precursor and product ion masses (with at least one decimal place) should be used in the MS/MS method for all analyses.

[d] Ions used for quantitation purposes.

[e] Argon used as collision gas.

[f] HFPO-DA is not stable in the ESI source and the $[M - H]^-$ yields a weak signal under typical ESI conditions. The precursor ion used during method development was $[M - CO_2 - H]^-$.

[g] The isotope dilution analogue used during method development was composed of the linear isomer exclusively.

[h] Analyte has multiple resolved chromatographic peaks due to linear and branched isomers. All peaks summed for quantitation purposes. To reduce bias regarding detection of branched and linear isomers, the *m/z* 80 product ion must be used for this analyte.

Table 7. LCMRL Results

Analyte	LCMRL Fortification Levels (ng/L)	Calculated LCMRL (ng/L)
PFBA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	13
PFMPA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.8
PFPeA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.9
PFBS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.5
PFMBA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.7
PFEESA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	2.6
NFDHA	4.0, 6.0, 10, 14, 20, 41, 82	16
4:2FTS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	4.7
PFHxA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	5.3
PFPeS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	6.3
HFPO-DA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.7
PFHpA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	2.6
PFHxS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.7
ADONA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.4
6:2FTS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	14
PFOA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	3.4
PFHpS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	5.1
PFNA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	4.8
PFOS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	4.4
9Cl-PF3ONS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	1.4
8:2FTS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	9.1
PFDA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	2.3
PFUnA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	2.7
11Cl-PF3OUdS	1.0, 2.0, 4.0, 6.0, 10, 14, 20	1.6
PFDoA	1.0, 2.0, 4.0, 6.0, 10, 14, 20	2.2

Table 8. Precision and Accuracy Data for Reagent Water

Analyte	**Low Fortification (ng/L)**	**Mean %R[a] (*n*=7)**	**%RSD[a]**	**High Fortification (ng/L)**	**Mean %R (*n*=5)**	**%RSD**
PFBA	10	128	8.6	80	98.4	2.4
PFMPA	10	108	4.5	80	98.1	2.2
PFPeA	10	107	4.9	80	99.6	3.6
PFBS	10	102	9.1	80	96.2	2.9
PFMBA	10	111	6.8	80	101	3.4
PFEESA	10	107	10	80	98.8	4.0
NFDHA	10	110	15	80	98.5	5.4
4:2FTS	10	94.4	14	80	100	5.7
PFHxA	10	102	8.0	80	97	7.7
PFPeS	10	99.5	19	80	101	7.8
HFPO-DA	10	102	9.7	80	102	4.7
PFHpA	10	108	7.0	80	104	4.1
PFHxS	10	103	9.0	80	97.7	5.5
ADONA	10	96.3	3.1	80	96.8	5.6
6:2FTS	10	109	15	80	111	11
PFOA	10	108	7.4	80	98.5	6.9
PFHpS	10	98.8	8.9	80	102	7.0
PFNA	10	109	6.2	80	99.6	5.6
PFOS	10	104	8.7	80	98.0	4.3
9Cl-PF3ONS	10	99.7	4.6	80	103	6.8
8:2FTS	10	100	17	80	100	13
PFDA	10	100	4.2	80	100	1.8
PFUnA	10	102	10	80	97.3	8.1
11Cl-PF3OUdS	10	106	5.3	80	102	6.1
PFDoA	10	101	6.2	80	96.3	5.1

[a] %R = percent recovery; %RSD = percent relative standard deviation

Table 9. P&A in Reagent Water: Isotope Dilution Analogue Recovery Data[a]

Analyte	Analogue Fortification (ng/L)	Mean %R[b,c] (n=7) P&A Low	%RSD[b,c]	Mean %R (n=5) P&A High	%RSD
$^{13}C_4$-PFBA	40	95.6	11	92.5	3.4
$^{13}C_5$-PFPeA	40	93.4	9.3	91.7	4.6
$^{13}C_3$-PFBS	40	98.6	9.6	107	6.6
$^{13}C_2$-4:2FTS	160	102	6.7	108	3.5
$^{13}C_5$-PFHxA	40	92.5	6.4	92.8	11
$^{13}C_3$-HFPO-DA	40	88.6	6.5	88.8	7.4
$^{13}C_4$-PFHpA	40	98.0	4.0	94.0	8.3
$^{13}C_3$-PFHxS	40	101	11	106	8.2
$^{13}C_2$-6:2FTS	160	109	9.5	99.8	4.7
$^{13}C_8$-PFOA	40	98.0	4.1	91.5	8.7
$^{13}C_9$-PFNA	40	97.1	4.9	92.1	8.4
$^{13}C_8$-PFOS	40	98.8	6.5	96.5	5.0
$^{13}C_2$-8:2FTS	160	106	13.9	108	8.7
$^{13}C_6$-PFDA	40	104	7.7	104	6.1
$^{13}C_7$-PFUnA	40	107	6.0	98.8	7.5
$^{13}C_2$-PFDoA	40	100	5.7	94.0	6.7

[a] P&A = “precision and accuracy”.

[b] %R = percent recovery; %RSD = percent relative standard deviation.

[c] Mean and %RSD of the isotope dilution analogue results for the fortified samples in the P&A study; number of replicates given in the header row of the table.

Table 10. Precision and Accuracy Data for Finished Ground Water[a]

Analyte	Low Fortification (ng/L)	Mean %R[b] (*n*=5)	%RSD[b]	High Fortification (ng/L)	Mean %R (*n*=5)	%RSD
PFBA	10	127	15	80	98.0	4.0
PFMPA	10	100	8.3	80	103	9.8
PFPeA	10	105	11	80	105	5.1
PFBS	10	111	12	80	101	10
PFMBA	10	99.0	4.6	80	100	2.3
PFEESA	10	101	3.5	80	107	8.8
NFDHA	10	95.1	17	80	98.5	18
4:2FTS	10	70.5	20	80	116	9.2
PFHxA	10	104	18	80	111	17
PFPeS	10	87.5	5.0	80	106	6.2
HFPO-DA	10	105	7.4	80	103	7.5
PFHpA	10	102	6.8	80	101	6.4
PFHxS	10	86.6	18	80	108	6.8
ADONA	10	97.6	8.1	80	94.2	6.9
6:2FTS	10	99.9	15	80	100	12
PFOA	10	95.8	8.1	80	104	9.8
PFHpS	10	94.0	6.3	80	113	6.0
PFNA	10	95.1	7.2	80	108	3.3
PFOS	10	[c]	[c]	80	109	5.8
9Cl-PF3ONS	10	92.7	7.2	80	111	7.9
8:2FTS	10	108	19	80	102	3.2
PFDA	10	90.8	9.8	80	104	7.1
PFUnA	10	98.3	8.8	80	105	3.0
11Cl-PF3OUdS	10	94.6	8.3	80	110	9.3
PFDoA	10	92.7	7.8	80	102	6.3

[a] Finished water from a ground water source. Hardness = 320 mg/L as $CaCO_3$. pH = 7.88 at 17 °C. Free Cl_2 = 0.64 mg/L. Total Cl_2 = 0.74 mg/L.

[b] %R = percent recovery, corrected for native concentration; %RSD = percent relative standard deviation.

[c] The spike level was below the ambient PFOS concentration of 25 ng/L.

Table 11. P&A in Finished Ground Water: Isotope Dilution Analogue Recovery Data[a]

Analyte	**Analogue Fortification (ng/L)**	**Mean %R**[b,c] **(*n*=6) P&A Low**	**%RSD**[b,c]	**Mean %R (*n*=6) P&A High**	**%RSD**
$^{13}C_4$-PFBA	40	89.5	4.4	81.3	7.8
$^{13}C_5$-PFPeA	40	94.0	4.2	84.6	7.7
$^{13}C_3$-PFBS	40	103	1.7	93.6	8.5
$^{13}C_2$-4:2FTS	160	107	6.1	105	2.6
$^{13}C_5$-PFHxA	40	93.8	9.8	75.8	16
$^{13}C_3$-HFPO-DA	40	77.8	8.5	72.0	9.8
$^{13}C_4$-PFHpA	40	90.5	8.4	83.3	10
$^{13}C_3$-PFHxS	40	101	7.8	94.7	6.4
$^{13}C_2$-6:2FTS	160	101	5.2	101	4.5
$^{13}C_8$-PFOA	40	89.5	5.7	82.8	10
$^{13}C_9$-PFNA	40	103	6.6	78.0	11
$^{13}C_8$-PFOS	40	101	7.6	89.7	4.5
$^{13}C_2$-8:2FTS	160	97.2	7.4	94.0	8.0
$^{13}C_6$-PFDA	40	98.7	6.3	82.3	15
$^{13}C_7$-PFUnA	40	102	4.3	82.6	8.0
$^{13}C_2$-PFDoA	40	98.8	4.6	81.2	10

[a] P&A = “precision and accuracy”.

[b] %R = percent recovery; %RSD = percent relative standard deviation.

[c] Mean and %RSD of the isotope dilution analogue results for the unfortified matrix sample and the fortified samples in the P&A study; number of replicates given in the header row of the table.

Table 12. Precision and Accuracy Data for a Surface Water Matrix[a]

Analyte	Low Fortification (ng/L)	Mean %R[b,c] (*n*=5)	%RSD[b]	High Fortification (ng/L)	Mean %R (*n*=5)	%RSD
PFBA	10	95.4	19	80	106	4.8
PFMPA	10	108	16	80	102	5.9
PFPeA	10	93	13	80	101	6.0
PFBS	10	111	17	80	98.3	2.7
PFMBA	10	93.0	12	80	103	3.0
PFEESA	10	95.6	15	80	99.1	2.4
NFDHA	10	102	14	80	101	2.5
4:2FTS	10	70.9	17	80	91.1	7.8
PFHxA	10	96.9	19	80	103	4.2
PFPeS	10	87.5	14	80	104	4.9
HFPO-DA	10	109	8.7	80	105	7.0
PFHpA	10	95.9	11	80	105	4.8
PFHxS	10	78.5	8.2	80	97.1	5.3
ADONA	10	94.3	7.9	80	95.8	6.0
6:2FTS	10	86.5	6.3	80	101	9.7
PFOA	10	91.9	9.8	80	98.7	4.9
PFHpS	10	88.4	14	80	106	3.4
PFNA	10	89.7	9.5	80	95.9	2.8
PFOS	10	95.1	11	80	105	8.0
9Cl-PF3ONS	10	82.4	5.0	80	94.1	3.9
8:2FTS	10	102	7.6	80	101	4.0
PFDA	10	87.3	12	80	98.5	8.0
PFUnA	10	96.9	5.4	80	95.2	2.7
11Cl-PF3OUdS	10	82.4	8.9	80	93.0	4.4
PFDoA	10	94.6	2.3	80	98.4	4.1

[a] Surface water matrix was sampled after the clarifier and prior to granular activated carbon within the drinking water treatment plant and chlorinated in our laboratory. pH = 8.1 at 20 °C. Free Cl_2 = 0.98 mg/L. Total Cl_2 = 1.31 mg/L. Total Organic Carbon (TOC) = 3.8 mg/L C.

[b] %R = percent recovery; %RSD = percent relative standard deviation.

[c] Corrected for native concentration.

Table 13. P&A in Surface Water Matrix: Isotope Dilution Analogue Recovery Data[a]

Analyte	**Analogue Fortification (ng/L)**	**Mean %R**[b,c] **(*n*=6) P&A Low**	**%RSD**[b,c]	**Mean %R (*n*=6) P&A High**	**%RSD**
$^{13}C_4$-PFBA	40	86.9	18	86.3	6.5
$^{13}C_5$-PFPeA	40	105	15	102	5.7
$^{13}C_3$-PFBS	40	98.6	11	99.8	4.5
$^{13}C_2$-4:2FTS	160	136	13	138	6.3
$^{13}C_5$-PFHxA	40	88.8	16	84.8	4.5
$^{13}C_3$-HFPO-DA	40	78.4	14	75.4	13
$^{13}C_4$-PFHpA	40	91.6	12	89.3	6.0
$^{13}C_3$-PFHxS	40	98.2	6.5	96.0	9.6
$^{13}C_2$-6:2FTS	160	110	9.7	109	8.4
$^{13}C_8$-PFOA	40	90.1	14	86.6	4.5
$^{13}C_9$-PFNA	40	91.0	14	87.2	6.0
$^{13}C_8$-PFOS	40	98.8	15	95.6	5.0
$^{13}C_2$-8:2FTS	160	101	9.8	97.3	11
$^{13}C_6$-PFDA	40	92.0	16	86.6	10
$^{13}C_7$-PFUnA	40	92.2	16	90.0	5.6
$^{13}C_2$-PFDoA	40	91.2	14	90.8	10

[a] P&A = “precision and accuracy”.

[b] %R = percent recovery; %RSD = percent relative standard deviation.

[c] Mean and %RSD of the isotope dilution analogue results for the unfortified matrix sample and the fortified samples in the P&A study; number of replicates given in the header row of the table.

Table 14. Aqueous Sample Holding Time Data[a]

Analyte	**Fortified Conc. (ng/L)**	**Day Zero Mean (ng/L)**	**Day Zero %RSD**	**Day 7 %Change**[b]	**Day 7 %RSD**	**Day 14 %Change**	**Day 14 %RSD**	**Day 21 %Change**	**Day 21 %RSD**	**Day 28 %Change**	**Day 28 %RSD**
PFBA	40	42	4.6	9.1	2.3	3.1	7.2	5.1	5.4	4.2	5.0
PFMPA	40	41	5.2	5.5	2.2	-7.8	5.1	1.0	6.3	-10	3.1
PFPeA	40	43	4.1	1.2	1.9	-2.2	6.5	-0.29	2.5	-6.5	5.8
PFBS	40	43	9.7	-1.9	3.6	-6.1	1.8	-4.0	2.5	-7.6	8.9
PFMBA	40	40	3.0	-2.5	3.7	-5.7	4.3	0.20	5.0	-6.6	6.3
PFEESA	40	39	3.2	2.6	5.7	-1.8	6.7	-2.4	4.5	-1.7	2.6
NFDHA	40	39	6.5	-4.0	7.2	-11	6.9	-3.8	5.2	-2.9	8.0
4:2FTS	40	43	9.7	-1.7	3.8	-2.6	9.6	-2.0	6.1	-0.34	5.3
PFHxA	40	42	5.2	-0.37	4.6	-2.61	5.6	-1.7	5.8	-2.3	7.6
PFPeS	40	41	3.2	5.6	7.5	-3.1	2.6	6.0	9.2	-11	9.4
HFPO-DA	40	42	5.1	6.2	4.8	3.2	9.2	2.1	2.1	-3.5	4.2
PFHpA	40	41	4.6	-0.042	2.4	-4.7	1.7	-2.9	3.6	-3.0	5.4
PFHxS	40	41	4.3	1.8	3.0	-1.8	1.8	-1.8	9.0	-0.99	6.8
ADONA	40	39	4.2	-4.3	3.1	-12	5.7	-6.2	5.9	-2.3	3.1
6:2FTS	40	41	7.5	-4.3	4.4	-0.74	9.4	2.5	6.0	-1.5	6.0
PFOA	40	41	5.4	-1.5	6.7	1.6	5.1	-2.0	4.9	-6.5	7.2
PFHpS	40	41	4.7	-2.4	5.4	1.2	3.1	0.30	3.2	2.9	7.2
PFNA	40	42	4.1	2.05	0.57	-6.0	4.9	-6.1	3.4	-9.5	3.4
PFOS	40	41	7.0	-2.1	4.7	-1.8	5.2	1.0	5.8	-1.6	5.3
9Cl-PF3ONS	40	40	3.5	1.6	4.8	-0.34	1.8	4.0	4.8	-2.6	10
8:2FTS	40	44	7.9	-0.36	2.5	-1.4	6.7	0.026	3.8	-3.6	6.9
PFDA	40	41	5.0	0.12	3.1	-2.7	3.8	-1.4	3.8	-2.4	7.0
PFUnA	40	39	3.9	-1.3	4.7	-12	1.2	3.7	3.1	-6.7	3.5
11Cl-PF3OUdS	40	40	4.9	-1.1	4.5	-9.4	5.1	-11.0	4.7	-12	7.3
PFDoA	40	39	4.4	9.5	6.5	-4.8	6.0	-3.4	5.8	-16	6.1

[a] Finished water from a surface water source. pH = 8.84 at 18 °C; total organic carbon (TOC) = 0.75 mg/L C (mean of 2019 first quarter plant records); free chlorine = 0.87 mg/L, total chlorine = 1.04 mg/L. Day Zero: *n*=7. All other events: *n*=5.

[b] %Change = percent change from Day Zero calculated as follows: (Day X mean concentration – Day Zero mean concentration) / Day Zero mean concentration * 100%, where X is the analysis day.

Table 15. *Extract Holding Time Data*[a]

Analyte	Fortified Conc. (ng/L)	Day Zero Mean (ng/L)	Day Zero %RSD	Day 14 %Change[b]	Day 14 %RSD	Day 21 %Change	Day 21 %RSD	Day 27 %Change	Day 27 %RSD
PFBA	40	42	4.6	-8.0	4.2	-4.4	0.89	-12	6.4
PFMPA	40	41	5.2	-3.9	4.5	-0.10	5.1	-3.9	12
PFPeA	40	43	4.1	-6.0	6.0	-0.55	4.8	-5.4	1.1
PFBS	40	43	9.7	2.6	2.0	6.6	2.3	2.9	3.6
PFMBA	40	40	3.0	-10	7.1	-4.8	5.3	-8.8	2.7
PFEESA	40	39	3.2	1.3	8.9	-3.6	2.1	-4.9	3.6
NFDHA	40	39	6.5	-10	3.9	-13	6.8	-11	3.1
4:2FTS	40	43	9.7	-4.7	8.5	-6.2	8.8	-7.3	8.5
PFHxA	40	42	5.2	-4.6	6.3	-20	3.0	-14	4.7
PFPeS	40	41	3.2	-6.7	8.6	-11	5.2	-10	4.5
HFPO-DA	40	42	5.1	-4.9	4.9	-4.7	5.1	-4.4	7.7
PFHpA	40	41	4.6	-1.9	1.9	-6.1	4.8	-8.7	7.8
PFHxS	40	41	4.3	-19	9.9	-21	8.4	-22	11
ADONA	40	39	4.2	-1.2	1.9	-7.8	6.4	-7.5	5.0
6:2FTS	40	41	7.5	-5.3	13	-7.6	5.8	-8.4	14
PFOA	40	41	5.4	-5.7	6.3	-2.2	4.2	-2.4	3.3
PFHpS	40	41	4.7	-8.7	7.3	-6.0	5.2	-3.2	4.2
PFNA	40	42	4.1	-5.8	5.6	0.17	3.2	-2.0	6.0
PFOS	40	41	7.0	-3.8	10	-4.2	2.5	-3.7	4.4
9Cl-PF3ONS	40	40	3.5	-5.8	7.7	-9.3	4.0	-8.6	4.7
8:2FTS	40	44	7.9	-4.7	6.3	-1.3	5.8	-6.4	2.9
PFDA	40	41	5.0	-3.7	5.3	-1.8	5.6	-4.8	3.1
PFUnA	40	39	3.9	6.2	4.0	0.63	7.5	-2.8	5.2
11Cl-PF3OUdS	40	40	4.9	-12	5.9	-18	4.6	-10	6.3
PFDoA	40	39	4.4	1.9	5.5	1.0	6.4	-2.6	3.3

[a] Finished water from a surface water source. pH = 8.84 at 18 °C; total organic carbon (TOC) = approximately 0.75 mg/L C (2019 first quarter plant records); free chlorine = 0.87 mg/L, total chlorine = 1.04 mg/L. Day Zero: *n*=7. All other events: *n*=7.

[b] %Change = percent change from Day Zero calculated as follows: (Day X mean concentration – Day Zero mean concentration) / Day Zero mean concentration * 100%, where X is the analysis day.

Table 16. Initial Demonstration of Capability (IDC) Quality Control Requirements

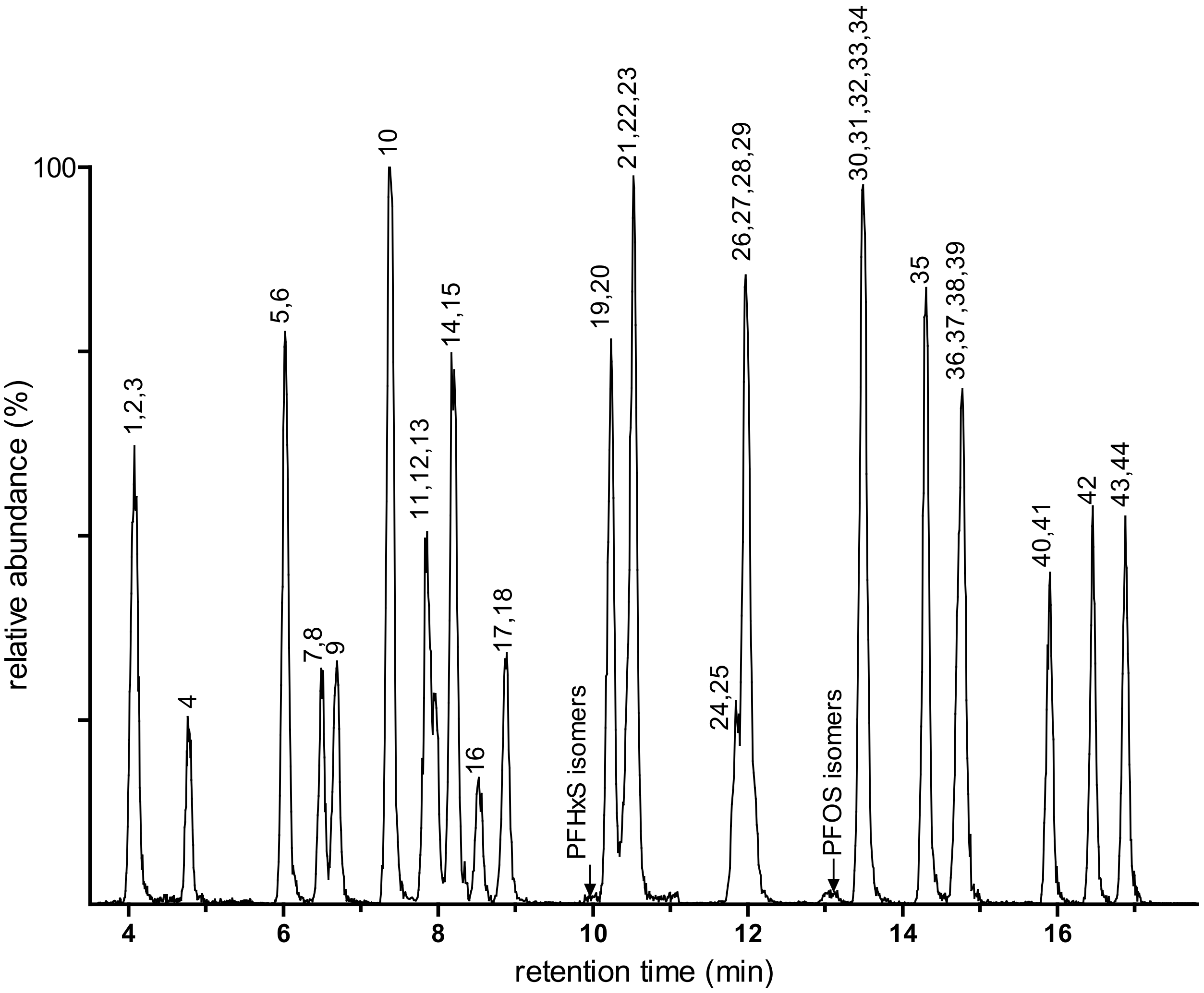
Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 10.2.2	Establish retention times for branched isomers	Each time chromatographic conditions change	All isomers of each analyte must elute within the same MRM window.
Section 9.1.1	Demonstration of low system background	Analyze a Laboratory Reagent Blank (LRB) after the highest standard in the calibration range.	Demonstrate that the method analytes are less than one-third of the Minimum Reporting Level (MRL).
Section 9.1.2	Demonstration of precision	Extract and analyze 7 replicate Laboratory Fortified Blanks (LFBs) near the mid-range concentration.	Percent relative standard deviation must be ≤20%.
Section 9.1.3	Demonstration of accuracy	Calculate mean recovery for replicates used in Section 9.1.2.	Mean recovery within 70–130% of the true value.
Section 9.1.4	MRL confirmation	Fortify and analyze 7 replicate LFBs at the proposed MRL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR meet the recovery criteria.	Upper PIR ≤150% Lower PIR ≥50%
Section 9.1.5	Calibration Verification	Analyze mid-level QCS.	Results must be within 70–130% of the true value.

Table 17. Ongoing Quality Control Requirements

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 10.3	Initial calibration	Use the isotope dilution calibration technique to generate a linear or quadratic calibration curve. Use at least 5 standard concentrations. Evaluate the calibration curve as described in Section 10.3.5.	When each calibration standard is calculated as an unknown using the calibration curve, analytes fortified at or below the MRL should be within 50–150% of the true value. Analytes fortified at all other levels should be within 70–130% of the true value.
Section 9.2.1	Laboratory Reagent Blank (LRB)	Include one LRB with each Extraction Batch. Analyze one LRB with each Analysis Batch.	Demonstrate that all method analytes are below one-third the Minimum Reporting Level (MRL), and that possible interference from reagents and glassware do not prevent identification and quantitation of method analytes.

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 9.2.3	Laboratory Fortified Blank	Include one LFB with each Extraction Batch.	For analytes fortified at concentrations ≤2 x the MRL, the result must be within 50–150% of the true value; 70–130% of the true value if fortified at concentrations greater than 2 x the MRL.
Section 10.4	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low-level CCC (concentrations at or below the MRL for each analyte) at the beginning of each Analysis Batch. Subsequent CCCs are required after every tenth field sample and to complete the batch.	The lowest level CCC must be within 50–150% of the true value. All other levels must be within 70–130% of the true value.
Section 9.2.4	Isotope performance standards	Isotope performance standards are added to all standards and sample extracts.	Peak area counts for each isotope performance standard must be within 50–150% of the average peak area in the initial calibration.
Section 9.2.5	Isotope dilution analogues	Isotope dilution analogues are added to all samples prior to extraction.	50%–200% recovery for each analogue
Section 9.2.6	Laboratory Fortified Sample Matrix (LFSM)	Include one LFSM per Extraction Batch. Fortify the LFSM with method analytes at a concentration close to but greater than the native concentrations (if known).	For analytes fortified at concentrations ≤2 x the MRL, the result must be within 50–150% of the true value; 70–130% of the true value if fortified at concentrations greater than 2 x the MRL.
Section 9.2.7	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicate (FD)	Include at least one LFSMD or FD with each Extraction Batch.	For LFSMDs or FDs, relative percent differences must be ≤30% (≤50% if analyte concentration ≤2 x the MRL).
Section 9.2.8	Field Reagent Blank (FRB)	Analyze the FRB if any analyte is detected in the associated field samples.	If an analyte detected in the field sample is present in the associated FRB at greater than one-third the MRL, the results for that analyte are invalid.
Section 9.2.9	Calibration Verification using QCS	Perform a Calibration Verification at least quarterly.	Results must be within 70–130% of the true value.

Figure 1. Example Chromatogram for Reagent Water Fortified with Method Analytes at 80 ng/L[a]



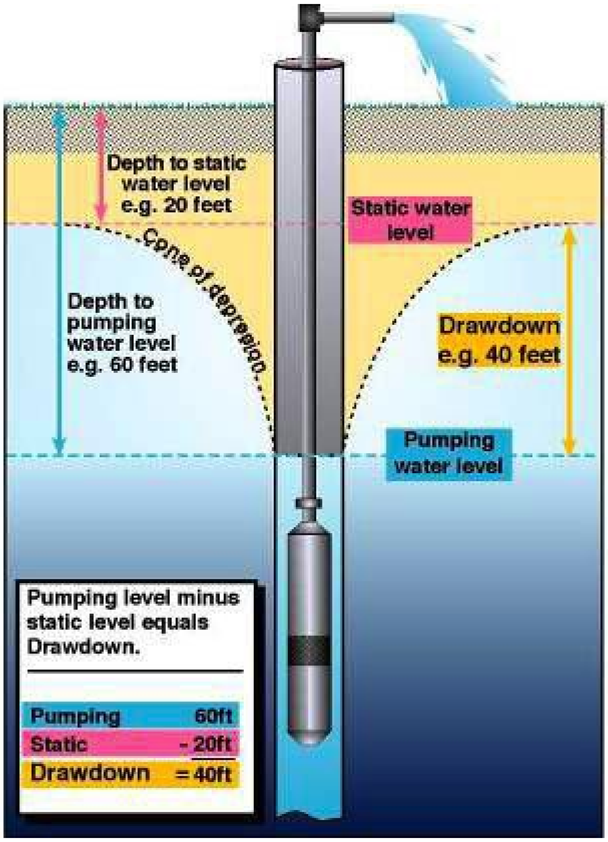
[a] Numbered peaks are identified in **Table 3**, **Table 4**, and **Table 5**.

APPENDIX B
OEPA TECHNICAL GUIDANCE MANUAL FOR HYDROGEOLOGIC INVESTIGATIONS AND GROUNDWATER MONITORING (OEPA TGM): CHAPTERS 4, 7, 10, AND 14

Ohio Environmental
Protection Agency

Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring

Chapter 4
Pumping and Slug Tests



John R. Kasich, Governor
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February 2018

Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring

Chapter 4

Pumping and Slug Tests

February 2018

Revision 2

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Preface

This document is part of a series of chapters incorporated in Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM), which was originally published in 1995. DDAGW now maintains this technical guidance as a series of chapters rather than as an individual manual. The chapters can be obtained at ***epa.ohio.gov/ddagw/gw_support.aspx***

The TGM identifies technical considerations for performing hydrogeologic investigations and ground water monitoring at potential or known ground water pollution sources. The purpose is to enhance consistency within the Agency and inform the regulated community of the Agency's technical recommendations and the basis for them.

Ohio EPA utilizes ***guidance*** to aid regulators and the regulated community in meeting laws, rules, regulations and policy. Guidance outlines recommended practices and explains their rationale. The methods and practices described in this guidance are not intended to be the only methods and practices available to an entity for complying with a specific rule. Unless following the guidance is specifically required within a rule, the Agency cannot require an entity to follow methods recommended within the guidance. The procedures used should be tailored to the specific needs and circumstances of the individual site, project and applicable regulatory program, and should not comprise a rigid step-by-step approach utilized in all situations.

Major Changes from April 2007 TGM

Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM) was first finalized in 1995. Chapter 4 (Pumping and Slug Tests) was revised in December 2006. This is the second revision to the chapter.

Section numbers were added to make the document easier to read.

References were updated, in particular, the references to ASTM standards and U.S. EPA guidance documents.

Additional information has been added on:

- Definition and clarification of "well skin effects" in slug testing
- Addition of guidance regarding use of appropriate well construction parameters in slug testing, including use of "effective" well construction parameters
- Terminology changed throughout document to make concepts flow better and easier to understand

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Chapter 4

Pumping and Slug Tests

Slug and pumping tests are used to determine in-situ properties of water-bearing formations and define the overall hydrogeologic regime. Such tests can determine transmissivity (T), hydraulic conductivity (K), storativity (S), yield, connection between saturated zones, identification of boundary conditions, and the cone of influence of a pumping well in an extraction system. The hydraulic properties that can be determined are particular to the specific test method, instrumentation, knowledge of the ground water system, and conformance of site hydraulic conditions to the assumptions of the test method (ASTM 4043-96 (2004)). The selection of test method(s) depends primarily on the hydrogeology of the area being tested. Secondarily, the method is selected based on the testing conditions specified by a particular method, such as the method of causing water level changes in the ground water zone or the requirements for observing water level responses.

To ensure proper test design, it is important to define objectives and understand site hydrogeology as much as possible. Methods, instruments and operating procedures should be specified in a workplan. Test results, methods and any departures from the workplan that were necessary during implementation of the workplan should be documented in the final report.

The purpose of this chapter of the Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) is to aid in the design and performance of slug and pumping tests, provide recommended quality assurance and quality control (QA/QC) procedures, and present a standardized approach to the presentation of the resulting data. This chapter covers various types of tests, including single well and multiple well. It includes a discussion of the advantages and disadvantages of the various tests and the minimum criteria that should be considered prior to, during and after implementation of the tests. The recommendations presented here are a subset of the larger hydrogeologic characterization process that is implemented when characterizing a site. The additional investigative tools necessary to adequately characterize a site, as well as recommendations for their use, are contained in other chapters of the TGM. This chapter does not cover pumping tests conducted for the purpose of determining whether a ground water zone can produce a sufficient amount of yield for water supply purposes.

1.0 Slug Tests

Slug tests are generally conducted to determine the horizontal K of a ground water zone. A slug test involves the abrupt removal, addition or displacement of a known volume of water and the subsequent monitoring of changes in water level as equilibrium conditions return. The measurements are recorded and analyzed by one or more methods. The rate of water level change is a function of the K of the formation and the geometry of the well or screened interval.

Slug tests generally are typically most useful in formations that exhibit low K, and thus may not be appropriate in fractured rock or formations with T greater than 250 m^2/day (2,690 ft^2/day) (Kruseman and de Ridder, 1990). However, a vacuum or slug test conducted in fractured or high T formations with a pressure transducer or an electronic data logger may produce accurate, defensible results in some instances.

Hydraulic properties determined by slug tests are representative only of the material in the immediate vicinity of the well. However, by performing a series of slug tests at discrete vertical intervals and tests in closely spaced wells, important information can be obtained about the vertical and horizontal variations of hydraulic properties for the site (Butler, 1998). It should be noted that due to the localized nature of hydraulic response, the test results might be affected by the properties of the well filter pack or "well skin effects" (for example, physical or geochemical alteration of near-well conditions resulting from drilling). Therefore, the results should be compared to known values for similar geologic media to determine if they are reasonable. Additionally, adjustments for well skin effects should be made, where appropriate (Butler, 1998).

If slug tests are used, the designer should consider the amount of displaced water, design of the well, number of tests, method and frequency of water level measurements, and the method used to analyze the data. Slug tests should be conducted in properly designed and developed wells or piezometers. If development is inadequate, the smearing of fine-grained material along the borehole wall may result in data that indicate an artificially low K. Drilling and sampling a well can cause geochemical changes that lead to similar effects on the aquifer pore spaces immediately surrounding a well. Such physical or geochemical alterations of near-well conditions from drilling and sampling are termed "well skin effects" (Butler, 1998) and could lead to poor estimation of contaminant migration potential. Well skin effects result from locally increasing the K near the well by opening fractures or intergranular porosity (positive skin) or by decreasing the K (negative skin) through: a) filling voids or coating borehole walls with drilling cuttings, or b) preferential closing of voids by chemical precipitate resulting from interaction of atmosphere with the saturated zone through installation and/or sampling of the well (Butler, 1998; Sevee, 2006).

Drilling methods, well design and installation, and well development are covered in TGM Chapters 6, 7 and 8, respectively. The design, analytical methods, and information that should be reported to document that the tests were conducted properly are discussed briefly below. Detailed practical guidelines for the design, performance and analysis of slug tests are provided by Butler (1998). Additional information can also be found in Black (1978), Chirlin (1990), Dawson and Istok (1991), Ferris et al. (1962), Kruseman and de Ridder (1990), and Lohman (1972), Batu (1988), and ASTM standards.

For some programs, workplans may need to be submitted prior to conducting tests to ensure that results will be relevant to regulatory and program goals. If needed, the workplan should discuss the components listed below for the design and performance of the slug tests and the method of analysis.

1.1 Design and Performance of Slug Test

1.1.1 Design of Well

Well depth, length and diameter of screen, screen slot size, and distribution of the filter pack should be known and based on site-specific boring information for a well to be used as a valid observation point. For example, equations used in data analysis incorporate the radii of the well and borehole. The nature of the materials comprising the screened interval (for example, thickness, grain size, and porosity of the filter pack) also must be known. Recommendations for monitoring well construction are provided in TGM Chapter 7.

1.1.2 Number of Tests

Properties determined from slug tests at a single location are not very useful for site characterization unless they are compared with data from tests in other wells installed in the same zone at or near the site. When conducted in large number, slug tests are valuable for determining subsurface heterogeneity and isotropy. The appropriate number depends on site hydrogeologic complexity.

1.1.3 Test Performance and Data Collection

Data collection should include establishment of water level trends prior to and following the application of the slug. Pre-test measurements should be made until any changes have stabilized and should be taken for a period of time, at least as long as the expected recovery period. Water level measurements in low-permeability zones may be taken with manual devices. Automatic data loggers should be used for tests of high-permeability zones. Slug tests should be continued until at least 85 percent recovery of the initial pretest measurement is obtained (U.S. EPA, 1986).

Whenever possible, water should be removed by either bailing or it should be displaced by submerging a solid body. According to Black (1978), an addition of water invariably arrives as an initial direct pulse followed by a subsequent charge that runs down the sides of a well. This may result in a response that is not instantaneous, which may subsequently influence the data (Figure 4.1). An advantage of displacement is that it allows for collection and analysis of both slug injection and slug withdrawal data. However, in wells where the screened interval intercepts the water table slug withdrawal tests are generally much more representative than slug injection tests.

The volume of water removed or displaced should be large enough to ensure that build-up or drawdown can be measured adequately, but it should not result in significant changes in saturated zone thickness (Dawson and Istok, 1991). Kruseman and de Ridder (1990) suggest water level displacement between 10 and 50 centimeters (Kruseman and de Ridder, 1990). Field procedures for slug tests are also described in ASTM D 4044-96 (2002).

1.2 Modified Slug Tests

In addition to removal or displacement of water, a change in static water level can be accomplished by pressurizing a well with air or water or by creating a vacuum. Packers are often used to seal the zone to be tested.

1.2.1 Packer Tests within a Stable Borehole

Horizontal K for consolidated rock can be determined by a packer test conducted in a stable borehole (Sevee, 2006). A single packer system can be used when testing between a packer and the bottom of the borehole. Two packer systems can be utilized in a completed borehole at any position or interval. A packer is inflated using water or gas. Water should be injected for a given length of time to test the packed-off zone.

Figure 4.1

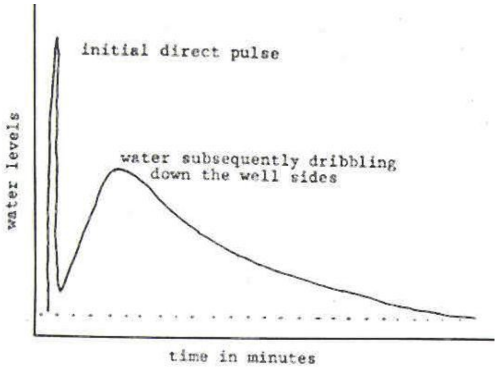

Figure 4.1. Results of a slug test with addition of water. Water arrives as an initial direct pulse followed by a subsequent charge that runs down the sides of the well (Source: Adapted from Black, 1978).

1.2.2 Pressure Tests

A pulse or a pressure test may be appropriate in formations where K can be assumed to be lower than 10^{-7} cm/sec. In a pulse test, an increment of pressure is applied into a packed zone. The decay of pressure is monitored over a period of time using pressure transducers with electronic data loggers or strip-chart recorders. The rate of decay is related to the K and S of the formation being tested. This test generally is applied in rock formations characterized by low K. Compensation must be made for well skin effects (Sevee, 2006) and packer adjustments during the test. An understanding of the presence and orientation of fractures is necessary to select an appropriate type curve to analyze test data (Sevee, 2006 and Sara, 2003). ASTM D4631-95 (2002) describes the pressure-pulse technique applied to low hydraulic conductivity bedrock.

1.2.3 Vacuum Tests

According to Orient et al. (1987), vacuum tests can be used to evaluate the K of glacial deposits and compare favorably to more conventional methods. In general, water level is raised by inducing vacuum conditions. Once it reaches the desired height and sufficient time has been allowed for the formation to return to its previous hydrostatic equilibrium, the vacuum is broken, and the recovery is monitored. The data is evaluated using the same techniques that are used to evaluate conventional slug test data.

1.3 Analysis of Slug Test Data

Mathematical methods/models for slug test data analysis are summarized in Table 4.1. Methods have been developed to deal with confined, unconfined, partial penetration and well skin effects. Calculation of K for a fully screened zone is achieved by dividing T by the entire thickness of the zone. A test of a partially penetrating well yields a T value that is only indicative of that portion of the zone that is penetrated by the well screen.

Table 4.1 Analysis Methods for Slug Tests.

General Assumptions

1) The ground water zone has an apparently infinite areal extent.
2) The zone is homogeneous and of uniform thickness over the area influenced by the test (except when noted in application column).
3) Prior to the test, the water table or piezometric surface is (nearly) horizontal over the area influenced and extends infinitely in the radial direction.
4) The head in the well is changed instantaneously at time to = 0.
5) The inertia of the water column in the well and the linear and non-linear well losses are negligible (for example, well installation and development process are assumed to have not changed the hydraulic characteristics of the formation).
6) The well diameter is finite; hence storage in the well cannot be neglected.
7) Ground water density and viscosity are constant.
8) No phases other than water (such as gasoline) are assumed to be present in the well or ground water.
9) Ground water flow can be described by Darcy's Law.
10) Water is assumed to flow horizontally.

	Application				
Method	**Ground Water Zone Type**	**Flow Condition**	**Can account for**		**Remarks**
			Partial Penetration	**Anisotropic**	
Cooper et al. (1967) (a,b,c)	Confined	Transient	No	No	Also described in ASTM D4104-91 (1992)
Bouwer and Rice (1976) Bouwer (1989) (a,b,c)	Unconfined or leaky*	Steady state	Yes	No	Can be used to estimate the K of leaky ground water zones that receive water from the upper-semi confining layer through recharge or compression
Hvorslev (1951) (a, c)	Confined or Unconfined	Transient	Yes	Yes	Differences of 0.3X to 0.5X can be observed when comparing the K calculated from other methods In some cases, can be applied to unconfined ground water zones, Fetter (2001)
Bredehoeft and Papadopulos (1980) (c)	Confined	Transient		Yes	Low to extremely low K (for example, silts, clays, shales)
Uffink (1984) (Oscillation Test) (b)	Confined	Transient		No	

Described in: a-Dawson and Istok (1991). b- Kruseman and de Ridder (1990); c-Butler (1998)

As alluded to in "Design of Well" above, slug test analysis formulas include well construction parameter inputs that must be actual or "effective," as applicable. For example, when artificial filter packs are more permeable than the surrounding formation, the "effective well screen radius" (for example, radius of the nominal well screen plus filter pack) is a more representative parameter than to the nominal well screen radius alone. The representativeness of well construction parameter estimates used in analysis formulas can have a significant effect on the representativeness of analysis results. Therefore, well construction parameter values or estimates used in each analysis should be documented and defensible. Butler (1998) for example, provides criteria for defensible estimates of effective well screen radius, effective well screen length and other well construction parameters.

Test results obtained are for the geologic material immediately surrounding the well intake, which invariably has been altered to some degree by the installation process.

Computer programs are available to evaluate slug test data. Only those programs that provide analysis of the data based on graphical curve matching, rather than simply least-squares analysis, and allow for the generation of data plots should be used.

1.4 Presentation of Slug Test Data

The specifics of slug tests should be documented to demonstrate that the tests were conducted properly and that the data and interpretations are representative of site conditions. At a minimum, the following should be specified:

- The design and implementation of the test including: Well construction (for example, depth, diameter and length of screen and filter pack).
- Method to displace the water, such as:
    - Dimension and weight of slug.
    - Composition of slug.
    - Manner in which the slug will be lowered and raised from the well.
    - Use of packers, and manner in which pressure will be delivered.
    - Chemical quality of water to be added.
- Frequency and method of water level measurements.
- Number and location of tests.
- All raw data.
    - Method. Name of analytical method(s) used; computer programs used for analysis should be referenced and all assumptions and limitations should be noted. For methods that employ type curves curve matching, the following should be provided.
    - The portion of data to which type curves are fit should be indicated on the plot.
    - If an analysis method employing a family of type curves is used, all curves selected to fit the data should be described.
- All data plots. Plots of change in hydraulic head versus time should be presented for all slug-tested wells. Plots should be on an arithmetic scale, and either double-logarithmic or semi-logarithmic scale, depending on the analysis technique. Time data should be depicted along the horizontal axis, and change in head along the vertical axis. All data points should be clearly labeled and identified in a legend. If multiple tests are presented on the same plot, the labeling should be distinct to differentiate between data sets.

- Sample calculations. Equations used for calculating hydraulic properties should also be included. While calculations of the values (for example, hydraulic conductivity, estimated transmissivity) can be presented on the data plots, the values themselves should be presented in tabular format in the report for all slug tested wells, all zones tested, and each data analysis method used.
- Any field conditions or problems that may influence the results.
- An evaluation and interpretation of the data (relating it to overall site conditions). In the event that calculations are available from other multiple- or single-well tests, the report should contain a discussion addressing how the most recent calculations compare with previously obtained values.

2.0 Single Well Pumping Tests

A single well test involves pumping at a constant or variable rate and measuring changes in water levels in the pumped well during pumping and recovery. Single well pumping tests can be used to determine transmissivity, hydraulic conductivity and yield of a ground water zone. They are also conducted to determine well loss, and optimizing rate and pump setting for a multiple well test. Single well tests are often used when water level recovery is too rapid for slug tests and no observation wells or piezometers are available. Single well tests generally will not identify impermeable boundaries, recharge boundaries, or interconnection between other ground water or surface water unless these conditions exist in very close proximity to the well being tested.

A step drawdown test is a type of single well test that is often used to optimize appropriate pumping rate and depth of pump setting used in a later multiple well test (Domenico and Schwartz, 1998). This test involves pumping at a constant rate for a period of time, the rate is then increased. This process generally is repeated through a minimum of three steps. The duration of each step generally should be a minimum of 60 minutes and should be long enough such that drawdown data plotted on a semilog plot fall on a straight line. References detailing the mechanics of a step test include Kruseman and de Ridder (1990), Driscoll (1986), Dawson and Istok (1991), and Batu (1998) and Walton (1996).

The drawdown in a pumped well is influenced by well loss and well-bore storage. Well loss is responsible for drawdown being greater than expected from theoretical calculations and can be classified as linear or non-linear. Linear loss is caused by compaction and/or plugging of subsurface material during well construction and installation and head loss in the filter pack and screen. Non-linear loss includes head loss from friction within the screen and suction pipe.

Since well-bore storage is large when compared to an equal volume of formation material, it must be considered when analyzing drawdown data from single well tests (Kruseman and de Ridder, 1990). The effects of well-bore storage on early-time drawdown data can be recognized by a log-log plot of drawdown (s_w) verses time (t). Borehole storage effects exist if the early-time drawdown data plots as a unit-slope straight line (Kruseman and de Ridder, 1990). Papadopulos and Cooper (1967) observed that the influence of well-bore storage on drawdown decreases with time (t) and becomes negligible at:

$$t = 25r_c^2/KD$$

where:

r_c = the radius of the unscreened part of the well

K = hydraulic conductivity

D = thickness of saturated zone.

2.1 Analysis and Presentation of Single Well Pumping Tests

Table 4.2 presents several methods for analyzing drawdown data for constant discharge, variable discharge, and step-discharge single well tests. Analysis of recovery test data (residual drawdown) is valuable with a single well pumping test. Methods for analysis are straight line methods, which are the same as for conventional pumping tests. However, with single well tests, one must account for the effects of well- bore storage when evaluating recovery (Kruseman and de Ridder, 1990). Recovery data may be more reliable then data collected during the pumping phase because pumping does not influence recovery. Available methods to analyze recovery are discussed in the Multiple Well Pumping Tests section of this chapter.

Information to document that single well tests have been appropriately performed and analyzed may be similar to documentation for either slug or multiple well pumping tests.

Table 4.2 Single well pumping tests.

General Assumptions

1) The ground water zone is infinite in aerial extent.
2) The zone is homogeneous, isotropic, and of uniform thickness over the area influenced by the test.
3) Prior to pumping, the piezometric surface is horizontal, or nearly so, over the area to be influenced.
4) The well penetrates the entire ground water zone and, thus, receives water by horizontal flow.
5) The water removed from storage is discharged instantaneously with decline of head.
6) Non-linear well losses are negligible.

The following assumptions/conditions apply to leaky confined ground water zones.

1) The aquitard is infinite in aerial extent.
2) The aquitard is homogeneous, isotropic and of uniform thickness.
3) The water supplied by leakage from the aquitard is discharged instantaneously with decline in head.

Method	Application		Remarks
	Ground Water Zone Type	Flow Condition	
Papadopulos and Cooper (1967) (a & b)	Confined	Transient	Early time data does not adequately reflect zone characteristics. May be difficult to match the data curve with appropriate type curves because of similarities of curves. Constant discharge. Equations take storage capacity of well into account.
Rushton and Singh (1983) (b)	Confined	Transient	More sensitive curve fitting than Papadopulos and Cooper method. Constant discharge.
Birsoy and Summers(1980) (b)	Confined	Transient	Variable discharge (zone is pumped stepwise or is intermittently pumped at constant discharge).
Hurr-Worthington (Worthington, 1981) (b)	Confined or leaky confined	Transient	Constant discharge. Modified Theis Equation.
Jacob's Straight Line Method (b)	Confined or leaky confined	Transient	Sensitive to minor variations in discharge rate. May be able to account for partial penetration if late-time data is used. Constant discharge.
Hantush (1959b) (b)	Leaky confined/ artesian	Transient	Flow through aquitard is vertical. Variable discharge.
Jacob and Lohman (1952)(b)	Confined/ artesian	Transient	If value of the effective radius is not known then storativity cannot be determined. Variable discharge (drawdown is constant).

a-Described in Dawson and Istok (1991), b-Described in Kruseman and de Ridder (1990)

3.0 Multiple Well Pumping Tests

A multiple well test is implemented by pumping a well continuously and measuring water level changes in both the pumped and observation wells during pumping or subsequent recovery. Properly designed and conducted multiple well tests can be used to define the overall hydrogeologic regime of the area being investigated, including T, S and/or specific yield of a zone. They also can help design municipal well fields, predict rates of ground water flow, determine interconnectivity between ground water zones, and design a remediation system.

Two basic types of multiple well pumping tests are constant discharge and variable discharge. The former is performed by pumping at a constant rate for the duration of the test, while the latter is distinguished by changes in rate. Measurements obtained from the pumping well generally are less desirable for calculating hydraulic properties because of the irregularities induced from the operation of the pump and well bore storage. Obtaining data from observation well(s) allows for characterization of the pumped zone over a larger area.

Test design and data analysis depends on the characteristics of the zone tested, the desired/required information to be evaluated and available funds. Design and analysis are summarized below. More detailed information can be found in Lohman (1972), Walton (1987), Dawson and Istok (1991) and Kruseman and de Ridder (1990).

3.1 Preliminary Studies

Pumping test methods are specific to the hydrogeology of the area being evaluated and the specific assumptions of the analytical solution of the chosen test method. Therefore, a prerequisite for selecting the most appropriate method is gathering as much information about the site as possible. Prior to testing, the following should be gathered:

- Geologic characteristics of the subsurface that may influence ground water flow.
- Type of water-bearing zone and its lateral and vertical extent.
- Depth, thickness and lateral extent of any confining beds.
- Location of recharge and discharge boundaries.
- Horizontal and vertical flow components (for example, direction, gradient).
- Location, construction and zone of completion of any existing wells in the area.
- Location and effects of any pumping wells.
- Approximate values and spatial variation of formation K, T and S.
- Seasonal ground water fluctuations and any regional trends.

This preliminary information can assist in the proper design of the test and the choice of a conceptual model. Test design also can be facilitated by preliminary conceptual modeling to predict the outcome of the test beforehand (Walton, 1987). This serves two purposes. First, it describes the ground water zone so that an appropriate data analysis method is evident. Second, it suggests deficiencies in observation well locations. Costs frequently are reduced by using existing wells (production, drinking, monitoring) rather than installing new ones. However, they need to be evaluated to determine whether they are properly constructed, located and equipped to be used for pumping and/or observation points. Single well tests should be conducted on the existing wells to determine whether they will respond to water level changes.

3.2 Pumping Test Design

As indicated, the design of a pumping test depends on the hydrogeologic environment and the purpose of the test. The designer should determine pumping well location (areal and depth) and design, pumping rate, pump selection, location and depth of observation wells, test duration, discharge rate measurements and devices, interval and method of water level measurements, and method of analyzing data.

3.2.1 Pumping Well Location

A pumping well should be located far enough away from hydraulic boundaries to permit recognition of drawdown trends before boundary conditions influence the data (Sevee, 2006). To minimize the effect of stream, river or lake bed infiltration, it should be located at a distance equal to or exceeding the ground water zone thickness from the possible boundary (Walton, 1987). However, if the intent is to induce recharge, then the pumping well should be located as close to the recharge boundary as possible (Sevee, 2006). The appropriate depth should be determined from exploratory boreholes or logs from nearby wells.

3.2.2 Pumping Well Design

The design of a pumping well depends on the hydrogeologic environment, the choice of conceptual model, and economics. Components to consider include diameter, length and depth of the screened interval, and screen slot configuration.

A general rule is to screen the well over at least 80 percent of the ground water zone thickness. This makes it possible to obtain about 90 percent or more of the maximum yield that could be obtained if the entire zone were screened, and allows horizontal flow toward the well to be assumed, which is an assumption that underlies almost all well-flow equations. Pumping wells completed in thick zones often have intake lengths less than 80 percent of the thickness. These wells are considered partially penetrating (Kruseman and de Ridder, 1990), and pumping would be expected to induce vertical flow components. As a result, corrections to the drawdown data may be necessary. Corrections are discussed later in this chapter.

The diameter of a pumping well depends on the method chosen to analyze the data and the estimated hydraulic properties. It must accommodate the pump, assure hydraulic efficiency and allow measurement of depth to water before, during and after pumping. Table 4.3 recommends casing diameters based on pumping rates; however, the final selection should be based on consultation with the pump manufacturer.

The screen slot size and filter pack material should be based on the grain size distribution of the zone being pumped (Kruseman and de Ridder, 1990). The screen should be factory slotted or perforated over no more than 40 percent of its circumference. Slots should be long and narrow or continuous. Slots produced manually are not recommended.

3.2.3 Pumping Rate

The rate(s) should be sufficient to ensure that the ground water zone is stressed and that drawdown can be measured accurately. The water table in an unconfined zone should not be lowered by more than 25 percent since it is the largest relative drawdown that can be corrected and analyzed with an analytical solution of the ground water flow equation (Dawson and Istok, 1991). The pumping rate for tests conducted in confined zones should not readily dewater the pumping well. Well efficiency and an appropriate pumping rate for a constant discharge test can be determined by conducting a step-drawdown test (See Single Well Tests).

Table 4.3 Recommended pumping well diameter for various pumping rates.

(Dawson and Istok, 1991, after Driscoll, 1986).

Pumping Rate		Diameter	
Gal/min	m³/day	(in)	(mm)
<100	<545	6	152
75-175	409-954	8	203
150-350	818-1,910	10	254
300-700	1,640-3,820	12	305
500-1,000	2,730-5,450	14	365
800-1,800	4,360-9,810	16	406
1,200-3,000	6,540-16,400	20	508

Other methods that may be useful to estimate an appropriate pumping rate include: 1) using an empirical formula to predict well specific capacity; and 2) predicting drawdown using analytical solutions. These methods are described by Dawson and Istok (1991). It should be noted that these techniques predict discharge rates that can be utilized to determine hydraulic parameters and should not be utilized to estimate an appropriate rate for capturing a contaminant plume.

3.2.4 Pump Selection

The pump and power supply must be capable of operating continuously at an appropriate constant discharge rate for at least the expected duration of the test. Pumps powered by electric motors produce the most constant discharge (Stallman, 1983).

3.3 Observation Well Number

The appropriate number of observation wells depends on the goals of the test, hydrogeologic complexity, the degree of accuracy needed, and the method employed to analyze the data. In general, at least three are recommended (Kruseman and de Ridder, 1990). If two or more are available, data can be analyzed by both time (x-axis) versus drawdown (y-axis) and distance (x-axis) versus drawdown (y-axis) relationships. Using both and observing how wells respond in various locations provides greater assurance that: 1) the calculated hydraulic properties are representative of the zone being pumped over a large area; and 2) any heterogeneities that may affect the flow of ground water and contaminants have been identified. In areas where several complex boundaries exist, additional wells may be needed to allow proper interpretation of the test data (Sevee, 2006).

3.3.1 Observation Well Design

In general, observation wells need to be constructed with an appropriate filter pack, screen slot size and annular seal, and must be developed properly. Practices for design and development of observation wells can be similar to those for monitoring wells (see TGM Chapters 7 and 8). The observation wells/piezometers should be of sufficient diameter to accommodate the measuring device.

3.3.2 Observation Well Depth

Fully-penetrating wells are desirable. The open portion of an observation well generally should be placed in the same horizon as the intake of the pumping well. When testing heterogeneous zones, it is recommended that an observation well be installed in each permeable layer. Additional wells should be placed in aquitards to determine leakage and interconnectivity (Kruseman and de Ridder, 1990).

3.3.3 Observation Well Location

Observation well location depends on the type of ground water zone, estimated transmissivity, duration of the test, discharge rate, length of the pumping well screen, whether the zone is stratified or fractured and anticipated boundary conditions. Placing observation wells 10 to 100 meters (33 to 328 feet) from the pumping well is generally adequate for determining hydraulic parameters. For thick or stratified, confined zones, the distance should be greater (Kruseman and de Ridder, 1990). Also, additional observation wells located outside the zone of influence of the pumping well are recommended to monitor possible natural changes in head.

In general, observation wells completed in a confined ground water zone can be spaced further from the pumping well than those completed in an unconfined zone. The decline in the piezometric surface of confined zones spreads rapidly because the release of water from storage is entirely due to compressibility of water and the ground water zone material. Water movement in unconfined zones is principally from draining of pores, which results in a slower expansion.

Under isotropic conditions, the distribution of the observation wells around the pumping well can be arbitrary. However, an even distribution is desirable so that drawdown measurements represent the largest volume as possible (Dawson and Istok, 1991). If feasible, at least three wells should be logarithmically spaced to provide at least one logarithmic cycle of distance-drawdown data (Walton, 1987). If anisotropic conditions exist or are suspected, then a single row of observation wells is not sufficient to estimate the directional dependence of transmissivity. A minimum of three observation wells, none of which are on the same radial arc, is required to separate the anisotropic behavior.

The length of the pumping well screen can have a strong influence on the distance of the observation wells from the pumping well. Partially penetrating pumping wells will induce vertical flow, which is most noticeable near the well. As a result, water level measurements taken from these wells need to be corrected; however, the effects of vertical flow become more negligible at increasing distances from the pumping well. For partially penetrating pumping wells, corrections to the drawdown data may not be necessary if the following relation holds true (Sevee, 2006; and Dawson and Istok, 1991):

$$MD \geq 1.5D\sqrt{\frac{K_H}{K_v}}$$

where:

MD = minimum distance between pumping well and observation well

D = saturated thickness

K_H = horizontal K

K_V = vertical K.

Drawdown measured in observation wells located less than the minimum distance should be corrected. Typically, horizontal K is ten times greater than vertical K. If this ratio is used, then the minimum distance becomes 1.5D/10. Note that partially penetrating wells located at or greater than the minimum distance may be too far away to show drawdown.

Anticipated boundary conditions (for example, an impervious zone or a recharging river) also can affect the placement of observation wells. Wells should be placed to either minimize the effect of the boundary or more precisely locate the discontinuity (Dawson and Istok, 1991). According to Walton (1987), to minimize the effect of the boundary on distance-drawdown data, wells should be placed along a line through the pumping well and parallel to the boundary. Observation wells also should be placed on a line perpendicular to the boundary. If more than one boundary is suspected or known, the wells should be located so that the effects on drawdown data encountered by the first boundary have stabilized prior to encountering the second boundary (Sevee, 2006).

Observation points in nearby surface water bodies can be monitored to help determine if interconnection exists between the ground water and surface water.

3.4 Duration of Pumping

The appropriate duration of a pumping test depends on the hydrogeologic setting, boundary conditions, degree of accuracy desired and objectives of the test. In general, longer tests are needed to address boundary conditions; while shorter tests may be acceptable to determine hydraulic parameters. Economic factors and time constraints also may be influential; however, economizing the period of pumping is not recommended. The cost of continuing a test is low compared to total costs, particularly when the wells have been specially constructed and positioned for test purposes (Kruseman and de Ridder, 1990).

Pumping tests commonly last from five hours to five days (Walton, 1962). In some cases, tests may need to be continued until the cone of depression has stabilized and does not expand as pumping continues (for example, drawdown does not appreciably increase/decrease). Such a steady state or equilibrium can occur within a few hours to weeks or never. According to Kruseman and de Ridder (1990), the average time to reach steady state in a leaking ground water zone is 15 to 20 hours. A test of a confined ground water zone should last a minimum of 24 hours. Three days or more should be allowed for tests conducted in unconfined zones because of the slow expansion of the cone of depression. The duration necessary to define the hydraulic parameters depends on the regional and local geologic/hydrogeologic setting. Plotting drawdown data during tests often reveals anomalies and the presence of suspected or unknown boundaries, and assists in determining test duration.

3.4.1 Discharge Rate Measurement

Variation in discharge rates produces aberrations in drawdown that are difficult to treat in data analysis. Engines, even those equipped with automatic speed controls, can produce variations up to 20 to 25 percent over the course of a day. The rate should never vary by more than five percent (Osborne, 1993). To obtain reliable data, discharge should be monitored, and adjustments made as needed.

The frequency of measurements depends on the pump, engine power characteristics, the well, and the zone tested. Discharge from electric pumps should be measured and adjusted (if necessary) at 5, 10, 20, 30, 60 minutes, and hourly thereafter. Other types of pumps may require more frequent attention; however, no "rule of thumb" can be set because of the wide variation in equipment response (Stallman, 1983).

3.4.2 Discharge Measuring Devices

Some discharge measurement techniques are more accurate than others and some allow for a convenient means of adjusting rate. A commercial water meter of appropriate capacity can be utilized. It should be connected to the discharge pipe in a way that ensures accurate readings. A disadvantage is the unavoidable delay in obtaining values at the start of the test, when pumping rate is being adjusted to the desired level (Driscoll, 1986). When discharge is low, the rate can be measured as a function of time to fill a container of known volume. The orifice weir is commonly used to measure discharge from high-capacity pumps. A manometer is fitted into the discharge pipe. The water level in the manometer represents the pressure in the pipe when the water flows through the orifice. Details on orifice design and interpretation of results can be found in Driscoll (1986). Finally, discharge rate can be obtained by water level measurements taken from weirs and flumes. The rate of flow is determined within known constriction dimensions placed in the discharge channel originating at the well head (Driscoll, 1986).

3.4.3 Interval of Water Level Measurements

Pre-test Measurements

Prior to the start of tests, water level data should be collected from the pumping and observation wells to determine existing trends for all zones to be monitored. The pumping phase should begin only if identified and recorded trends are expected to remain constant. As a general rule, the period of observation should be at least twice the length of the estimated time of pumping (Stallman, 1983). Water levels should be measured and recorded hourly for all zones. In addition, the barometric pressure should be monitored, at least hourly, to determine the barometric efficiency of ground water zone(s), which may be useful in correcting the drawdown data. Barometric efficiency is discussed later in this chapter.

Measurements During Pumping

The appropriate time interval for water level measurements varies from frequent at the beginning of a test, when water-levels are changing rapidly, to long at the end of the test, when change is slow. Typical intervals for the pumping well and observation wells located close to the pumping well are given in Tables 4.4 and 4.5, respectively. Though specified intervals need not be followed rigidly, each logarithmic cycle should contain at least 10 data points spread through the cycle (Stallman, 1983). Frequent readings are essential during the first hour since drawdown occurs at a faster rate in the early time interval. For wells further away and those located in zones above or below the pumping zone, the measurements recommended by Table 4.5 within the first few minutes of the pumping test are less important (Kruseman and de Ridder, 1990).

Table 4.4 Range of interval between water-level measurements in the pumping well (Kruseman and de Ridder, 1990).

Time Since Start of Pumping	Time Interval
0 to 5 minutes	0.5 minutes
2 to 60 minutes	5 minutes
60 to 120 minutes	20 minutes
120 to shutdown of the pump	60 minutes

Table 4.5 Range of intervals between water-level measurements in observation wells (Kruseman and de Ridder, 1990).

Time Since Start of Pumping	Time Interval
0 to 2 minutes	approx. 10 seconds
2 to 5 minutes	30 seconds
5 to 15 minutes	1 minute
50 to 100 minutes	5 minutes
100 minutes to 5 hours	30 minutes
5 hours to 48 hours	60 minutes
48 hours to 6 days	3 times a day 1 time a day
6 days to shutdown of the pump	

According to Stallman (1983), it is not necessary to measure water levels in all wells simultaneously, but it is highly desirable to achieve nearly uniform separation of plotted drawdowns on a logarithmic scale. All timepieces used should be synchronized before the test is started, and provisions made to notify all participants at the instant the test is initiated.

Measurements During Recovery

After pumping is completed, water level recovery should be monitored with the same frequency used during pumping. Measurements should commence immediately upon pump shut down and continue for the same duration as the pumping phase, or until the water levels have reached 95 percent of the initial, pre-pumping static water level. A check valve should be used to prevent backflow of water in the riser pipe into the well, which could result in unreliable recovery data.

3.5 Water Level Measurement Devices

The most accurate recording of water level changes is made with fully automatic microcomputer-controlled systems that use pressure or acoustic transducers for continuous measurements. Water levels can also be determined by hand, but the instant of each reading must be recorded with a chronometer. Measurements can be performed with floating steel tape equipped with a standard pointer, electronic sounder or wet-tape method. For observation wells close to the pumped well, automatic recorders programmed for frequent measurements are most convenient because water level change is rapid during the first hour of the test. For detailed descriptions of automatic recorders, mechanical and electric sounders, and other tools, see Driscoll (1986), Dalton et al. (2006), and ASTM D4750-87 (2001). TGM Chapter 10 contains a summary of manual devices.

The measurement procedure should be standardized and the instrument calibrated prior to the start of the test. Transducers should be calibrated by a direct method, and the calibration should be checked at the conclusion of the recovery test.

3.6 Discharge of Pumped Water

Water extracted during a pumping test must be discharged properly and in accordance with any applicable laws and regulations. At sites with contaminated ground water, the discharge may need to be containerized and sampled to assess the presence of contaminants and, if necessary, treated and/or disposed at an appropriate permitted facility.

It is not the intent of this document to define Ohio EPA policy on disposal of pumped water. In general, the water should be evaluated to determine if it is characteristically a waste. If the ground water has been contaminated by a listed hazardous waste, the ground water is considered to "contain" that waste, and must therefore be managed as such. Disposal must be at a permitted hazardous waste facility. Treatment must be in a wastewater treatment system that is appropriate for the waste and meets the definitions contained in OAC rule 3745-50-10.

If containerization is not necessary, then pumped water must be discharged in a manner that prevents recharge into any zone being monitored during the test. At a minimum, the water should be discharged 100 to 200 meters from the pumped well. This is particularly important when testing unconfined zones. At no time should the discharge water be injected back into the subsurface. A permit for discharge via stream or storm sewer may be required (contact the Division of Surface Water, Ohio EPA).

3.7 Decontamination of Equipment

Decontamination of equipment is important throughout an in-situ test. Contact of contaminated equipment with ground water (or a well) may cause a measuring point to be unsuitable for water quality investigations. Details on appropriate methods can be found in TGM Chapter 10.

4.0 Correction to Drawdown Data

Prior to using the drawdown data collected from a pumping test, it may be necessary to correct for either external sources or effects induced by the test. Barometric pressure changes, tidal or river fluctuations, natural recharge and discharge, and unique situations (for example, a heavy rainfall) may all exert an influence. In confined and leaky ground water zones, changes in hydraulic head may be due to influences of tidal or river-level fluctuations, surface loading or changes in atmospheric pressure.

Diurnal fluctuations in water levels can occur in unconfined zones due to the differences between night and day evapotranspiration. Corrections to measurements may be needed for unconfined ground water zone data due to a decrease in saturated thickness caused by the pumping test. Also, corrections may be necessary if the pumping well partially penetrates the zone tested. By identifying pre-test water level trends in zone(s) of interest, long and short-term variations can be eliminated from the data if their impacts are significant during the pumping phase (Figure 4.3).

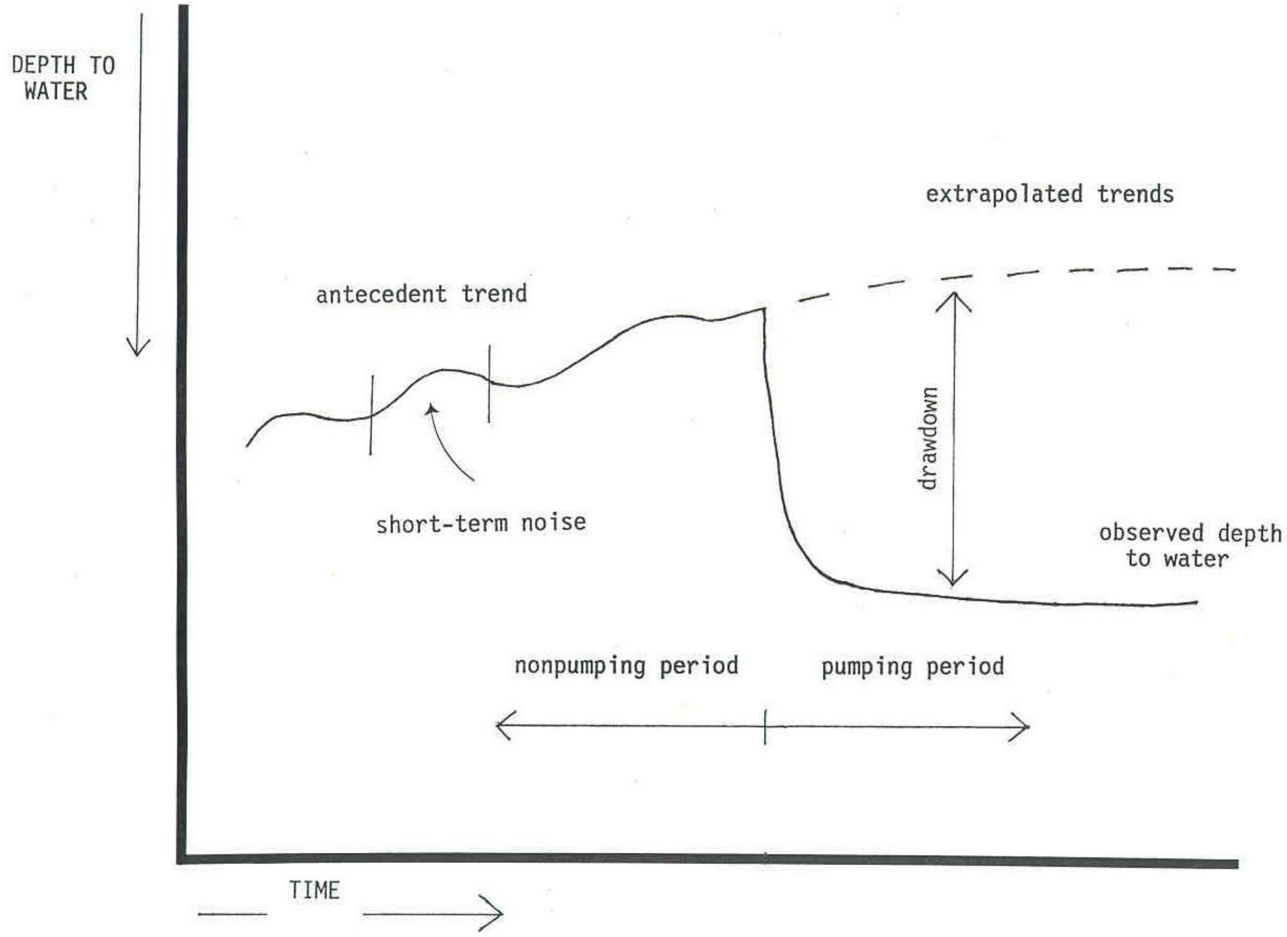

Figure 4.3 Hydrograph for hypothetical observation well showing definition of drawdown (adapted from Stallman, 1983).

To determine if corrections are necessary, measurements should be taken during the test in observation wells unaffected by the pumping. Hydrographs of the pumping and observation wells covering a sufficient period of pre-test and post-recovery periods can help determine if the data needs to be corrected and to correct the drawdown data. If the same constant water level is observed during the pre-testing and post-recovery periods, it can safely be assumed that no external events exerted an influence (Kruseman and de Ridder, 1990).

4.1 Barometric Pressure

Data for confined and leaky zones needs to be corrected for the amount of rise in water levels resulting from a decrease in atmospheric pressure and/or the amount of fall resulting from an increase. To make the correction, the barometric efficiency (BE) of the zone needs to be determined. The BE can be calculated by the following equation [Dawson and Istok (1991) and Kruseman and de Ridder (1990)]:

$$BE = \frac{\partial h}{\partial \rho / Y_w} \times 100\%$$

where:

∂h = change of head in observation well

∂p = change in atmospheric pressure

Y_w = specific weight (density) of water

If the change in hydraulic head is plotted versus the change in pressure (measured column height) and a best-fit straight line is drawn, then the slope of the line is the BE. From changes in atmospheric pressure observed during the test and the BE, the change in water level due to changes in barometric pressure can be calculated and the drawdown data can be corrected. When artesian zones are tested, barometric pressure (to a sensitivity of +/- 0.01 inch of mercury) should be recorded continuously throughout the testing period. Barometric efficiency typically ranges between 0.20 and 0.75 (Kruseman and de Ridder, 1990).

4.2 Saturated Thickness

The saturated thickness of an unconfined zone decreases during pumping tests; however, most conceptual models assume that it remains constant. This assumption can be accepted if the saturated thickness does not decrease more than 25 percent. If the decrease is greater than 25 percent, then the drawdown data should be corrected prior to analysis (Dawson and Istok, 1991).

According to Jacob (1944), data for unconfined zones can be corrected for saturated thickness change with the following equation:

$S_{corrected} = s - s^2/2m$ where:

$S_{corrected}$ = corrected drawdown

m = initial saturated thickness

However, this correction is based on the Dupuit-Forchheimer assumption (ground water flows horizontally and hydraulic gradient is equal to the slope of the water table). Neuman (1975) showed that this assumption is not valid for an unconfined until the later portion of the test when the drawdown matches the Theis type curve. Therefore, the correction is not recommended with early and intermediate data (Dawson and Istok, 1991).

4.3 Unique Fluctuations

Data cannot be corrected for unique events such as a heavy rain or sudden fall or rise of a nearby river that is hydraulically connected to the zone tested. However, in favorable circumstances, some allowances can be made for the resulting fluctuations by extrapolating data from a controlled piezometer outside the zone of influence. In most cases, the data collected is rendered worthless and the test must be repeated when the situation returns to normal (Kruseman and de Ridder, 1990). It is also important to understand the effects of nearby industrial or municipal pumping wells prior to conducting a pumping test. Also, it may be necessary to monitor/evaluate the effects of surficial loading (for example, passing trains) on water level measurements.

4.4 Partially Penetrating Wells

In some cases, a ground water zone is so thick that it is not justifiable to install a fully penetrating well, and the zone must be pumped by a partially penetrating well. Partial penetration causes vertical flow in the vicinity of the well, which results in additional head loss. As indicated earlier, this effect decreases with increasing distance from the pumping well and no correction is necessary if the observation well is at a distance greater than 1.5D/KH/KV. Various methods have been developed to correct data for the effects of partially penetrating wells. These were discussed in detail by Kruseman and de Ridder (1990). Table 4.6 lists the methods and their general applications.

4.5 Noordbergum Effect

The Noordbergum effect (also called the Mandel-Cryer effect) is observed in observation wells monitored in an upper or lower zone above the pumping zone. A rise in water levels may occur in these units due to compression of the aquitard and an increase in pore pressure or, equivalently, a hydraulic buildup (instead of the expected drawdown). The effects generally occur early and die with time. See Sara (2003) for additional explanation.

Table 4.6 Corrections for partially penetrating effects (information derived from Kruseman & de Ridder, 1990).

Method	Application	Original Source
Huisman Method I	- confined - steady state	Anonymous, 1964
Huisman Method II	- confined - unsteady state - time of pumping relatively short	Hantush (1961 a, 1961 b)
Hantush Modification of Theis Method	- confined - unsteady state - time of pumping relatively short	Hantush (1961 a, 1961 b)
Hantush, Modification of Jacob Method	- confined - unsteady state - time of pumping relatively long	Hantush (1961 b)
Weeks', "Modification of Walton and the Hantush Curve Fitting Methods"	- leaky - steady state flow	Weeks (1969)
Streltsova's Curve Fitting Method	- unconfined - anisotropic - unsteady state	Streltsova (1974)
Neuman's Curve- Fitting Method	- unconfined - anisotropic	Neuman (1974, 1975, 1979)

5.0 Analysis of Multiple Well Pumping Test Data

Many methods (for example, Theis, Cooper-Jacob, etc.) and computer software programs exist for interpreting multiple well pumping test data. The hydraulic properties computed by a particular method can only be considered correct if the assumptions included in the conceptual model on which the method is based are valid for the particular system being tested. Because the computed values depend on the choice of conceptual model used to analyze the data, the selection of an appropriate model is the single most important step in analysis (Dawson and Istok, 1991).

It is beyond the scope of this document to detail or discuss the various models. Tables 4.7 through 4.11 can be used for a preliminary selection of a method. In addition, ASTM Method D4043-96 (2004) provides a decision tree for the selection of a test method and ASTM Methods D4106-96 (2004) and D4105-96 (2002) offer information on determining hydraulic parameters. In addition to ASTM standards, information on aquifer analysis conceptual models and/or programs can be found in: Batu (1998) Dawson and Istok (1991), and Kruseman and de Ridder (2000).

Data collected during a pumping test are subject to a variety of circumstances that may be recognized in the field or may not be apparent until data analysis has begun. In either case, all information (including field observations) must be examined during data correlation and analysis.

5.1 Presentation of Multiple Well Tests Data

The guidelines below recommend the minimum criteria for how multiple well test data should be compiled, presented and summarized to document that the hydraulic properties of the zone(s) of interest have been adequately determined.

- Preliminary evaluation of hydrogeologic conditions, including all data used to plan and design the test.
- Summary of the design and implementation of the pumping tests including, but not limited to:
    - Geologic zone into which the pumping well is completed (for example, areal extent, thickness, lateral and vertical extent).
    - Pumping well construction (justification should be provided if the well screen is partially penetrating).
    - Duration of pumping.
    - Rate of pumping and method for determination. Location of all observation wells.
    - Geologic zone(s) to be monitored (including depths, thickness, spatial relationship to the pumped zone).
    - Observation and pumping well construction.
    - Method of water level measurements (for each well).
    - Methods for gathering data used to correct drawdown and establishment of existing trends in water levels.
    - Procedures for the discharge and disposal (if necessary) of pumped water.
    - Date and time pumping began and ended.
- Raw data, including water level measurements, time of measurement in minutes after pumping started or ended, drawdown, pumping rates, etc. should be included in tabular form. All data should be expressed in consistent units. Water level in nearby surface water bodies should also be provided, if taken. If the data set is large, it may be provided on disk.
    - Data plots and type curves. All graphs and data plots should be labeled clearly.

  - Data plots of (for example, drawdown versus time) should be presented for the pumping well and each observation well on double-logarithmic and semi- logarithmic paper. Time data (in minutes) should be depicted along the horizontal axis, and drawdown should be depicted along the vertical axis. For semi-logarithmic plots, drawdown should be presented along the vertical arithmetic axis.
  - The horizontal scale should be the same for all data plots.
  - All data points on the plots should be clearly labeled. In the event data from multiple wells are presented on the same plot, the labeling should be distinct to enable differentiation between sets of data, and be identified in a legend.
  - Data plots of drawdown versus distance from the pumping well should be presented; calculations of hydraulic properties based on these plots should be used to corroborate calculations made from time drawdown data plots.
  - Data plots of residual drawdown versus time since pumping stopped should be presented for recovery data.
  - Data plots of discharge rate versus time should be presented.
  - For data depicted on double-logarithmic plots, the following requirements should be met: If a single type curve has been used to analyze the data, the type curve should be presented directly on the data plot.
  - If an analysis method employing a family of type curves has been used, all curves selected to fit the data (including both early and late time responses to pumping, if applicable) should be depicted directly on the data plot, and a discussion addressing the applicability of using multiple type curves should be included in the site investigation report.
  - Match point values should be identified on data plots.
  - For data depicted on semi-logarithmic plots, the portion of the data to which a straight line is fit should be indicated on the plot.
- Calculations. Equations used for calculating hydraulic properties should also be included in the report.
- In the event any boundaries are encountered by the cone of depression during the test, the report should contain: (1) a reference to the data plot on which the boundary's impact can be observed; (2) identification of the type of boundary; and (3) a discussion addressing the boundary's effect on the hydraulics at the site. For pumping wells, an evaluation of casing storage effects should be included
- Comments noting any external events (for example, change in weather patterns, passage of train or heavy machinery). In the event drawdown data need adjustment due to external effects or reduction in saturated thickness, separate data plots depicting both adjusted and unadjusted drawdown versus time and versus distance should be presented for the appropriate wells. Any plots, graphs, or equations used to determine the magnitude of drawdown adjustment should also be presented.
- Data analysis method and/or programs, including assumptions, limitations and their applicability to the site.
- In the event a computer program is used to perform the analysis, only those software programs that provide analysis of the data based on graphical curve matching, rather than least-squares analysis, and allow for the generation of data plots should be used.

- Interpretation of the data using both results of the test and other available hydrogeologic information.

5.2 Recovery Tests

Recovery tests (also called residual drawdown tests) involve measuring water level rise after the pump is shut down. These tests provide an independent check on the transmissivity and storativity determined from a pumping test. The results should be used in conjunction with calculations obtained from the pumping phase to estimate the true hydraulic properties of the zone(s) of interest. Results of a recovery test can be more reliable than pumping test results because recovery is not influenced by the erratic fluctuations that can be characteristic of pumping.

As with the early portions of the pumping phase in which water levels drop rapidly, water levels rise rapidly during early portions of the recovery phase and are followed by a decreasing rate of water level rise. It is therefore important to establish the same schedule for obtaining water level measurements during the initial portions of the recovery phase as that used during the pumping phase (Kruseman and de Ridder, 1990). Table 4.12 provides methods for analyzing recovery data.

At a minimum, the following information should be provided: date and time the pumping phase ended and the recovery phase began; initial and final water levels for the recovery phase; time since pumping stopped (in minutes); measured water level; residual drawdown; and records of any noteworthy occurrences.

Table 4.7 Multiple-well, constant discharge pumping tests, unconfined ground water zone.

General Assumptions

1) The ground water zone is unconfined and bounded below by an aquiclude.
2) All layers are horizontal and extend infinitely in the radial extent.
3) The ground water zone is homogeneous, isotropic (unless noted) and of uniform thickness.
4) Prior to pumping, the water table is horizontal over the area that will be influenced by the test.
5) Ground water density and viscosity are constant.
6) Ground water flow can be described by Darcy's Law.
7) Head losses through well screen and pump intake are negligible.
8) The ground water zone is compressible and completely elastic.
9) The zone has been pumped long enough that equilibrium has been reached.
10) Drawdown is small compared to the saturated thickness (for example, no more than 25 percent).
11) Pumping and observation wells are screened over the entire saturated thickness (unless noted).
12) Ground water flow above the water table is negligible.

	Can Account For			
Method	**Flow Conditions**	**Partial Penetration**	**Other**	**Remarks**
Neuman's Curve Fitting Method (Neuman, 1972) (a,b)	Transient	No	anisotropic conditions	Theory should be valid for piezometers with short screens provided that the drawdowns are averaged over the saturated thickness (Van der Kamp, 1985)
Thiem-Dupuit's Method, (Thiem, 1906) (b)	Steady state	No		Steady state will only be achieved after long pumping time Does not give accurate description of drawdown near the well Assumptions ignore the existence of a seepage face at the well and the influence of the vertical velocity component
Boulton and Streltsova (1976)	Transient	Yes	storage in the well anisotropy	
Neuman (1974) (a)	Transient	Yes	anisotropy	

a Described in Dawson and Istok, 1991

b Described in Kruseman and de Ridder, 1990

Table 4.8 Multiple-well, constant-discharge pumping tests, confined ground water zones.

General Assumptions

1) The ground water zone is confined and bounded above and below by aquicludes.
2) The ground water zone is homogeneous, isotropic (unless noted in special conditions) and of uniform thickness over the area influenced by the test.
3) All layers are horizontal and extend infinitely in the radial extent.
4) Prior to pumping, the piezometric surface is horizontal and extends infinitely in the radial direction.
5) Ground water density and viscosity are constant.
6) Ground water can be described by Darcy's Law.
7) Head losses through well screen and pump intake are negligible.
8) Ground water flow is horizontal and is directed radially to the well.
9) Pumping well and observation wells are screened over the entire thickness of the ground water zone.

Additional assumptions for unsteady state flow.

1) The water removed from storage is discharged instantaneously with decline of head.
2) The diameter of the well is small, i.e., the storage in the well can be neglected.

Method	Application			Remarks
	Can Account For			
	Flow Conditions	Partial Penetration	Other	
Thiem (1906) (a,b)	Steady state	No		Equation should be used with caution and only when other methods cannot be applied. Drawdown is influenced by well losses, screen and pump intake.
Theis (1935) (a,b)	Transient	No		Because there may be a time lag between pressure decline and release of stored water, early drawdown data may not closely represent theoretical drawdown data.
Hantush (1964) (b)	Transient	Yes	Anisotropy in the horizontal plane	Inflection point method can be used when the horizontal and vertical hydraulic conductivities can be reasonably estimated.
Jacob's Method (Cooper and Jacob, 1946) (b)	Transient	No		Can also be applied to single well pump tests. Condition that u values are small usually is satisfied at moderate distances from the well within an hour or so. at $u < 0.05$ or 0.10, error introduced is two and five percent respectively. Based on Theis Equation, straight line method based on drawdown versus time on semi-log paper.

Table 4.8 (continued). Multiple-well, constant discharge pumping tests, confined.

Method	Application			Remarks
	Can Account For			
	Flow Conditions	Partial Penetration	Other	
Weeks (1969) (b)	Transient	Yes	Anisotropy in the vertical plane	Similar procedure can be applied to leaky ground water zones.
Papadopulos (1965) (a)	Transient	No	Anisotropy in horizontal plane	Minimum of three observation wells.
Papadopulos and Cooper (1967) (a)	Transient	No	Well Storage	Pumping rate is the sum of the ground water entering in the pumping well from the zone and the rate of decrease of water stored in well casing.
Neuman's Extension of Papadopulos (Neuman et al., 1984) (b)	Transient	No	Anisotropy in the horizontal plane	More reliable results can be obtained by conducting three pumping tests. The zone is penetrated by at least three wells, which are not on the same ray.
Hantush (1966) (b)	Transient	No	Anisotropy in the horizontal plane	If the principal direction of anisotropy is known, drawdown data from two piezometers on different rays is sufficient. If not, three wells on different rays will be needed. Use of Theis (1906) or Cooper and Jacob (1946).
Hantush and Thomas (1966) (b)	Transient	No	Anisotropy in the horizontal plane	Apply methods for confined isotropic ground water zones to the data for each ray of piezometers.

a Described in Dawson and Istok (1991)

b Described in Kruseman and de Ridder (1990)

Table 4.9 Multiple-well, Constant discharge pumping tests, leaky ground water zones.

General Assumptions

1) The ground water zone is leaky.
2) The ground water zone and aquitard have seemingly infinite and areal extent.
3) The ground water zone and aquitard are homogeneous, isotropic (unless noted), and of uniform thickness over the area influenced by the test.
4) Prior to pumping, the piezometric surface and the water table are horizontal over the area that will be influenced by the test.
5) The well penetrates the entire thickness of the zone and thus receives water by horizontal flow (unless noted).
6) The flow in the aquitard is vertical.
7) The drawdown in the unpumped ground water zone (or aquitard) is negligible.
8) Ground water flow can be described by Darcy's Law.

Additional assumptions for transient conditions:

1) Water removed from storage and the water supplied by leakage from the aquitard is discharged instantaneously with decline of head.
2) The diameter of the well is very small, for example, the storage in the well can be neglected.

	Can Account For			
Method	**Flow conditions**	**Partial Penetration**	**Other**	**Remarks**
De Glee (1930 & 1951) (b)	steady state	No		
Hantush (1960) (b)	Transient	No	Takes into account storage changes in the aquitard	Only the early-time drawdown should be used to satisfy the assumption that the drawdown in the aquitard is negligible. Generally is Theis equation plus an error function.
Hantush-Inflection Point (1956) (a,b)	Transient	No		Accuracy depends on accuracy of extrapolating the maximum drawdown. Two different methods, one requires one piezometer, and the other requires data from two piezometers.
Hantush-Jacob (1955) (b)	Steady state	No		
Lai and Su (1974) (a,b)	Transient	No		
Neuman-Witherspoon (1972) (b)	Transient	No		Need to calculate transmissivity using one of the other methods.

Table 4.9 (continued). Multiple-well, constant discharge, pumping tests, leaky.

Method	Can Account For			Remarks
	Flow Conditions	Partial Penetration	Other	
Hantush-Jacob (1955) (a)	Transient	No		Drawdown in the source bed can be neglected when KD of source bed is >100 KD of ground water zone. Ground water zone is bounded above by aquitard and an unconfined ground water zone and bounded below by an aquiclude. Ground water flow in the aquitard is vertical.
Walton (1962) (b)	Transient	No		To obtain the unique fitting position of the data plot with one of the type curves, enough of the observation data should fall within the period when leakage effects are negligible.
Hantush (1966) (b)	Transient	No	Anisotropic in horizontal plane	Similar to Hantush's methods for confined zone except initial step uses methods to calculate the hydraulic parameters.
Weeks (1969) (b)	Transient	Yes	Anisotropic in the vertical plane	Similar process can be conducted for confined zone.

a Described in Dawson and Istok, 1991

b Described in Kruseman and de Ridder, 1990

t = time since start of pumping, S' = aquitard storativity, D'= saturated thickness of aquitard, D = saturated thickness of the ground water zone, K'= hydraulic conductivity of aquitard

Table 4.10 Pumping tests, variable discharge.

Method*	Application	Assumptions	Remarks
Birsoy and Summers (1980)	- Confined - Transient - Pumped step-wise or intermittently at variable rates	- General assumptions for confined ground water zones.	Tedious process
Aron and Scott (1965)	- Confined - Transient - Discharge rate decreases	- General assumptions for confined ground water zones. - Discharge rate decreases with time sharpest decrease occurring soon after the start of pumping.	Analogous to the Jacob Method
Hantush (1964)	- Confined - Transient	- Standard assumptions for confined ground water zones. - At the start of the tests, the water level in the free flowing well drops instantaneously. At t>0 drawdown is constant and its discharge rate is variable.	
Hantush-De Glee Method (Hantush, 1959b)	- Leaky - Transient - Fully penetrating well	- Standard assumptions for leaky ground water zones (see leaky section). - At the start of the tests, the water level in the free flowing well drops instantaneously. At t>0 drawdown is constant and its discharge rate is variable.	

* Methods described in Kruseman and de Ridder (1990).

Table 4.11 Methods of analysis for pumping tests with special conditions.

Ground Water Zone Condition	Flow	Type	Models and Sources*
One or more recharge boundaries	Steady State	Confined or Unconfined	Dietz (1943)
One or more straight recharge boundaries	Unsteady State	Confined or Unconfined	Stallman (in Ferris et al., 1962)
One recharge boundary	Unsteady State	Confined or Unconfined	Hantush (1959a)
Bounded by two fully penetrating boundaries	Unsteady State	Leaky or Confined	Vandenberg (1976 and 1977)
Wedge shaped ground water zones	Unsteady State	Confined	Hantush (1962)
Water table slopes	Steady State	Unconfined	Culmination Point Method (Huisman, 1972)
	Unsteady State	Unconfined	Hantush (1964)
Two layered ground water zone, unrestricted cross flow Pumping well does not penetrate entire thickness	Unsteady State	Confined	Javandel-Witherspoon (1983)
Leaky two-layered ground water zone, separated by aquitard with cross-flow across aquitard	Steady State	Leaky	Bruggeman (1966)
Large diameter well	Unsteady State	Confined	Papadopulos (1967), Papadopulos and Cooper (1967)
Large diameter well	Unsteady State	Unconfined	Boulton and Streltsova, (1976)

* Sources are described in Kruseman and de Ridder, 1990.

Table 4.12 Recovery test methods (discussed in Kruseman and de Ridder, 1990).

Method	Application	Source
Theis Recovery Methods	- Confined Unsteady state - Recovery after constant discharge	Theis (1935)
	- Leaky Unsteady state - Recovery after constant discharge	Vandenberg (1975) Hantush (1964)
	- Unconfined - Recovery after constant discharge - Late recovery data	Neuman (1975)
	- Unconfined - Recovery after constant drawdown	Rushton and Rathod (1980)
Birsoy and Summers	- Unconfined - Recovery after variable discharge	Birsoy and Summers (1980)

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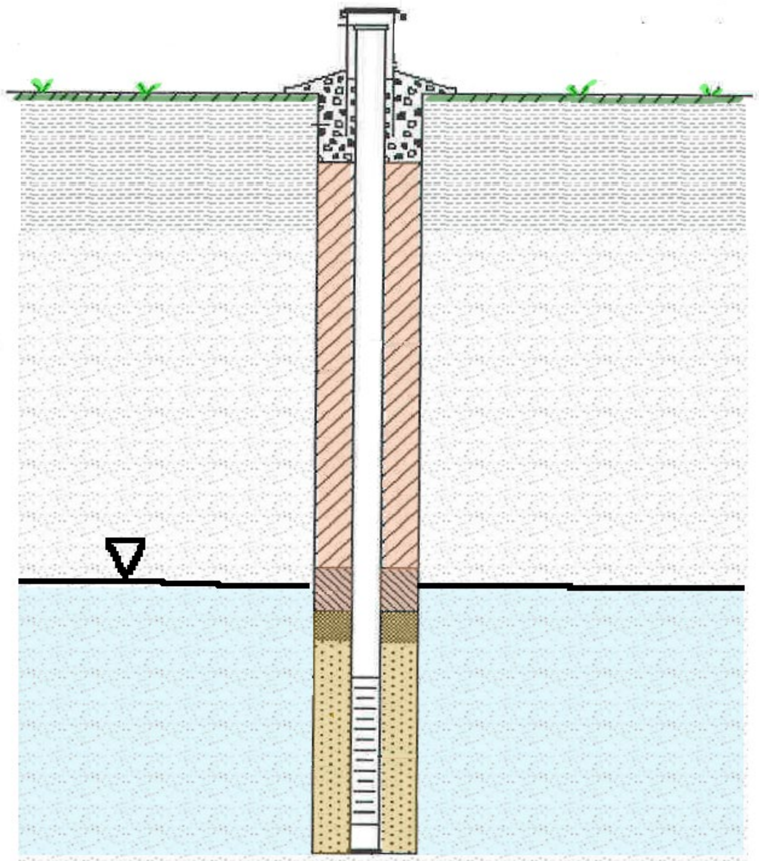
State of Ohio
Environmental Protection Agency

Division of Drinking and Ground Waters

Technical Guidance Manual for Ground Water Investigations

Chapter 7

Monitoring Well Design and Installation



February 2008

Governor : Ted Strickand
Director : Chris Korleski

TECHNICAL GUIDANCE
MANUAL FOR
GROUND WATER INVESTIGATIONS

CHAPTER 7

Monitoring Well Design and Installation

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Revision 1

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PREFACE

This document is part of a series of chapters incorporated in Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM), which was originally published in 1995. DDAGW now maintains this technical guidance as a series of chapters rather than as an individual manual. The chapters can be obtained at http://www.epa.state.oh.us/ddagw/tgmweb.aspx

The TGM identifies technical considerations for performing hydrogeologic investigations and ground water monitoring at potential or known ground water pollution sources. The purpose is to enhance consistency within the Agency and inform the regulated community of the Agency's technical recommendations and the basis for them. In Ohio, the authority over pollution sources is shared among various Ohio EPA divisions, including the Emergency and Remedial Response (DERR), Hazardous Waste Management (DHWM), Solid and Infectious Waste (DSIWM), and Surface Water (DSW), as well as other state and local agencies. DDAGW provides technical support to these divisions.

Ohio EPA utilizes ***guidance*** to aid regulators and the regulated community in meeting laws, rules, regulations and policy. Guidance outlines recommended practices and explains their rationale. The Agency may not require an entity to follow methods recommended by this or any other guidance document. It may, however, require an entity to demonstrate that an alternate method produces data and information that meet the pertinent requirements. The procedures used to meet requirements usually should be tailored to the specific needs and circumstances of the individual site, project, and applicable regulatory program, and should not comprise a rigid step-by-step approach that is utilized in all situations.

MAJOR CHANGES FROM THE FEBRUARY 1995 TGM

The Ohio EPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) was finalized in 1995. This guidance document represents an update to Chapter 7 (Monitoring Well Design and Installation). Listed below are the major changes from the 1995 version.

1. Deleted language cautioning against the use of multi-level wells. Added information on multi-level well systems.
2. Added text indicating that vertical water profiles can be obtained with passive sampling techniques.
3. Revised text to state that PVC is preferable to PTFE for monitoring well screens when organics are present. Studies have shown that PTFE sorbs organic compounds at a higher rate than does PVC.
4. Added language stating that a filter pack can be much less thick than previously recommended.
5. Added language describing the use of pre-packed screen wells.
6. Changed the recommendation for selecting the screen slot size of a naturally packed well from a slot that retains 30 to 60% of the filter pack to one that retains 70%.
7. Added information on methods for creating high-solids bentonite.
8. Revised text to note potential problems with using a bentonite/cement mixture. However, the guidance does not rule it out as a potential sealant for monitoring wells. Some literature has indicated problems with the use of a bentonite as an additive to neat cement for well sealing. Because of this, the Ohio rules applying to drinking water wells do not allow the use of a bentonite/cement mixture (OAC 3745-09). However, there are also articles that favor its use, and many states still allow (and recommend) it.
9. Added section on procedures for installation of neat cement grout.
10. Added recommendation that, due to its potential to affect ground water chemistry, bentonite sealing material should be placed a minimum of 3 to 5 feet above the top of the well screen.
11. Included references to new documents that have become available since 1995, including:
    - Updated existing references.
    - Added new ASTM reference for installation of pre-packed screens.
    - Added new ASTM reference for maintenance and rehabilitation of ground water monitoring wells.
    - Added reference to the Technical Guidance for Ground Water Investigation Chapter 15 - Use of Direct Push Technologies for Soil and Ground Water Sampling.

TABLE OF CONTENTS

CHAPTER 7

MONITORING WELL DESIGN AND INSTALLATION

To collect representative ground water samples, it is necessary to construct monitoring wells to gain access to the subsurface. This chapter covers installation and construction of single-riser/limited interval wells, which are designed such that only one discrete zone is monitored in a given borehole, and multiple interval wells designed to measure multiple discrete depth intervals at a single location. Whether a single riser or multiple interval well is installed, it is important that efforts focus on intervals less than 10 feet thick and be specific to a single saturated zone.

All monitoring wells should be designed and installed in conformance with site hydrogeology, geochemistry, and contaminant(s). While it is not possible to provide specifications for every situation, it is possible to identify certain design components. Figure 7.1 is a schematic drawing of a single-riser/limited interval well. The ***casing*** provides access to the subsurface. The ***intake*** consists of a filter pack and screen. The ***screen*** allows water to enter the well and, at the same time, minimizes the entrance of filter pack materials. The ***filter pack*** is an envelope of uniform, clean, well-rounded sand or gravel that is placed between the formation and the screen. It helps to prevent sediment from entering the well. Installation of a filter pack and screen may not be necessary for wells completed in competent bedrock. The ***annular seal*** is emplaced between the borehole wall and the casing and is necessary to prevent vertical movement of ground water and infiltration of surface water and contaminants. ***Surface protection***, which includes a surface seal and protective casing, provides an additional safeguard against surface water infiltration and protects the well casing from physical damage.

DESIGN OF MULTIPLE-INTERVAL SYSTEMS

It is often necessary to sample from multiple discrete intervals at a given location if more than one potential pathway exists or a saturated zone is greater than 10 feet thick. Chapter 5 - Monitoring Well Placement discusses the concepts involved in selecting zones to monitor. Multiple-interval monitoring can be accomplished by installing single-riser/limited interval wells in side-by-side boreholes (well clusters) or using systems that allow sampling of more than one interval from the same borehole (multi-level wells, well nests, or single-casing, long-screen wells). Multiple-interval monitoring may be useful to:

- Determine the hydraulic head distribution.
- Measure temporal changes in vertical hydraulic head.
- Determine vertical contaminant distribution.
- Provide long-term multilevel water quality monitoring.

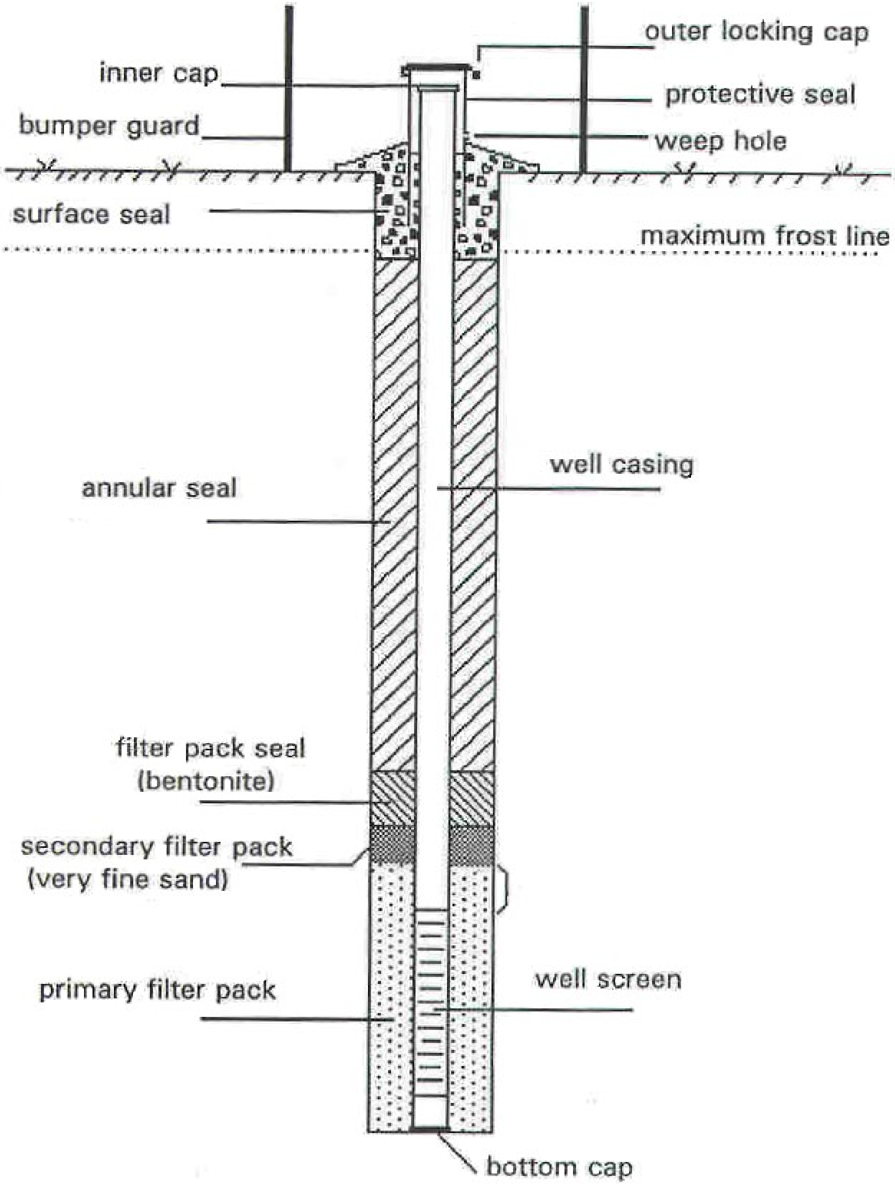

Figure 7.1 Cross-section of a typical single-riser/limited interval monitoring well.

WELL CLUSTERS

When monitoring multiple intervals at one location, single-riser/limited interval wells are often installed in adjacent, separate boreholes. These well clusters can be used to determine vertical gradients when distinct differences in head exist. They may be used to monitor discrete zones or evaluate chemical stratification within a thick zone. If flow direction has been determined prior to installation, the shallow well should be placed hydraulically upgradient of the deeper well to avoid the potential influence on its samples caused by the presence of grout in the annular space of the deeper well.

MULTI-LEVEL WELLS

Multi-level wells allow sampling of more than one interval in a single borehole. These levels are isolated within the well either by packers or grout. Probes, lowered into the casing, can locate, isolate and open a valve into a port coupling to measure the fluid pressure outside the coupling or obtain a sample. Individual tubes run from sampling levels to the surface.

The use of multiple-level monitoring wells in Ohio has been limited due to: 1) cost of installation, 2) difficulty in repairing clogs, and 3) difficulty in preventing and/or evaluating sealant and packer leakage. Detailed workplans (including construction and installation, methods to measure water levels and obtain samples, references to situations where these types of wells have been used successfully, and advantages and disadvantages) should be submitted prior to installing multi-level systems.

Several systems are commercially available for obtaining multi-level monitoring of a single borehole. Most consist of casing or tubing with monitoring ports located at user-selected intervals. In one system, however, a lining containing intermittent sampling ports is placed in the borehole. The systems may be sampled with small diameter pumps and bailers, or using proprietary samplers that go with the monitoring system. See Nielsen and Schalla (2006) for more information on multi-level well systems.

NESTED WELLS

Nested wells involve the completion of a series of single-riser wells in a borehole. Each well is screened to monitor a specific zone, with filter packs and seals employed to isolate the zones. Nested wells are not recommended because they are difficult to install in a manner that ensures that all screens, filter packs, and seals are properly placed and functioning. It is more efficient to install single-riser wells for each interval to ensure that representative samples can be collected. Aller et al. (1991) indicated that individual completions generally are more economical at depths less than 80 feet. According to Nielsen and Schalla (2006), the cost of installing well clusters is comparable to the cost for nested wells. Well clusters can enable savings on sampling and future legal costs that may be necessary to prove the accuracy of nested wells.

SINGLE-CASING, LONG-SCREEN WELLS

Single-casing, long-screen wells are monitoring wells that, in general, are screened across the entire thickness of a water-bearing zone. If purging is performed immediately before sampling, only composite water samples are yielded, which are not adequate for most monitoring studies. If natural, flow-through conditions can be maintained, vertical water quality profiles can be obtained with passive sampling techniques. Vertical profiling may be a cost effective initial assessment to determine the depth of final wells.

Long-screen wells are not appropriate for detection monitoring. Furthermore, these wells can allow cross-contamination between different zones and, therefore, should not be used in contaminated areas.

CASING

The purpose of casing is to provide access to the subsurface for sampling of ground water and measurement of water levels. A variety of casing types have been developed. Items that must be considered during well design include casing type, coupling mechanism, diameter, and installation.

CASING TYPES

Three categories of casing are commonly used for ground water monitoring, including fluoropolymers, metallics, and thermoplastics (Aller et al., 1991). All have distinctive characteristics that determine their appropriateness.

Fluoropolymers

Fluoropolymers are synthetic plastics composed of organic material. They are resistant to chemical and biological attack, oxidation, weathering, and ultraviolet (UV) radiation. They have a broad useful temperature range, a high dielectric constant, a low coefficient of friction, display anti-stick properties, and have a greater coefficient of thermal expansion than most other plastics and materials (Aller et al., 1991). Standard properties of the various materials have been provided by Aller et al. (1991).

The most common fluoropolymer used for monitoring wells is polytetrafluoroethylene (PTFE). It can withstand strong acids and organic solvents and, therefore, it is useful for environments characterized by the presence of these chemicals. It maintains a low tensile strength, which theoretically limits installation of Schedule 40 PTFE to an approximate depth of 250 ft[1]. It is also very flexible, which makes it difficult to install with the retention of straightness that is needed to ensure successful insertion of sampling or measurement devices. Dablow et al. (1988) found that the ductile nature of PTFE can result in the partial closing of screen slots

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[1] The maximum depth for PTFE casing depends on site hydrogeology. If the casing largely penetrates unsaturated soils, the depth may be limited to approximately 100 feet. However, if the casing is placed mostly in water-bearing zones, then depth may be as great as 375 feet.

due to the compressive forces of the casing weight. This makes slot size selection very difficult. PTFE is costly, generally ten times more expensive than thermoplastics. Studies by Gillham and O'Hannesin (1990), Parker et al. (1990), and Parker and Raney (1993) (in Nielsen and Schalla, 2006), found that PTFE showed higher sorption rates than PVC of organic compounds. These studies concluded that PVC was a better material to use when organics are present.

Metallics

Metallic materials include low carbon, carbon, galvanized, and stainless steel. Metallics are very strong and rigid and can be used to virtually unlimited depths. Corrosion problems are the major disadvantage for low carbon, carbon, and galvanized casings, as electrochemical and chemical attack alters water sample quality. U.S.EPA (1992) has listed the following as indicators of corrosive conditions (modified from Driscoll, 1986):

- Low pH (< 7.0).
- Dissolved oxygen exceeds 2 ppm.
- Hydrogen sulfide in quantities as low as 1 ppm.
- Total dissolved solids (TDS) greater than 1000 ppm.
- Carbon dioxide exceeds 50 ppm.
- Chloride (Cl^-), bromide (Br^-), and fluoride (F^-) content together exceeds 500 ppm.

According to Barcelona et al. (1983), flushing before sampling does not minimize the bias of low carbon steel due to the inability to predict the effects of disturbed surface coatings and corrosion products accumulated at the bottom of the well. Due to their high corrosion potential, all metallics except stainless steel are unacceptable for monitoring wells.

Stainless steel is manufactured in two common types, 304 and 316. Type 304 is composed of iron with chromium and nickel. Type 316's composition is the same as Type 304's, but includes molybdenum, which provides further resistance to sulfuric acid solutions. Stainless steel is readily available in a wide variety of diameters.

Stainless steel can perform quite well in most corrosive environments. In fact, oxygen contact develops an external layer that enhances corrosion resistance (Driscoll, 1986). However, several studies cite the formation of an iron oxide coating on the surface of stainless steel casing that forms in long-term exposure to ground water that can have unpredictable effects on the adsorption capacity of the casing material (Nielsen and Schalla, 2006). Under very corrosive conditions, stainless steel can corrode and release nickel and chromium into ground water samples (Barcelona et al., 1983). Combinations and/or extremes of the factors indicating corrosive conditions generally are an indication of highly corrosive environments. For example, Parker et al. (1990) found that both 304 and 316 showed rapid rusting (<24 hrs.) when exposed to water containing chloride above 1000 mg/l, and a study by Oakley and Korte (in Nielsen and Schalla, 2006) noted corrosion of stainless steel at even lower chloride levels (600-900 mg/L). Like PTFE, stainless steel is relatively expensive in comparison with thermoplastics. Nielsen and Schalla (2006) and Aller et al. (1991) provided additional information on the properties of stainless steel.

Thermoplastics

Thermoplastics are composed of large, synthetic organic molecules. The most common type used for monitoring wells is polyvinyl chloride (PVC), while a material used less often is acrylonitrile butadiene styrene (ABS). These materials are weaker, less rigid, and more temperature-sensitive than metallics. Thermoplastics are very popular due to their light weight, high strength to weight ratio, low maintenance, ease of joining, and low cost.

Common, acceptable PVC types are Schedule 40 and Schedule 80. The greater wall thickness of Schedule 80 piping enhances durability and strength, provides greater resistance to heat attack from cement, and allows construction of deeper wells. Only rigid PVC should be used for monitoring wells. Flexible PVC is composed of a high percentage of plasticizers (30 - 50%), which tend to degrade and contaminate samples (Jones and Miller, 1988). All PVC casing should meet Standard 14 of NSF International. This standard sets control levels for the amount of chemical additives to minimize leaching of contaminants (NSF International, 1988). Additional specifications have been provided by Nielsen and Schalla (2006) and Aller et al. (1991).

Drawbacks of PVC include brittleness caused by ultraviolet (UV) radiation, low tensile strength, relative buoyancy in water, and susceptibility to chemical attack. It is immune to corrosion and is resistant to most acids, oxidizing agents, salts, alkalies, oils, and fuels (NWWA/PPI, 1981). Additionally, Schmidt (1987) showed that no degradation of PVC occurred after six months immersion in common gasolines. However, studies have shown that high concentrations (parts-per-thousand or percentage concentrations) of tetrahydrafuran, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexane degrade PVC (Nielsen and Schalla, 2006). Barcelona et al. (1983) reported that low molecular weight ketones, aldehydes, amines, and chlorinated alkenes and alkanes may cause degradation. Studies by Ranney and Parker (1995, 1997) and Parker and Ranney (1994b, 1995, 1996), showed that PVC is degraded when exposed to higher concentrations (0.2 and 0.4, or 20% and 40% of the solubility limit of the solvent in water) of aromatic hydrocarbons, aromatic and aliphatic chlorinated solvents, ketones, anilines, aldehydes and nitrogen-containing organic compounds. It is recommended that PVC not be used in situations where the material may be exposed to concentrations of known solvents or swelling agents of PVC greater than 25% of the solubility limit of the solvent or swelling agent (Nielsen and Schalla, 2006).

TYPE SELECTION

Many regulated parties choose PVC casing because of its lower cost; however, well integrity and sample representativeness are more important criteria. The high cost of analysis and the extreme precision of laboratory instruments necessitate the installation of wells that produce representative samples. Above all, the burden of proof is on the regulated party to demonstrate that casing is appropriate. The proper selection can be made by considering casing characteristics in conjunction with site conditions.

Casing characteristics include strength, chemical resistance, and chemical interference potential. The ***strength*** must withstand the extensive tensile, compressive, and collapsing forces involved in maintaining an open borehole. Since the forces exerted are, in large part, related to well depth, strength often is important when planned depth exceeds the maximum range of the weakest acceptable material (100 to 375 ft. - PTFE). In these instances, either stainless steel or PVC should be chosen. Strength can be the overriding factor because the concern for chemical resistance and interference become insignificant if an open borehole cannot be maintained. Nielsen and Schalla (2006) provided specific strength data for commonly used materials.

The casing also must withstand ***electrochemical corrosion and chemical attack*** from natural ground water and any contaminant(s). Chemical resistance is most important in highly corrosive environments, when contaminants are present at extremely high levels, and when wells are intended to be part of a long-term monitoring program. For extended monitoring in corrosive environments, PTFE and PVC are preferred over stainless steel because of the potential for the metallic material to degrade. If high concentrations of organics (parts per thousand) are present, either PTFE or stainless steel should be selected. PVC should not be used if a PVC solvent/softening agent is present or the aqueous concentration of a solvent/softening agent exceeds 25% of its solubility in water. It is suitable in most situations where low (parts per billion to low parts per million) levels of most organic constituents are present (Nielsen and Schalla, 2006).

The casing also should not interfere with sample quality by ***adding (leaching) or removing contaminants.*** In most cases, the magnitude of this interference is a function of the ground water's contact time with the casing. The longer the contact, the greater the potential for leaching and sorption. Various studies have been conducted [Barcelona and Helfrich (1988), Curran and Tomson (1983), Gillham and O'Hannesin (1990), Jones and Miller (1988), Miller (1982), Parker and Jenkins (1986), Parker et al. (1990), Reynolds and Gillham (1985), Schmidt (1987), Sykes et al. (1986), Tomson et al. (1979), Hewitt (1992, 1994), Parker and Ranney (1994)] to compare the sorbing and leaching characteristics of the three favored materials. No conclusive results have been obtained to indicate that any one is best. Most of these studies involved contact lasting days, weeks, and even months and, therefore, the results cannot be correlated to field conditions where contact is often minimal because sampling is generally conducted soon after purging.

In many cases, concern about sorption or leaching may be exaggerated. Barcelona et al. (1983) and Reynolds and Gillham (1985) both concluded that the potential sorption biases for casing may be discounted due to the short contact after purging. Also, Parker et al. (1990) indicated that sorption of various constituents never exceeded 10 percent in the first 8 hours of their tests. They concluded that, on the basis of overall sorption potential for organic and inorganic compounds, PVC is the best compromise.

In summary, the appropriate casing should be determined on a case-by-case basis. PVC is acceptable when free product is not present and the solubility limits of organic contaminants are not approached (e.g., levels that exceed 0.25 times the solubility). Ohio EPA recognizes the difficulty inherent in establishing a "cut-off" level for when aqueous concentrations of organics cause failure of PVC. To be certain that casing will retain integrity, particularly when monitoring is planned for long periods of time (e.g., 30 years), Ohio EPA may recommend a more resistant casing when aqueous concentrations are relatively high but still below the criteria mentioned above.

HYBRID WELLS

Casing not in contact with the saturated zone generally is not subject to attack. Therefore, it may be possible to install less chemically resistant material above the highest seasonal water level and more inert material where ground water continually contacts the casing. Such a "hybrid well" commonly is installed to reduce costs. For example, when monitoring a zone with high concentrations of organics, stainless steel could be installed opposite the saturated materials, while PVC could be used opposite the unsaturated materials. Thus, resistant, more expensive casing would be present where contact with highly contaminated ground water may occur, while less resistant, inexpensive casing would be present where contact does not occur.

Variations in ground water levels caused by seasonal or pumping effects should be taken into account when planning the casing material configuration (Nielsen and Schalla, 2006). Different varieties of steel never should be installed in the same well. Each type is characterized by its own electro-chemical properties. Installation of different types in contact can increase the potential for corrosion.

COUPLING MECHANISMS

Casing sections should be connected using threaded joints that provide for uniform inner and outer diameters along the entire length of the well. Such "flush" coupling is necessary to accommodate tools and sampling devices without obstruction and to help prevent bridging during the installation of the filter pack and annular seal. It should be noted that thread types vary between manufacturers and matching can be difficult. A union among non-matching joints should never be forced, otherwise structural integrity of the joint and the entire well could be compromised. To alleviate these problems, the American Society of Testing and Materials has developed Standard F 480-90 (1992) to create a uniformly manufactured flush-threaded joint. Most manufacturers now produce the F 480 joint, which is available in both PVC and stainless steel.

Solvent cements should never be used because they are known to leach organics. Metal fasteners such as rivets or screws should not be used to supplement threaded joints. Use of such fasteners can reduce the effective inner well diameter, and may damage pumps or other tools lowered into the well (Nielsen and Schalla, 2006).

It is recommended that either nitrile, ethylene propylene, or Viton O-rings be used between sections to prevent the seal and/or affected water from entering (Nielsen and Schalla, 2006). Nielsen and Schalla (2006) indicated that Teflon tape can be used in place of O-rings, although it does not ensure as good a seal. Although welding stainless steel can produce a flush joint that is of equal or greater strength than the casing itself, this method is not used as commonly as threaded joints due to the extra assembly time, welding difficulty, corrosion enhancement, ignition danger, and the potential to lose materials into the well (Nielsen and Schalla, 2006). Threaded steel casing provides inexpensive, convenient connections. It should be noted that threaded joints reduce the tensile strength of the casing; however, this does not cause a problem for most shallow wells. Also, threaded joints may limit or hinder the use of various sampling devices when thin-walled stainless steel (Schedules 5 and 10) is employed. Thin-walled casing is too thin for threads to be machined, so the factory welds a short, threaded section of Schedule 40 stainless steel pipe to the end of the thin-walled pipe. These joints are made to be flush on the outside, but not the inside.

If hybrid wells are installed, it is essential that the joint threads be matched properly. This can be accomplished by purchasing casing screen that is manufactured to ASTM F480-90 (1992) standard coupling.

DIAMETER

Choice of casing diameter is site-specific. Small wells are considered to be less than 4 inches in diameter. Wells installed using conventional drilling methods are generally 2 or 4 inches in diameter. Wells installed by direct push technologies (see Chapter 15 – Use of Direct Push Technologies for Soil and Ground Water Sampling) have diameters of 2 inches to as small as 0.5 inch. Advantages of small diameter wells are as follows:

- Water levels require less time to recover after purging.
- They produce a smaller volume of purged water that must be disposed.
- Construction costs are lower.
- They are more easily installed by driven, direct push, jetting, or hollow stem augers.

Some disadvantages of small diameter wells include:

- Access may be limited for sampling devices.
- Filter packs and seals are more difficult to install.
- They offer a lower depth capability due to lesser wall thickness.
- Development can be more difficult.
- Less ground water is pumped during a hydraulic test or a remediation extraction.
- The amount of available water may be too small for chemical analyses.
- Slower recovery after water removal.

CASING INSTALLATION

Casing should be cleaned thoroughly before installation. Strong detergents and even steam cleaning may be necessary to remove oils, cleansing solvents, lubricants, waxes, and other substances (Curran and Tomson, 1983; Barcelona et al., 1983). It is strongly recommended that only factory-cleaned materials be used for monitoring wells. Casing can be certified by the supplier and individually wrapped in sections to retain cleanliness. If it has not been factory-cleaned and sealed, it should be washed thoroughly with a non-phosphate, laboratory grade detergent (e.g., Liquinox) and rinsed with clean water or distilled/deionized water as suggested by Curran and Tomson (1983) and Barcelona et al. (1983). The materials should be stored in a clean, protected place to prevent contamination by drilling and site activities.

When installing casing, it is important that it remain centered in the borehole to ensure proper placement and even distribution of the filter pack and annular seal. In addition, centering helps ensure straightness for sampling device access. If a hollow-stem auger is used, no additional measures are necessary because the auger acts as a centralizing device. If casing is installed in an open borehole, centralizers made of stainless steel or PVC can be used. They are adjustable and generally attached just above the screen and at 10 to 20 foot intervals along the riser. If centralizers are used, measures should be taken to prevent them from bridging the filter pack and seal material during their installation.

If the well screen and riser are significantly lighter than the buoyant force of the fluid in the borehole, the casing assembly may require ballast to offset the tendency of the materials to float in the borehole. The riser may be ballasted by filling it with water of a known and acceptable source or with water previously removed from the borehole. Alternatively, hydraulic rams on the drill rig may be used to push the riser into the borehole (ASTM D5092-04).

INTAKES

Although every well is unique, most have a screen and filter pack comprising the well intake. Monitoring wells in cohesive bedrock may incorporate open borehole intakes.

FILTER PACK

Wells monitoring unconsolidated and some poorly consolidated materials typically need to have a screen (discussed later) surrounded by more hydraulically conductive material (filter pack). In essence, the filter pack increases the effective well diameter and prevents fine-grained material from entering.

Types of Filter Packs

Filter packs can be classified by two major categories, natural and artificial. ***Natural packs*** are created by allowing the formation to collapse around the screen. In general, natural packs are recommended for formations that are coarse-grained, permeable, and uniform in grain size. Grain size distribution of the formation should be determined through a sieve analysis of samples from the formation. According to Nielsen and Schalla (2006), natural packs may be suitable when the effective grain size (sieve size that retains 90%, or passes 10%) is greater than 0.010 inch and the uniformity coefficient (the ratio of the sieve size that retains 40% and the size that retains 90%) is greater than 3. Ideally, all fine-grained particles are removed when the well is developed, leaving the natural pack as a filter to the surrounding formation.

Installation of ***artificial packs*** involves the direct placement of coarser-grained material around the screen. The presence of this filter allows the use of a larger slot size than if the screen were in direct contact with the formation. Artificial packs generally are necessary where: 1) the formation is poorly sorted; 2) the intake spans several formations and/or thin, highly stratified materials with diverse grain sizes; 3) the formation is a uniform fine sand, silt or clay; 4) the formation consists of thinly-bedded materials, poorly cemented sandstones, and highly weathered, fractured, and solution-channeled bedrock; 5) shales and coals that provide a constant source of turbidity are monitored; and 6) the borehole diameter is significantly greater than the diameter of the screen (Aller et al., 1991), (Nielsen and Schalla, 2006). Artificial packs generally are used opposite unconsolidated materials when the effective grain size is less than 0.010 inches and when the uniformity coefficient is less than 3.0 (Nielsen and Schalla, 2006). Pre-packed well screens (discussed below) may also be used to install an artificial filter pack. The filter pack for these screens is installed at the surface, ensuring an effective filter pack.

An artificial pack may include two components. The ***primary pack*** extends from the bottom of the borehole to above the top of the screen. In some cases, it may be desirable to place a ***secondary pack*** directly on top of the primary pack. Its purpose is to prevent the infiltration of the annular seal into the primary pack, which can partially or totally seal the screen.

Nature of Artificial Filter Pack Material

The artificial pack material should be well-sorted, well-rounded, clean, chemically inert, of known origin, and free of all fine-grained clays, particles and organic material. Barcelona et al. (1983) recommended clean quartz sand or glass beads. Quartz is the best natural material due to its non-reactive properties and availability. Crushed limestone should never be used because of the irregular particle size and potential chemical effects. Materials should be washed, dried, and packaged at the factory, and typically are available in 100 lb. bags (approximately one cubic foot of material) (Nielsen and Schalla, 2006).

The material should be based on the formation particle size. If chosen grains are too small, it is possible that loss of the pack to the formation can occur (Nielsen and Schalla, 2006), which could lead to the settling of the annular seal into the screened interval. On the other hand, if the grains are too large, the pack will not effectively filter fine-grained material, leading to excessively turbid samples. For these reasons, the universal application of a single well screen/filter pack combination to all formations should be avoided (ASTM D5092-04).

The primary pack generally should range in grain size from a medium sand to a cobbled gravel. Most materials are available in ranges, such as 20- to 40-mesh (0.033 to 0.016 inches, Table 7.1). The grain size of the primary filter pack should be determined by multiplying the 70% retention size of the formation by a factor of 3 to 6 (U.S. EPA, 1975). A factor of 3 is used for fine, uniform formations; a factor of 6 is used for coarse, non-uniform formations. Where the material is less uniform and the uniformity coefficient ranges from 6 to 10, it may be necessary to use the 90% retention (10% passing) size multiplied by 6 (Nielsen and Schalla, 2006). This is to ensure that the bulk of the formation will be retained. The ratio of the particle size to the formation grain size should not exceed 6, otherwise, the pack will become clogged with fine-grained material from the formation (Lehr et al., 1988). If the ratio is less than 4, a smaller screen slot size will be necessary, full development of the well may not be possible, and well yield may be inhibited. When monitoring in very heterogeneous, layered stratigraphy, a type of pack should be chosen that suits the layer with the smallest grain size.

It is preferred that the filter pack be of uniform grain size. Ideally, the uniformity coefficient should be as close to 1.0 as possible and should not exceed 2.5 (Nielsen and Schalla, 2006, ASTM D5092-04, 2005). Uniform material is much easier to install. If non-uniform material is used, differing fall velocities cause the materials to grade from coarse to fine upwards along the screen. This can result in the loss of the upper fine-grained portion to the well during development.

The secondary filter pack material should consist of a 90% retention sieve size (10% passing) that is larger than the voids of the primary pack to prevent the secondary pack from entering the primary pack (Nielsen and Schalla, 2006). In general, the secondary 90% retention size should be one-third to one-fifth of the primary 90% retention size (Nielsen and Schalla, 2006).

Dimension of Artificial Filter Pack

The filter pack should be thick enough to completely surround the well screen. The well annulus should be large enough to preclude bridging of the filter-pack material. Centering of the well screen in the borehole will ensure adequate space for an effective filter pack. Driscoll (1986) states that the mechanical filtration function of the filter pack can be achieved with a filter pack of only 2 to 3 grains in thickness. Filter packs of less than a half inch thick have been successfully used in pre-packed well screens that are installed in direct push boreholes (Nielsen and Schalla, 2006).

The primary pack should extend from the bottom of the screen to at least 3 feet above its top (Nielsen and Schalla, 2006). In deeper wells (i.e., >200 feet), the pack may not compress initially. Compression may occur after installation of the annular seal, which may allow the seal to be in close contact with the screen. Therefore, additional pack material may be needed to account for settling and, at the same time, provides adequate separation of the seal and the screen. However, extension of the pack should not be excessive because it enlarges the zone that contributes ground water to the well, which may cause excess dilution. The length of the secondary pack should be 1 foot or less.

Artificial Filter Pack Installation

Methods that have been used for artificial pack installation include tremie pipe, gravity emplacement, reverse circulation, and backwashing (Nielsen and Schalla, 2006). The material should be placed in a manner that prevents bridging and particle segregation. Bridging can cause large voids and may prevent material from reaching the intended depth. Segregation can cause a well to produce turbid samples. During installation, regular measurements with a weighted tape should be conducted to determine when the desired height has been reached, and also act as a tamping device to reduce bridging. The anticipated volume of filter pack should be calculated.[2] Any discrepancy between the actual and calculated volumes should be explained.

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[2] Anticipated filter pack volume can be calculated by determining the difference in volume between the borehole and casing (using outside diameter of the well) from the bottom of the borehole to the appropriate height above the well screen.

Table 7.1 Common filter pack characteristics for typical screen slot sizes (From Nielsen and Schalla, 2006).

Size of Screen Opening [mm (in.)]	Slot No.	Sand Pack Mesh Size	1% Passing Size (D_1) (mm)	Effective Size (D_{10}) (mm)	30% Passing Size (D_{30}) (mm)	Range of Uniformity Coefficient	Roundness (Powers Scale)	Fall Velocities[a] (cm/s)
0.125(0.005)	5	40-140	0.09-0.12	0.14-0.17	0.17-0.21	1.3-2.0	2-5	6-3
0.25 (0/010)	10	20-40	0.25-0.35	0.4-0.5	0.5-0.6	1.1-1.6	3-5	6-6
0.50 (0.020)	20	10-20	0.7-0.9	1.0-1.2	1.2-1.5	1.1-1.6	3-6	14-9
0.75 (0.030)	30	10-20	0.7-0.9	1.0-1.2	1.2-1.5	1.1-1.6	3-6	14-9
1.0 (0.040)	40	8-12	1.2-1.4	1.6-1.8	1.7-2.0	1.1-1.6	4-6	16-13
1.5 (0.060)	60	6-9	1.5-1.8	2.3-2.8	2.5-3.0	1.1-1.7	4-6	18-15
2.0 (0.080)	80	4-8	2.0-2.4	2.4-3.0	2.6-3.1	1.1-1.7	4-6	22-16

[a] Fall velocities in centimeters per second are approximate for the range of sand pack mesh sizes named in this table . If water in the annular space is very turbid, fall velocities may be less than half the values shown here. If a viscous drilling mud remains in the annulus, fine particles may require hours to settle.

The preferred method for artificial pack installation is to use a ***tremie pipe*** to emplace material directly around the screen (Figure 7.2). The pipe is raised periodically to help minimize bridging. The pipe generally should be at least 1 inch ID, but larger diameters may be necessary where coarser-grained packs are being installed. When driven casing or hollow-stem augering is used to penetrate non-cohesive formations, the material should be tremied as the casing and auger is pulled back in one to two foot increments to reduce caving effects and ensure proper placement (Nielsen and Schalla, 2006). When installing wells through cohesive formations, the tremie pipe can be used after removal of the drilling device.

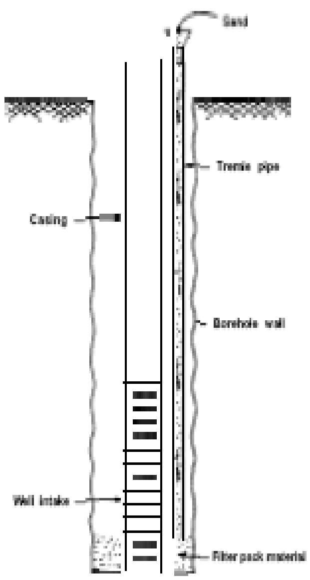

Figure 7.2. Installation of artificial filter pack material with a tremie pipe. (Source: Aller et al., 1991).

Gravity emplacement is accomplished by allowing material to free-fall to the desired position around the screen. Placement by gravity should be restricted to shallow wells with an annular space greater than 2 inches, where the potential for bridging or segregation is minimized (Nielsen and Schalla, 2006). For low-yielding formations, it may be possible to bail the borehole dry to facilitate placement; however, segregation is generally not a problem if the pack has a uniformity coefficient of 2.5 or less. Gravity placement also can cause grading if the material is not uniform. In addition, formation materials are often incorporated during placement, which can contaminate the pack and reduce its effectiveness. For most cases, gravity placement is not recommended.

Reverse circulation involves the insertion of a sand and water mixture through the annulus. Sand is deposited around the screen as the water returns to the surface through the casing. Due to the potential water quality alteration, this method generally is not recommended.

Sand is deposited around the screen as the water returns to the surface through the casing. Due to the potential water quality alteration, this method generally is not recommended.

Backwashing is accomplished by allowing material to free-fall through the annulus while clean water is pumped down the casing. The water returns up the annulus carrying fine-grained material with it. This creates a more uniform pack; however, the method is not commonly used for monitoring well installation and generally is not recommended due to the potential for alteration of ground water quality. Nonetheless, it is sometimes used for placing packs opposite non-cohesive heaving sands and silts.

SCREEN

The screen provides an access point to a specific portion of a ground water zone, as well as providing a barrier to keep unwanted formation particles out of ground water samples.

Screen Types

Recommended screen compositions are stainless steel, PTFE, and PVC. The same discussion and concerns for casing materials apply to screens. Only manufactured screens should be used, since these are available with slots sized precisely for specific grain sizes. Field-cut or punctured screen should never be used, due to the inability to produce the necessary slot size and the potential for the fresh surface to leach or sorb contaminants. A bottom cap or plug should be placed at the base of the screen to prevent sediments from entering and to ensure that all water enters the well through the screen openings.

Slotted and continuous slot, wire-wound screen are the common types used for monitoring wells. In deep wells, slotted screen generally retains structural integrity better than wire-wound; however, continuous slot, wire-wound screens provide almost twice the open area of slotted casing. More open area per unit length enhances well recovery and development. A slot type should be chosen that provides the maximum amount of open area in relation to the effective porosity of the formation. Opinions vary regarding the optimum percentage of open area needed for effective hydraulic performance of well screens. Though it has been suggested that a range of open areas from 8 to 38% do not differ significantly in well performance, Driscoll (1986) recommended that the percentage of open area should be at least equal to the effective porosity of the formation and filter pack. In common situations with 8 to 30 percent effective porosities, continuous slot screens are preferred, although not required. A high percentage of open area is of greater importance when wells are installed in fine-grained formations where smaller slot sizes and fine-grained filter packs are required (Nielsen and Schalla, 2006).

Pre-Packed Screen Wells

A pre-packed screen is an assembly consisting of an inner slotted screen surrounded by a wire mesh sleeve that acts as a support for filter media. The pre-packed screen assemblies can either be shipped with filter media already packed within the mesh sleeve or can be shipped without filter media and packed with filter sand in the field. Refer to ASTM D5092-04 for appropriate sizing of filter pack material. Pre-packed well screens help eliminate problems in the placement of filter pack around the screens of small diameter wells. In fine-grained formations pre-packed screens may be best for ensuring proper filter pack placement.

(ASTM D5092-04). The wells are sealed and grouted using the same procedure described for conventionally completed DPT wells. ASTM D6725-04 provides additional guidance on the use of pre-packed wells.

Slot Size

When selecting a screen slot size for an artificially filter-packed well, a sieve analysis should be conducted on the pack material. The selected size should retain at least 90% of the pack. In many situations it is preferable to retain 99% (Nielsen and Schalla, 2006 and ASTM D 5092-90, 1994). See Table 7.1 for a guide to the selection of slot sizes for various packs.

For naturally-packed wells, the screen should retain at least 70% of the pack (Nielsen and Schalla, 2006, ASTM D5092-04). For additional information on pack and screen selection, see Aller et al. (1991), Nielsen and Schalla, (2006), and ASTM D 5092-90 (1994).

It should be noted that if a PTFE screen is used in a deep well, a slightly larger slot size than predicted should be selected due to the material's lower compressive strength, which allows the openings to compress (Dablow et al., 1988).

Length

Screen length should be tailored to the desired zone and generally should not exceed 10 ft. A 2 to 5 ft. screen is desirable for more accurate sampling and discrete head measurements. Longer screens produce composite samples that may be diluted by uncontaminated water. As a result, concentrations of contaminants may be underestimated. In addition, if vertical flow is present, the well screen may provide a pathway for redistribution of contaminants, and possible cross-contamination of the formation (Nielsen and Schalla, 2006). Furthermore, the screen should not extend through more than one water-bearing zone to avoid cross-contamination. When a thick formation must be monitored, a cluster of individual, closely spaced wells, screened at various depths, can be installed to monitor the entire formation thickness. The length of screens that monitor the water table surface should account for seasonal fluctuation of the water table. For related information on screen length, refer to Chapter 5 – Monitoring Well Placement.

OPEN BOREHOLE INTAKES

When constructing monitoring wells in competent bedrock, an artificial intake is often unnecessary because an open hole can be maintained and sediment movement is limited. Installing a filter pack in these situations may be difficult due to loss of material into the surrounding formation. In some cases, however, intakes are a necessary component of bedrock wells. A screen and filter pack should be installed in highly weathered, poorly cemented, and fractured bedrock (Nielsen and Schalla, 2006). They are usually necessary when monitoring the unconsolidated/consolidated interface in Ohio.

Open hole wells often are completed by casing and grouting the annulus prior to drilling into the monitoring zone. In cases where the zone has been drilled prior to sealing the annulus, a bridge (cement basket or formation packer shoe) must be set in the hole to retain the grout/slurry to the desired depth (Driscoll, 1986).

If an open hole well is installed, the length of open hole generally should not exceed 10 feet to prevent sample dilution. To maintain a discrete monitoring zone in consolidated formations, the casing should be extended and grouted to the appropriate depth to maintain the 10 foot limit. Driven casing may be necessary to avoid loss of the annular seal into the surrounding formation.

ANNULAR SEALS

The open, annular space between the borehole wall and the casing must be sealed properly to: 1) isolate a discrete zone, 2) prevent migration of surface water, 3) prevent vertical migration of ground water between strata, and 4) preserve confining conditions by preventing the upward migration of water along the casing. An effective seal requires that the annulus be filled completely with sealant and the physical integrity of the seal be maintained throughout the lifetime of the well (Aller et al., 1991).

MATERIALS

The sealant must be of very low permeability (generally 10^{-7} to 10^{-9} cm/sec), capable of bonding with casing, and chemically inert with the highest anticipated concentration of chemicals expected. Cuttings from the existing borehole, no matter what the type of materials, should never be used. They generally exhibit higher permeability and cannot form an adequate seal. The most common materials used are bentonite and neat cement grout. Each has specific, unique, and desirable properties. These materials are discussed briefly here. Additional information can be found in Michigan DEQ (2007), ASTM Method C-150 (2007), and Nielsen and Schalla (2006).

Bentonite

Bentonite is composed of clay particles that expand many times their original volume when hydrated. The most acceptable form is a sodium (Na) rich montmorillonite clay that exhibits a 10- to 12-fold expansion when hydrated. Other types, such as calcium (Ca) bentonite, are less desirable because they offer lower swelling ability and surface area to mass ratios. However, other types should be considered if Na bentonite is incompatible with the formation or analyses of concern. For example, the capability of bentonite may be adversely affected by chloride salts, acids, alcohols, ketones, and other polar compounds. Ca bentonite may be more appropriate for calcareous sediments.

Bentonite is available in a variety of forms, including pelletized, coarse grade, granular and powder. ***Pellets*** are uniform in size and consist of compressed, powdered Na montmorillonite. They typically range from 1/4 to 1/2 inch in size. Pellets expand at a relatively slower rate when compared to other forms. ***Coarse grade***, also referred to as crushed or chipped, consists of irregularly shaped, angular particles of montmorillonite that range from 1/4 to 3/4 inches in size. ***Granular*** particles range from 0.025 to 0.10 inches in size. ***Powdered*** bentonite is pulverized montmorillonite, factory-processed after mining. Powered and granular forms are generally mixed with water to form a slurry.

Risk of losing a slurry to the underlying filter pack and surrounding formation should be considered. Bentonite slurry with less than 30 percent solids can lose its affinity for water, thus losing water to the formation (Listi, 1993). Bentonite used for drilling fluids/drilling fluid mud has a low solids content and therefore forms poor seals, so they are not suitable as annular seal materials (Edil et al., 1992). High-solids bentonite (>30% clay solids) has been developed specifically for monitoring well construction and provides an effective seal. High-solids bentonite slurries may also be formed by the addition of a swelling inhibitor to slow the swelling of the bentonite power, or addition of granular bentonite to bentonite slurry just prior to emplacement with a tremie pipe (Nielsen and Schalla, 2006).

Neat Cement Grout

Neat cement grout is comprised of portland cement and water, with no aggregates added. It is a hydraulic cement produced by pulverizing cement clinker consisting essentially of hydrated calcium silicates, and usually containing one or more forms of calcium sulfate as an interground addition. Several types of portland cements are manufactured to accommodate various conditions. Table 7.2 lists the types as classified by ASTM C150-07(2007). Type I is most commonly used for monitoring wells.

Air-entraining portland cements have been specially processed to form minute air bubbles within the hardened structure. The air-entraining materials are added during the grinding of the clinker. The finished product is more resistant to freeze-thaw action. Air-entraining cements are designated with an "A" after the ASTM cement type. They have been used to construct water supply wells; however, they are less desirable than standard cements because of their greater permeability. Therefore, air-entraining varieties are not recommended for subsurface sealing of monitoring wells.

Water added to the neat cement should be potable and contain less than 500 ppm total dissolved solids (Nielsen and Schalla, 2006). Low chloride and sulfate concentrations also are desirable (Campbell and Lehr, 1973). As the water to cement ratio increases, the compressive strength of the cement decreases and shrinkage increases. The American Petroleum Institute recommends a ratio of 5.2 gallons of water per 94 pound sack of cement. Additional water makes it easier to pump, but adversely affects the grout's sealing properties. Excess water can cause shrinkage and separation of the cement particles, which compromises seal integrity (Nielsen and Schalla, 2006).

Table 7.2 ASTM cement designation (modified from Michigan DEQ, 2007).

CEMENT TYPE	DESCRIPTION
Type I	General purpose cement suitable where special properties are not required. Most common type of cement used for grouting.
Type II	Moderate sulfate resistance. Lower heat of hydration than Type I.
Type III	High early strength. Not commonly used. Ground to finer particle size, which increases surface area and reduces curing time period before drilling may resume from 48 hours to 12 hours.
Type IV	Low heat of hydration cement designated for applications where the rate and amount of heat generated by the cement must be kept to a minimum. Develops strength at a lower rate than Type I. Not commonly used.
Type V	Sulfate-resistant cement for use where ground water has a high sulfate content.
Type IA, IIA, and IIIA	Air entraining cements for the same use as Types I, II, and III. Not recommended for monitoring well construction.

The major disadvantages of neat cement are its heat of hydration, shrinkage upon curing, and its effect on water quality. During curing, heat is released, which is generally of little concern for monitoring wells. If large volumes of cement are used or the heat is not rapidly dissipated, the resulting high temperatures can compromise the integrity of PVC casing. However, the borehole for most monitoring wells is small, and heat significant enough to cause damage generally is not created.

Shrinkage is undesirable because it causes cracks and voids. Bentonite is sometimes added to cement slurry to reduce shrinkage, the bentonite causing the mixture to expand as it hydrates and swells. Bentonite is also added to improve the cement’s workability, reduce the weight and density of the slurry, and reduce the set strength of the cement seal. Several authors, however, have shown bentonite to be chemically incompatible with cement so that the bentonite does not swell, and indeed reduces the capacity of the slurry to swell (Calhoun, 1988, Listi, 1993). Sodium ions in the bentonite are replaced by calcium ions in the cement through ion exchange, reducing the capacity of the bentonite to swell. Cement also releases OH^- ions as it sets, which causes the bentonite to flocculate, reducing its swelling ability. Christman et. al (2002) found that cement-bentonite grout showed evidence of dryness and variable consistency. If used, cement-bentonite grout should be used with care (ASTM 5092-04, Cristman, et. al, 2002).

Upon setting, neat cement grouts often lose water into the formation and affect water quality. Neat cement typically ranges in pH from 10 to 12; therefore, it is important to isolate the annular seal from the screen and filter pack. This may be accomplished by placing a very fine-grained secondary filter pack, 2 to 3 feet thick, above the primary filter pack (Nielsen and Schalla, 2006).

SEAL DESIGN

Annular seals should incorporate measures to prevent infiltration into the filter pack. Contact with the seal can cause sampled ground water to be artificially high in pH. Additionally, bentonite has a high cation exchange capacity, which may affect the chemistry of samples (Aller et al., 1991). In the saturated zone, a 2-foot pure bentonite seal can minimize the threat of infiltration. Above the bentonite seal, neat cement or bentonite grouts should be placed in the remainder of the annulus to within a few feet of the surface.

SEAL INSTALLATION

Bentonite

Annular seals should be installed using techniques that prevent bridging, which may cause gaps, cracking or shrinking. Surface water and/or contaminants potentially can migrate through any voids created. Bentonite that comes in contact with ground water may affect the chemistry of the ground water due to its high pH and high cation exchange capacity. Cations in the molecular structure of the bentonite may exchange with cations existing in the ground water. Because of this, bentonite sealing material should be placed a minimum of 3 to 5 feet above the top of the well screen. Use of a secondary filter pack above the primary filter is also recommended (Nielsen and Schalla, 2006). The bentonite seal above the filter pack is commonly installed by placing granular bentonite, bentonite pellets, or bentonite chips around the casing by dropping them directly down the annulus. If feasible, this practice is acceptable for wells less than 30 feet deep if a tamping device is used. However, for wells deeper than 30 feet, coarse-grained bentonite should be placed by means of a tremie pipe.

The bentonite should be allowed to hydrate or cure prior to sealing the remainder of the annular space. This will help prevent the grout from penetrating into the screened interval. Because bentonite chips or pellets require~~s~~ a sufficient quantity and quality of water in order to achieve and retain hydration, bentonite chips or pellets generally should only be used in the saturated zone. If a two foot bentonite seal is desired in the unsaturated zone, granular bentonite should be used. It should be added and hydrated in lifts of 2 to 3 inches using water that is potable and free of analytes of concern (Nielsen and Schalla, 2006).

For the remainder of the annulus, sealants should be in slurry form (e.g., cement grout, bentonite slurry) and should be placed with a tremie pipe (Figure 7.4). The grout should be mixed using a paddle-type mechanical mixer or by circulating the grout through a pump to disintegrate the lumps (ASTM 50-92-04). The grout should be placed with a tremie pipe. The bottom of the pipe should be equipped with a side discharge deflector to prevent the slurry from jetting a hole through the filter pack. The seal should be allowed to completely hydrate, set, or cure in conformance with the manufacturer's specifications prior to completing the surface seal and developing the well.

Neat Cement

Neat cement should not be poured into the annulus unless there is at least 3 inches between the casing and borehole, the annulus is dry, and the grout is being placed within 30 feet of the surface. If the neat cement grout is poured through standing water the mixture may be diluted or bridging may occur (Nielsen and Schalla, 2006). A neat cement grout should be mixed as with bentonite grout. A tremie pipe should be used for placement and inserted in the annulus to within a few inches of the bottom of the space using a side discharge port.

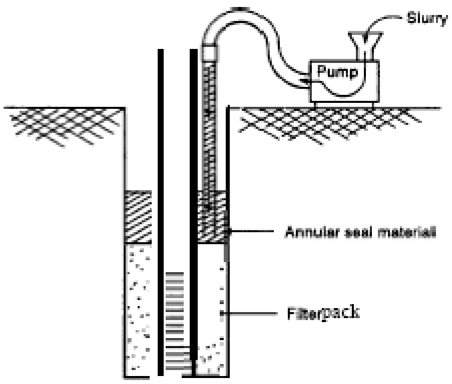

Figure 7.3 Tremie pipe emplacement of annular seal material (Source: Aller et l., 1991).

SURFACE SEAL/PROTECTIVE CASING COMPLETIONS

A surface seal is used to prevent surface runoff from entering the well annulus. The surface seal and protective casing also serve to provide protection from accidental damage or vandalism.

SURFACE SEAL

A neat cement or concrete surface seal should be placed around a protective casing to a depth just below the frost line (3-5 ft.). If the same material was used in the annular seal, the surface seal can be a continuation; otherwise, the surface seal is installed directly over the annular seal after settling and curing. The surface seal should slope away from the well and extend beyond the edge of the borehole to divert surface water. Air-entraining cements may be desirable in cold climates to alleviate cracking caused by freezing and thawing.

ABOVE-GROUND COMPLETIONS

Whenever possible, monitoring wells should extend above the ground surface to prevent surface water from entering and to enhance visibility. From the frost line upward, a steel protective casing should encompass the well. The protective casing should be at least two inches larger in diameter than the inner casing, extend above it, and have a locking cap. The lock should be protected by plastic or rubber covers so the use of lubricants to free and maintain locking mechanisms can be avoided. A small drain or "weep hole" should be located just above the surface seal to prevent the accumulation of water between the casings (See Figure 7.1). This is especially useful in cold climates, where the freezing of trapped water can damage the inner casing. In areas susceptible to flooding, the protective casing should extend high enough to be above flood level (Nielsen and Schalla, 2006). A permanent reference point on the well inner casing must be surveyed to the nearest 0.01 ft. This permanent marker should be used for all water level measurements. Additionally, the well identification number or code should be marked permanently and clearly.

Bumper or barrier guards should be placed beyond the edge of the surface seal or within 3 to 4 feet of the well (See Figure 7.1). These guards are necessary to reduce and prevent accidental damage from vehicles. Painting the guard posts yellow or orange and installing reflectors can increase visibility and help prevent mishaps.

FLUSH-TO-GROUND COMPLETIONS

Flush-to-ground completions are discouraged because the design increases the potential for surface water infiltration; however, they are occasionally unavoidable. This type of completion is generally used only when the location of a well would disrupt traffic areas such as streets, parking lots, and gas stations, or where easements require them (Nielsen and Schalla, 2006).

If flush-to-ground completion is installed, very careful procedures should be followed. A secure subsurface vault generally is completed in the surface seal, allowing the well casing to be cut below grade. The vault should be traffic-rated, and constructed of steel, aluminum, or a high-strength plastic composite material (Nielsen and Schalla, 2006). An expandable locking cap on the casing and a water-proof gasket should be installed around the vault lid to prevent surface water infiltration. The gasket should be inspected at regular intervals and properly maintained to ensure a watertight seal (Nielsen and Schalla, 2006). The completion should be raised slightly above grade and sloped away to help divert surface water. It should be marked clearly and locked to restrict access. This is especially important at gas stations to prevent the misidentification of wells as underground tank filling points. In cold-weather areas where parking lots and roads may be cleared of snow with snowplows, the well vault should be set slightly below the surrounding concrete or asphalt to prevent shearing off of the vault lid by the blade of a snowplow. Flush-to-ground well completions should never be installed in low-lying areas that undergo flooding (Nielsen and Schalla, 2006).

DOCUMENTATION

During monitoring well installation, pertinent information should be documented, including design and construction, the drilling procedure, and the materials encountered (see Chapter 3 for a listing of the particular geologic information needs). Accurate "as-built" diagrams should be prepared that, in general, include the following:

- Date/time of start and completion of construction.
- Boring/well number.
- Drilling method and drilling fluid used.
- Borehole diameter and well casing diameter.
- Latitude and longitude.
- Well location (± 0.5 ft.) with sketch of location.
- Borehole depth (± 0.1 ft.).
- Well depth (± 0.1 ft.).
- Casing length and materials.
- Screened interval(s).
- Screen materials, length, design, and slot size.
- Casing and screen joint type.
- Depth/elevation of top and bottom of screen.
- Filter pack material/size, volume calculations, and placement method.
- Depth/elevation to top and bottom of filter pack.
- Annular seal composition, volume, and placement method.
- Surface seal composition, placement method, and volume.
- Surface seal and well apron design/construction.
- Depth/elevation of water.
- Well development procedure and ground water turbidity.
- Type/design of protective casing.
- Well cap and lock.
- Ground surface elevation (± 0.01 ft.).
- Surveyed reference point (± 0.01 ft.) on well casing.
- Detailed drawing of well (include dimensions).
- Point where water encountered.
- Water level after completion of well development.

In addition, the following should be documented in work plans (when appropriate) and reports:

- Selection and rationale materials for selection of casing and screen.
- Selection and rationale for well diameter, screen length, and screen slot size.
- Filter pack selection and emplacement.
- Annular sealant selection and emplacement.
- Security measures.
- Locations and elevations of wells.
- Well development.

A complete, ongoing history of each well should be maintained. This can include sample collection dates, dates and procedures for development, water level elevation data, problems, repairs, personnel, and methods of decommissioning. This information should be kept as a permanent on-site file, available for agency review upon request.

On July 18, 1990, Ohio House Bill 476 went into effect. This bill requires that all logs for monitoring wells drilled in Ohio be submitted to the Ohio Department of Natural Resources, Division of Water (ODNR). The ODNR can be contacted for further information.

MAINTENANCE AND REHABILITATION

The condition of wells must be maintained to keep them operational and insure that representative samples can be obtained. The maintenance program should be site-specific and take into account all information that could affect well physical and chemical performance (ASTM Method D 5978-96(2005)).

Maintenance consists of conducting inspections and periodic checks on performance. Proper documentation (see previous section) is needed to serve as a benchmark for evaluation, as well as to track well maintenance activities. Current conditions should be compared to as-built diagrams and previous measurements. Maintenance includes, but is not limited to, the following:

- Ensuring visibility and accessibility.
- Inspecting locks for rusting.
- Inspecting surface pad and seals for cracking.
- Checking survey marks to insure visibility.
- Determining depth (see Chapter 10 for recommended procedures).
- Removing sediments (if needed).
- Evaluating performance by doing hydraulic conductivity tests.
- Evaluating turbidity and re-developing or replacing well if turbidity increases.
- Evaluating well construction using geophysical logs or down hole cameras.

Routine inspections generally can be conducted during sampling. Additional evaluation can be conducted by comparing new ground water quality data and with previous data. If the maintenance check indicates a problem, rehabilitation should be conducted. Well rehabilitation activities include redevelopment to remove fine-grained materials or entrapped pollutants from the well. See Chapter 8: Monitoring Well Development for further information on well development.

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Ohio Environmental Protection Agency

Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring

Chapter 10

Ground Water Sampling

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Ohio Environmental Protection Agency

Division of Environmental Response and Revitalization
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and Division of Materials and Waste Management

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Preface

This document is part of a series of chapters incorporated in Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM), which was originally published in 1995. DERR now maintains this technical guidance in collaboration with DDAGW and DMWM as a series of chapters rather than as an individual manual. These chapters can be obtained at ***epa.ohio.gov/derr/gw_support#184203976-technical-guidance-manual-tgm.***

The TGM identifies technical considerations for performing hydrogeologic investigations and ground water monitoring at potential or known ground water pollution sources. The purpose of the guidance is to enhance consistency within the Agency and inform the regulated community of the Agency's technical recommendations and the basis for them.

Ohio EPA utilizes ***guidance*** to aid regulators and the regulated community in meeting laws, rules, regulations and policy. Guidance outlines recommended practices and explains their rationale. The methods and practices described in this guidance are not intended to be the only methods and practices available to an entity for complying with a specific rule. Unless following the guidance is specifically required within a rule, the Agency cannot require an entity to follow methods recommended within the guidance. The procedures used should be tailored to the specific needs and circumstances of the individual site, project and applicable regulatory program, and should not comprise a rigid step-by-step approach utilized in all situations.

Changes from the May 2012 Manual

The Ohio EPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) was first finalized in 1995 and subsequently updated in February 2006 (Revision 1) and May 2012 (Revision 2). This guidance document represents an update (Revision 3) to Chapter 10 (Ground Water Sampling). Listed below are the technical changes from the 2012 version of Chapter 10.

1. Updated formula for calculating water volume in a one-foot section of well casing and associated table.
2. Updated sampling mechanisms and associated table.
3. Added general information related to sampling PFAS.
4. Updated Field Conditions section for additional conditions that could affect the quality of the .sample.
5. Updated water level measurements section and associated table.
6. Updated reference list.

Table of Contents

Chapter 10
Ground Water Sampling

This chapter summarizes procedures for collecting ground water samples from monitoring wells. It focuses on the planning and preparation prior to sampling, types of sampling and purging equipment, field procedures, quality control sampling, and documentation to ensure that samples represent the quality of water obtained from the sampled interval. When selecting protocol, it is important to understand the impacts that removing water from a well can have on the chemistry of the water. Therefore, impacts to sample integrity are also discussed. The chapter also provides some information on the selection of analytical methods and laboratory quality assurance. Understanding the purpose of sampling with respect to the regulatory program requirements and planning in advance is very important. In addition, site location, age, other potential sources, the proximity of water supply wells, and sampling for the analysis of additional constituents may be useful. Consistent sampling and analytical methodology are integral to quality monitoring data.

The primary objective of most ground water monitoring programs is to collect a sample that represents the in-situ ground water quality. However, the working definition of "representative" is not always the same for all programs. For example, those interested in characterizing ground water for the purpose of evaluating it as a potable water supply may be more interested in volumetric-averaged concentrations in the ground water zone (Nielsen and Nielsen, 2006). Monitoring programs may also be designed to determine "worst-case" conditions. Therefore, prior to starting any monitoring program, the data quality objectives need to be determined to ensure the collection of data that are of adequate quality to support decision making (See U.S. EPA, 2006).

The goal in sample collection is to sample in a manner that results in the least disturbance or change in the chemical and physical properties of the water. The guidelines provided here are intended to assist in choosing the most appropriate methods. Site-specific circumstances may require alternative approaches that are not specified. In these cases, the appropriate regulatory authority should be contacted to establish an acceptable approach. In addition, rules may specify issues such as frequency of sample collection, filtration, frequency and accuracy of water level measurements, and parameters for analysis. Requirements for documentation of field and laboratory procedures may also be specified. Appropriate divisions within Ohio EPA should be consulted when planning a ground water sampling program.

The choice of equipment and methodology should be based on an understanding of the hydrogeology of the area and the purpose of the data collection. Each technique has disadvantages and advantages. Because different techniques may yield different results, the best approach is to be consistent throughout an investigation to facilitate the comparison of data values over time (ASTM D4448). When necessary, changes in sampling strategies should be discussed with Ohio EPA prior to implementation.

Although the chapter is intended specifically for the sampling of conventional monitoring wells, the procedures may be useful for other types of ground water sampling, such as direct push technology and water supply wells. Additional information on direct push can be found in Chapter 15-Use of Direct Push Technologies for Soil and Ground Water Sampling. Additional considerations for sampling a water supply well can be found in Appendix A of this chapter.

1.0 Factors Influencing Sample Quality

Many aspects of the sampling process can affect the chemistry and physical properties of ground water when it is being collected. As a result, a sample may not represent the actual quality of the ground water. Therefore, the potential effects need to be considered in any sampling program.

1.1 Well Construction and Development Concerns

1.1.1 Well Construction

A detailed understanding of the local hydrogeology is critical for proper monitoring well construction. Wells must be properly placed with respect to the targeted saturated zone, grouted and sealed. The screen must not interconnect multiple saturated zones. Otherwise, the chemistry and physical properties of a ground water sample may be affected by poor well construction. Ground water samples from wells that have inadequate filter packs, are improperly grouted, or have misplaced screens may have ground water flowing through their intakes that is not represent the ground water quality of the saturated zone. This may be due to grout contamination, water seeping down the casing, or mixing from the surface or other ground water zones.

1.1.2 Well Development

Prior to sampling the well for the first time, care should be taken to properly develop the well. Proper well development creates a graded filter pack around the well screen. It reduces the sample turbidity by removing the fine particulate matter. If a well has not been properly developed, then sample quality may be affected by the sediments in the water. If the well begins to silt up over time, the well may need to be redeveloped. Chapter 8 - Monitoring Well Development, Maintenance, and Redevelopment, discusses proper development techniques and when a well can be considered properly developed.

1.1.2.1 Time Interval Between Well Installation and Well Development.

Development should not be implemented until the seal has cured and settled to prevent pulling uncured grout into the sand pack. The time interval between well installation and development is a function of well construction, type of grout, and conditions under which the grout was installed. For example, neat cement (Type 1) generally cures within 48 hours (Gaber and Fisher, 1988, State Coordinating Committee on Ground Water, 2015); however, if the cement grout column is located mostly above the water column, then 24 hours may be sufficient. Bentonite-based grouts tend to set within 24 to 48 hours. Bentonite granules, chips or pellets, above the sand pack will reduce the potential of contaminating the sand pack with grout during development activities; thus, reduce the time interval between construction and development. A 3/4-inch direct push well installed with dry granular bentonite grout may require less than 24 hours

Ideally, a time of 48 hours is recommended (U.S. EPA, 2001b). However, shorter time frames may be acceptable as discussed above. If shorter time frame is used, then justification should be documented. It is ultimately the responsibility of the environmental professional to demonstrate that the ground water samples collected from the well are representative of the formation water and are not impacted by grout contamination.

1.1.2.2 Time Interval Between Well Development and Sampling

Prior to sampling a well, sufficient time should be allowed for equilibration with the formation after development. The time interval between well development and sampling is dependent on physical equilibrium (i.e., return to static water level conditions), chemical equilibrium between the well and saturated zone, well drilling and construction, and data quality objectives.

Physical equilibrium (return to static water level conditions) is verified by measuring the water level in the well. Depending on the well diameter and saturated zone characteristics, the time required to return to physical equilibrium could range from several minutes to several days to over a month.

Evaluating chemical equilibrium is a more complicated matter. A simple method for determining when a monitoring well and the surrounding formation materials are in chemical equilibrium is not currently available. The degree to which a well disturbs the saturated zone chemistry depends on the drilling method, installation technique, construction, development technique and hydrogeologic environment (Striggow et al., 2008; Kim 2003; Lapham et al. 1995). All of these factors influence the amount of time needed for well materials to achieve chemical equilibrium with the surrounding formation materials and ground water. For example, a 2-inch monitoring well installed in bedrock using air rotary would require more time to chemically stabilize after development than a ¾-inch direct-push well with a pre-packed screen, because installation of the 2-inch monitoring well causes more formation damage and occupies a greater volume of the saturated zone. Several days may be required for the 2-inch well to stabilize with the surrounding formation, whereas the direct-push well may stabilize within a day.

Ohio EPA recommends that ground water samples not be collected from a newly-developed (or redeveloped) well until the well has physically stabilized, i.e., returned to static water level conditions. In addition, ground water sampling should be delayed until the well materials have had sufficient time to achieve chemical equilibrium with the surrounding saturated zone. While rigorous scientific techniques are not currently available to substantiate such a time frame (U.S. Army Corps of Engineers 1998), consideration should be given to the drilling method, installation technique, construction, development technique and hydrogeologic environment (Striggow et al., 2008; Kim 2003; Puls and Barcelona 1996; Lapham et al. 1995; Aller et al., 1991). For shallow (< 25 ft), small diameter (< 2 inch) monitoring wells installed using direct push methods, Ohio EPA recommends a post-development stabilization period of at least 24 hours prior to sampling. For deeper (≥ 25 ft) direct-push wells or deeper (25 to 50 ft), larger diameter (2 to 4 inch) “traditional” monitoring wells installed in unconsolidated sediments using augers or rotary drilling methods, Ohio EPA recommends a post-development stabilization period of at least 72 hours prior to sampling. For deep (> 50 ft) traditional monitoring wells installed in unconsolidated sediments or installed in bedrock, Ohio EPA recommends a post-development stabilization period of at least one week (7 days) prior to sampling. Monitoring wells installed in low permeability silt, clay or shale will generally require a longer stabilization period than wells installed in sand or gravels or more permeable bedrock types **(**U.S. Army Corps of Engineers 1998; Izraeli et al. 1992.)

1.2 Effects Caused by Change in Sample Environment

Transfer of ground water from *in-situ* to atmospheric conditions can alter its chemistry significantly unless proper sampling techniques are used. Aeration/oxidation, pressure, and temperature changes are three major causes of chemical alteration.

1.2.1 Aeration/Oxidation

Upon exposure to the atmosphere, the oxidation state of ground water samples can increase due to the addition of oxygen. Dissolved species such as iron (Fe), manganese (Mn), arsenic (As), and cadmium (Cd) may be oxidized from a reduced state (Gillham et al., 1983), which can cause them to precipitate from solution. The oxidation of Fe is particularly important for sample stability. Ground water may contain high concentrations of dissolved Fe due to anoxic (low oxygen) subsurface conditions. Upon exposure, it can oxidize rapidly and precipitate ferric hydroxide, resulting in a decrease in pH that may alter sample integrity further [$2Fe^{3+} + 6H_2O \rightarrow 2Fe(OH)_{3(s)}$) + $6H^+$]. Ferric hydroxide is known to remove contaminants from solution including, but not limited to, copper (Cu), zinc (Zn), cobalt (Co), cadmium (Cd), arsenic (As) and lead (Pb). Due to oxidation other metals may be dissolved or desorbed and become mobile. While constituents such as Pb do not necessarily change oxidation state, if the solid Pb is adsorbed to changes oxidation state and is dissolved, it releases Pb and other absorbed metals/constituents/trace elements. Alternatively, when oxidized other metals tend to dissolve and become mobile, such as chromium (Cr)…While it may often be difficult to prevent redox changes, acidification, and refrigeration of samples being analyzed for metals should prevent metals from precipitating or reacting to alter oxidation state.

1.2.2 Pressure Differences

Pressure changes caused by the release of ground water into a well may cause shifts in chemical equilibrium (US EPA, 2002) Ground water may have high partial pressures of carbon dioxide (CO_2) gas and, upon exposure, degas CO_2. This is known to cause increases in pH by up to 0.5 to 1 Standard Units (S.U.) and may cause various metals to dissolve or precipitate. If volatile organic compounds (VOCs) are present, sudden pressure changes can cause their volatilization. This will result in a negative bias with respect to true VOC concentration.

1.2.3 Temperature Differences

The temperature of a sample may change because of differences between ambient air and subsurface conditions. A primary concern is an increase in temperature, which may kinetically favor redox reactions and promote increased biodegradation and volatilization (US EPA, 2002).

1.3 Effect Due to Sampling Technique

The method and design of the sampling device potentially can alter samples (US EPA, 2002). Tools that allow air to contact ground water (see Section 3.0-Sampling and Purging Equipment) can potentially aerate samples, as discussed above. Devices can leach contaminants into samples or sorb contaminants from them. Also, improper decontamination of equipment can alter samples.

2.0 Planning and Preparation

The success of any ground water sampling event hinges on the planning and preparation conducted prior to entering the field. The sampling procedures should be documented in a written plan. Items that should be included in the written plan are summarized below. Procedures and event planning and preparation should be evaluated carefully and be appropriate for the associated Ohio EPA program and the intended use of the sampling data. This should also include an evaluation of the analytes selected.

2.1 Written Plan

Written, detailed, site-specific protocol should be developed to document sampling and analysis procedures. The protocol can be incorporated into a single, stand-alone document (sometimes called a sampling and analysis plan) or can comprise a section of a more comprehensive document. Protocol should provide sufficient detail for personnel to properly operate equipment and perform procedures and techniques in a manner that will generate representative data. The circumstances and conditions under which procedures and techniques will be implemented should be clearly described.

The submittal, format, and/or disposition may or may not be specified by rule. In all cases, the plan or other protocol should meet all requirements of the associated Ohio EPA program and provide data that are appropriate for the investigative purposes and that meet data quality objectives. In general, a plan may include (at a minimum) the components listed in Table 10.1.

Table 10.1 ***GENERAL COMPONENTS[1] OF A GROUND WATER SAMPLING AND ANALYSIS PLAN (SAP)***

Parameter selection • organics • metals	**Sampling frequency** • quarterly, semi-annual, annual • quality control samples	**Decontamination procedures** • equipment • IDW management
Field procedures prior to sampling ground water: • well inspection • water level measurements (including meter type and level of accuracy) • total depth of well • detection and sampling of immiscible liquids • field analyses • purging of well	**Well purging, including but not limited to:** • methods • criteria completion • equipment • disposal of water **Sample withdrawal:** • methods • equipment	**Field measurements of ground water:** • parameters (e.g., pH, temperature, and conductivity) • description and calibration of field equipment • description of field analysis procedures
Sample handling: • order of collection • filtration[2] • preservation (type and when/how added) • containers with labels • holding times • shipping	**Documentation:** • field logbook or sampling documentation forms[3] • standardized chain-of-custody forms • sample analysis request sheet • field QA/QC samples	**Laboratory analysis:** • analytical methods • detection limits • laboratory QA/QC samples • description of data validation methods reporting requirements and format

2.2 Sampling Event Planning and Preparation

Before any sampling begins, planning and preparation should be a high priority. All personnel should be familiar with site-specific written protocol and trained in the proper use of the equipment. All equipment and paperwork should be organized. Instruments should be in working order, properly decontaminated, and calibrated. Field logs, sheets, or other documents used to record notes should be organized. Arrangements with the laboratory

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[1] Additional components may be necessary on a site-by-site basis.

[2] Check whether the regulatory program allows filtering of ground water samples. Note that the Ohio solid waste regulations do not allow filtering at municipal landfills.

[3] See Section 4.10 - Documentation for items that may need to be included.

should be made to ensure that samples can be handled and analyzed within the required holding times and to obtain labels, appropriate containers, and preservatives. The following are general checklists for preparation procedures and equipment:

2.2.1 Preparation Procedures

Determine the following:

- Sampling date, time, and location
- Total sampling and travel time to insure appropriate lab arrangements
- Number and type of analyses needed from each location
- Purge water management practices
- Decontamination procedures
- Safety procedures
- Number of field blanks, equipment rinsates, trip blanks and duplicates needed
- Sample volumes needed, total number of samples, and container type
- Samples to be filtered (if appropriate)
- Appropriate equipment
- All equipment is properly calibrated and in working order
- Bailer volume (if necessary)
- Number and type of containers needed
- Number and type of necessary preservatives
- All chain-of-custody procedures

In addition, Review the construction, sampling history and recharge rate of each well. Be aware of any nearby production wells that may affect measured water levels

2.2.2 General Supply and Equipment Checklist

- SAP
- Keys to locks on wells
- Map of site, well locations, and underlying geology
- Field notebook, logbook, and/or field sampling forms
- Indelible marking pens
- Appropriate lab analysis and chain-of-custody forms
- Preservatives
- Filtration equipment
- Ice
- Coolers for ice and samples
- Purging and sampling devices
- Appropriate tubing
- Appropriate sample containers and labels
- Field monitoring meters (e.g., water level, pH, specific conductance, temperature)
- Calibration instructions and standard testing solutions for field monitoring equipment
- Calibrated bucket (to determine volume of purged water)
- Tool box
- Extra batteries
- Safety equipment
- Calculator
- Plastic sheeting
- Decontamination solutions and equipment
- Flashlight
- Photoionization detector (PID) or organic vapor analyzer (OVA)
- Equipment for detecting immiscible fluids (e.g., interface probe or clear bailer)
- Contact information for site, facility, and laboratory
- Emergency contact information

2.3 Sampling Frequency

For sites that require a ground water monitoring program, regulations may specify sampling frequencies. For other cases where contaminants have been identified and no regulatory requirements have been identified, the following hydrogeologic considerations in determining sampling frequencies are provided. Frequencies may be determined by site hydrogeology. U.S. EPA (1992) suggested using the Darcy equation to determine average linear velocity of ground water (see Chapter 3). If velocity is relatively low, less frequent sampling may be required. High velocity necessitates the need for more frequent sampling. Linear flow velocity can be used to determine an interval that yields an independent sample. Sample independence is an important concept for statistical and analytical data analysis (U.S. EPA, 2009). Barcelona et al. (1985) provided a graph based on hydraulic parameters that can be useful. Barcelona et al. (1989) indicated that data collected over a period of two years or more is often needed to establish seasonal trends before an adequate frequency can be selected.

The type of contaminant source (i.e., spill, intermittent source, or continuous source) should also be considered for sites with releases and known contamination (Barcelona et al., 1985). Spills tend to move as a slug/plume through the subsurface, potentially limiting the sampling time frame at a particular well as the slug passes. Intermittent sources may produce slugs with high and low concentration trends to develop. Continuous sources may produce a large plume requiring a sampling frequency based on ground water flow velocity.

2.4 Parameter Selection

Parameter selection depends on whether the purpose of sampling is to 1.) quantify the general quality of the ground water;2.) identify the presence of any contamination, or 3.) identify site as the specific source of contamination.

2.4.1 Parameters to Characterize General Quality

Parameters used to characterize general quality can include: pH, alkalinity, total dissolved solids (TDS), turbidity, dissolved oxygen (DO), oxidation/ reduction potential (ORP), fluoride (F^-), hydrogen sulfide (H_2S), total hardness and non-carbonate hardness, specific conductance, chloride (Cl^{-1}), nitrate (NO_3^{-1}), sulfate (SO_4^{-2}), phosphate (PO_4^{-3}), silicate (SiO_2), sodium (Na^{+1}), potassium (K^{+1}), calcium (Ca^{+2}), magnesium (Mg^{+2}), ammonium (NH_4^{+1}), total iron (Fe), and manganese (Mn). The results can provide an overall picture of ground water geochemistry that is useful to site characterization. For example, an understanding of geochemistry can help in determining chemical species present (e.g., AsO_3^{-2} vs. AsO_4^{-3}) and mobility in the subsurface. Certain parameters (e.g., anions, cations, pH, TDS, specific conductance) are helpful in evaluating releases of inorganic contaminants, while other parameters (chloride, iron, nitrate, sulfate, DO, ORP, and alkalinity) can be used to evaluate changes in ground water chemistry caused by the release and biodegradation of organic contaminants**.** Regulated entities (such as municipal or hazardous waste landfills) may be required to establish a sampling program that includes some of the above-mentioned parameters.

2.4.2. Parameters to Characterize Contamination

When ground water contamination is known, suspected, or being investigated as part of a monitoring program, parameters specific to the waste material, history of the site/facility, or chemicals of concern (COCs) usually are necessary. Rules may also dictate specific parameters. When ground water contamination is known or suspected, entities may be required to monitor additional site-specific parameters[4]**.**

Past waste constituents, handling practices, and age of site should be considered. Because waste released to the environment may chemically change through time, potential breakdown products should be considered. If accurate disposal records are available and waste constituents are well documented, the list of parameters can be relatively limited. The list should be more extensive if handling practices are poorly understood, or if needed to differentiate source. In more industrial areas, source of contamination may not be evident using the common contaminant criteria alone and require advanced techniques/analysis such as multivariate statistics, principle component analysis, hierarchical cluster analysis, time series modeling, and GIS analysis techniques. If this is the case, parameters should also be consistent with other regulated sites that may be contaminated the same area/region in order to properly compare sampled groundwater and identify contaminating source. Monitoring suites of parameters (e.g., volatiles, semi-volatiles, metals, etc.) may be necessary when specific waste constituents are not known. Where rule/policy allows, lists may be narrowed as the investigation progresses and waste constituents and chemicals of concern become better defined.

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[4] Ohio EPA recommends that, in some cases (e.g., characterizing known ground water contamination), that the laboratory be requested to report all constituents listed in a method's target analyte list whether they are detected or quantified or not. This ensures that breakdown products are also considered.

3.0 Sampling and Purging Equipment

Site-specific hydrogeology, geochemistry, types of contaminants, and well design determines the specific equipment recommended. Ultimately, the chosen equipment should employ inert material, not subject samples to negative pressures or high positive pressures and minimize exposure of samples to the atmosphere (ASTM D4448). The following are specific criteria and characteristics for equipment/device selection.

3.1 Criteria for Selection

In general, the choice of a device should be based on the ***characteristics of the device*** in combination with the ***characteristics of the site/project*** as listed in the following sections.

3.1.1. Device Characteristics

Characteristics of devices are:

- ***Device composition*** - The chosen device should have sample-contacting parts made of "inert" materials that limit the potential for bias through sorption or leaching of contaminants, degradation, or corrosion. For components requiring rigid material (casing, screen, bailers etc.), the acceptable materials are fluorocarbon polymer (e.g., Teflon®), stainless steel (316 and 304), and polyvinyl chloride (PVC). Disposable bailers can also be composed of polyethylene and polypropylene. When sampling for organics, pump tubing should be composed of fluorocarbon polymer, or fluorocarbon polymer-lined polyethene. Polyethene tubing is also acceptable for sampling for inorganics (USGS, 2014; Yeskis and Zavala, 2002, ASTM D4088). Refer to Section 3.2 for types of equipment and the limitations of their use based on material composition when sampling for organic/inorganic constituents. Special material and design considerations are needed to ensure compatible materials are used when sampling for Per- and Polyfluoroalkyl Substances (PFAS), as discussed in Section 3.2.10 below.
- ***Device design and technique of use*** - The device should deliver samples with minimal atmospheric exposure, should not apply negative pressures (vacuum), and should limit agitation, both in the well and in the transfer process (ASTM D6634). Furthermore, the tool should not introduce air or non-inert gas into samples as part of its lift mechanism.
- ***Flow rate control and capacity*** - When pumps are used, low flow rates are desirable to limit agitation and turbulent flow, especially for VOCs (Barcelona et al., 1985, U.S. EPA, 1986a). The ability to maintain a steady low flow varies significantly. If the device is being used for purging and sampling, then it should be capable of being operated at variable flow rates suitable for both applications. Flow control that involves "valving" should be avoided, since it can cause pressure changes and subsequent sample alteration. Instead, a mechanism that directly controls the rate (i.e., a rheostat to vary the power supplied to an electric submersible pump) should be utilized.
- ***Operation and Maintenance*** - The device should be easy to operate and maintain. If personnel are not properly trained, the margin of potential error is greater. The device should be designed for in-field maintenance. Mechanically simple equipment that can be easily repaired with inexpensive, replaceable parts is preferable. If decontamination is necessary, the device should be easy to decontaminate. Devices that are constructed to minimize the surface area contacting ground water samples and that are easy to disassemble and reassemble are best. Use of dedicated or disposable equipment at each well or sampling point eliminates the need for decontamination, saving valuable field time and reducing the potential for cross contamination of samples.
- ***Device reliability, durability, and portability*** - The device should operate reliably for extended periods and be able to withstand a variety of chemical and physical environments. Dedicated equipment may need to withstand extended contact with ground water and any existing contamination. Equipment that is transported into locations where access is limited should be sufficiently portable. Excess weight and volume of battery packs, generators, air compressors, tubing, etc. can limit portability.
- ***Capital, operation, and maintenance costs*** - These should be considered however, they should not

be overriding factors. Obtaining a sample that is representative of site conditions should be of more importance than cost, particularly when the costs of well installation, chemical analysis, and possible litigation resulting from discrepant analytical results are considered. These costs often far outweigh equipment purchase costs (Nielsen and Yeates, 1985).

3.1.2 Site/Project Characteristics

Characteristics of sites/projects that should be considered are:

- **Project and data quality objectives –** What is the purpose of the sampling? Are samples being collected for compliance evaluation, risk assessment or field screening?
- ***Monitoring Well Diameter*** - The device should be compatible with the diameter of the well. Most sampling equipment is not designed to be used in all wells.
- ***Well Obstructions or Constrictions*** - These can hinder the entry and retrieval of sampling equipment. For example, casing joints may not be flush and could prevent insertion. Also, a well that is not plumb can restrict access. For example, a well installed in an area with slope stability issues can be crimped, bent, or broken from the slope movement.
- ***Depth to the Sampling Interval*** – As well depth increases, greater lift capacity is required and sampling time generally increases, which may limit the desirability of labor-intensive devices. Options generally become limited as depth increases.
- ***Parameters of Interest*** - The suitability of various devices may depend on the parameters of greatest concern. Some devices perform better for inorganics, while some are more suitable for VOCs. Some materials contained within or frequently used with ground water sampling equipment are not suitable for sampling for PFAS (refer to Section 3.2.1).
- ***Presence of Non-Aqueous Phase Liquids (NAPLs)*** - The equipment should be capable of detecting the presence of either light or dense NAPLS if they are potentially present.
- ***Saturated Zone Characteristics and Ground Water Chemistry*** - The equipment should be appropriate for the saturated zone yield, the screen or open borehole length, the presence of stratification (causing vertical variation in yield) within the screened saturated zones, and the available water column in the well. Additionally, the sampling equipment should be compatible with ambient ground water chemistry, unusually low (<5.5.U.) or high (>9.5.U.) pH conditions, the presence of gas, etc.
- ***Temporal (Seasonal) Variations*** - The sampling equipment should be operable over seasonal variations in saturated zone temperature, yield and water level elevation.

3.2 Types of Equipment

The following is a discussion of commonly used sampling equipment available. Table 10.3 (see end of Section 3.2.10) summarizes the recommended devices. Devices not mentioned may be acceptable if they are peer-reviewed and have been demonstrated to be capable of collecting representative samples. For additional information, see ASTM D4448, ASTM D6634, Barcelona et al. (1985), Nielsen and Yeates (1985), Electric Power Research Institute (EPRI, 1985, 1987), Gillham et al. (1983), Nielsen and Nielsen (2006), KEMI (2015), Parker (1994), Pohlman and Hess (1988), U.S. EPA (1992), and Yeskis and Zavala (2002).

3.2.1 Grab Samplers

Grab samplers collect a sample at discrete depths without being pumped or lifted to the surface by gas or air. Grab samplers are commonly used to collect ground water include bailers and syringe samplers.

3.2.1.1 Bailers

Bailers are the most portable of all sampling devices. A bailer can be constructed of virtually any rigid or flexible material, including materials that are inert to chemical contaminants. For sampling ground water, acceptable compositions include Teflon®, stainless steel, PVC, polyethylene, and polypropylene. The cord used to raise and lower the bailer should be made of a non-reactive substance (e.g., Teflon-coated wire/rope, polypropylene).

Bailers are readily available in a variety of diameters. Their diameter should be 75% (or less) of the inside diameter of the well casing to allow for adequate clearance. There are several types of bailers (ASTM D6634, ASTM D6699):

- A ***top filling*** bailer is designed such that water flows through its top. Because of the agitation of the sample, this bailer is only appropriate for sampling light, non-aqueous phase liquids (LNAPL).
- A ***single check*** valve bailer (open bailer) has a valve at its bottom that seals the sample chamber when the bailer is withdrawn.
- A ***double check*** valve bailer (point source bailer) is designed to sample discrete zones in a water column. Water flows through valves at both ends as the bailer is lowered. When the desired level is reached, the bailer is pulled back, both valves close, and water from the interval is retained. However, if appropriate procedures are not carefully followed, samples collected may not be representative of the depth interval of interest. The double check valve bailer is also effective in collecting dense, non-aqueous phase liquids (DNAPLs).
- A **differential pressure** bailer consists of a sealed canister body with two small diameter tubes of different heights. The bailer is rapidly lowered into the well. When the descent has stopped, differences in hydrostatic pressure between the two tubes allow the bailer to fill through the lower tube as air is displaced through the upper tube. This minimizes the exposure of the sample to air, especially if the bailer is fitted with internal 40-millimeter vials for direct sample bottle filling. However, because the bailer is lowered rapidly, it will agitate the water column.

Some studies have demonstrated that levels of VOCs in samples obtained with bailers are statistically lower than in samples obtained with other devices (Imbrigiotta et al. 1988; Tai et al. 1991). In addition, bailing can cause increased turbidity (Puls and Powell, 1992; Puls et al., 1992; Backhus et al., 1993). In contrast, a literature survey by Parker (1994) found that bailers can recover representative samples under certain circumstances and that loss of volatile and oxidizable analytes can be reduced by careful use of bottom-emptying devices and a study comparing results from a bottom-emptying bailer and a Keck® helical-rotor pump operated at low flow pumping rates determined that differences in VOC concentrations were relatively small (Karkins, 1996).

Bailers may not be the best available technology. However, they may be the only practicable option for sampling some ground water zones. Bailers may be preferred where the water column is shallow, or the saturated zone is very deep. They may be preferred when concentrations of contaminants are extremely high because they are easier to decontaminate and are less expensive to replace than pumps. Disposable bailers eliminate the need to decontaminate.

Rapid addition or withdrawal of a bailer can cause surging within the well that may cause increased turbidity, loss of volatiles, aeration, degassing of samples, and affect the level of development of the well. Personnel sampling with bailers need to be properly trained since the results are highly dependent on the skill, care, and consistency of the operator. This training should be documented in the SAP. If samples from bailing are turbid, then it should be determined whether sampling with a low flow method would produce less turbid samples.

When bailing, ***double check valve bottom-draining*** bailers are recommended. This allows for lessened sample disturbance during transfer to the container. The bailer should be composed of Teflon®, stainless steel, PVC, polyethylene, or polypropylene. Either fluorocarbon polymer-coated or colorless (white) polypropylene cord should be used to lower and raise the bailer. Polypropylene cord is inexpensive enough to be discarded after one use. A bailer should always be lowered and raised slowly to minimize sample agitation associated with degassing, aeration, and turbidity and to the extent possible, avoid hitting the sides of the well. A tripod and pulley may be used to remove the bailer.

Pouring water from the top of a bailer directly into a container or to a transfer vessel may agitate/aerate the sample and alter its chemistry; therefore, such pouring is discouraged.

3.2.1.2 Syringe Samplers

Syringe samplers may be used for low-volume sampling for inorganics and non-volatile organics. These samplers can operate at great depths to provide discrete samples from specific intervals or zones. A sample container is pressurized or evacuated and lowered into a well. The sample is collected by opening the container or releasing the pressure, drawing water into the sampler (Nielsen and Nielsen, 2006). The syringe sampler is withdrawn, and the sample is transferred to a collection bottle, or alternatively, the syringe sampler can be utilized as the sample container.

Syringe devices cannot be used for purging large volumes and are ineffective for collecting large samples. In addition, ground water containing high concentrations of suspended solids may cause the syringe device to leak (U.S. EPA, 1992). Researchers have concluded that these samplers are inferior in comparison to other devices when sampling for VOCs (lmbrigiotta et al., 1988). Therefore, syringe samplers are not recommended.

3.2.2 Bladder Pumps

A bladder pump consists of a flexible bladder inside a rigid housing. Water enters the bladder from the bottom and is squeezed to the surface through a discharge line by gas pressure applied to the outside of the bladder. An air compressor and regulator turn the pressure on and off, allowing new water to enter the bladder and the cycle is repeated. The separate bladder chamber does not allow the sample to come in contact with the compressed air. Check valves at the top and bottom prevent backwash from the sample tube and bladder. Flow can be readily controlled and low rates of 100 millimeters per minute (ml/min) are easily obtainable. Teflon® bladders and Teflon®/stainless steel outer shells are recommended.

Bladder pumps have been used to depths greater than 200 feet and are available in sizes designed for 2-inch or smaller wells. The need for a power source and compressed air limits their mobility. Portable power sources are commercially available.

Potential problems with bladder pumps include sediment damaging the inner bladder and high suspended solids concentrations causing failure of check valves for some models (Nielsen and Nielsen 2006). Strainers or screens are available that attach below the bladder to filter material. Note that samples collected through a strainer or screens are not considered to be filtered.

Bladder pumps are generally recognized as the best overall sampling device for both inorganic and organic constituents (U.S. EPA, 1992). Muska et al., (1986) found that bladder pumps generate reproducible analytical results. Kasper and Serkowski (1988) concluded that the sampling rate and reliability of the bladder pump outperformed both the gas and mechanically driven piston pumps. Tai et al. (1991) concluded that a bladder pump yielded representative recoveries of VOCs compared to a control sample. Pohlmann and Hess (1988) determined that bladder pumps are suitable for collecting samples for almost any constituent.

Bladder pumps are recommended for purging and sampling. Whenever possible, the pump should be dedicated to the well. Doing so eliminates the need to transport and decontaminate the pump, thereby reducing the potential for cross contamination as well as saving time and reducing project cost.

3.2.3 Electrical Submersible Pumps

A variety of electrical submersible pumps are available. In the past, electrical submersible pumps were primarily designed for use in water supply wells and were difficult to use for contaminant monitoring purposes. However, manufacturers have since designed low-flow electrical submersible pumps for 2-inch diameter monitoring wells that can collect representative samples. Submersible pumps designed for ground water sampling incorporate non-sorptive materials (e.g., stainless steel, Teflon®, etc.) that are appropriate for collecting VOCs and other sensitive parameters. One disadvantage is that the heat generated by the motor could increase sample temperature, resulting in the loss of dissolved gases and VOCs and subsequent precipitation of trace metals (Nielsen and Nielsen, 2006) Therefore, after sampling, it is recommended that a sample be withdrawn and the temperature measured to assess whether the pump has increased the water temperature. Another disadvantage is the number of intricate parts, which may cause decontamination and maintenance to be time-consuming and difficult.

Two types of submersible pumps available are the centrifugal and the progressive cavity (helical-rotor) pumps. Both are positive displacement devices.

3.2.3.1 Centrifugal Submersible Pump

Centrifugal submersible pumps designed for 2-inch monitoring wells are usually cooled and lubricated with water rather than hydrocarbon-based coolants and lubricants that could contaminate samples. The electric motor spins or rotates an impeller (or series of impellers) that causes water to be accelerated outward and then upward into and through the pump's discharge lines. The higher the pumping rate, the greater the potential for sample alteration by agitation, increased turbulence, and pressure changes. Therefore, a variable-speed centrifugal submersible pump capable of low-flow purging and sampling is essential for collecting a representative sample. Low-flow centrifugal submersible pumps appear to perform similarly to low-flow bladder pumps with respect to preserving sample integrity.

3.2.3.2 Progressive Cavity (Helical-Rotor) Pumps

Progressive cavity (helical-rotor) pumps are appropriate for collecting sensitive samples if low-flow pumping rates are used. An electric motor at the base turns a corkscrew-like helical rotor near the top. The helical rotor causes an upward movement of water trapped in the vacuities of the rotor and the water moves up and through the discharge line. A check valve at the top ensures that water in the discharge line (sampling tube) does not re-enter the pump. A controller box at the surface allows for variable flow rates.

3.2.4 Gas-Driven Piston Pumps

Although not commonly used, the gas-driven piston pump is acceptable if the parts contacting samples are chemically inert (i.e., will not affect sample representativeness). This device utilizes gas pressure to drive a piston between two chambers, one for gas and one for water. Gas is injected through one of two tubes to lower the piston in the gas chamber, allowing water to fill the upper water chamber. Pressure is then applied to a separate tube that pushes the piston upward and propels the sample to the surface. Water and gas remain separated. These pumps can operate at great depths and collect large-volume samples. Disadvantages are that valves and pistons are known to be damaged by fine-grained sediments and mobility is limited by the need for a gas supply. Additionally, the valving mechanism may cause a series of pressure drops that could cause sample degassing and pH changes (U.S. EPA, 1992).

3.2.5 Suction Lift Pumps

Suction lift pumps deliver samples by applying a vacuum at the surface. The negative pressure is applied by a portable pump attached to a tube lowered into the well. Suction pumps are limited by practical suction limits, which restrict their use to wells with water to approximately 25 feet below ground.

Surface centrifugal and ***peristaltic*** are the two major types of suction lift pumps. The peristaltic offers greater advantages over the surface centrifugal. Surface centrifugal pumps must be primed before being operated and should employ a vacuum flask to prevent contact of the sample with moving parts. Peristaltic pumps are self-priming and create a vacuum by a series of rotating wheels that compress the sample tubing. As the sample only contacts the tubing when using a peristaltic pump, no moving parts need to be decontaminated. Usually, disposable tubing is used. Peristaltic pumps generally cause less agitation than surface centrifugal pumps.

Suction lift pumps are very portable, widely available, and relatively inexpensive. Flow rates are controlled easily, providing adequate rates for sampling. These devices typically can be used in wells of any diameter and plumbness. Concerns with use of peristaltic pumps for sampling VOCs include potential for degassing due to negative pressures, potential for sorption of contaminants to flexible tubing, and potential for contribution of organic compounds from the flexible tubing (Striggow et al., 2017). The National Council of Industry for Air and Stream Improvement (NCASI, 1984) found a 10 to 30 percent loss in VOC concentrations from peristaltic/vacuum flask systems compared to results for bailers, bladder pumps, or submersible pumps. Imbrigiotta et al. (1988) also attributed losses of VOCs due to the vacuum created by peristaltic pumps.

To address these concerns, Ohio EPA recommends:

1. Use Compatible Tubing

Using compatible tubing reduces the risk of losses of VOCs due to adsorption to the tubing or addition of contaminants from the tubing (i.e., material leaching).

- Ensure the sample tubing (drop-tubing / discharge tubing) is compatible with COCs being sampled.
  - Low-density polyethylene (LDPE), high-density polyethylene (HDPE), and Teflon®-lined tubing are all commonly used and generally compatible with most COCs (VOCs, semivolitile organic compounds [SVOCs], metals). ***NOTE:*** *Teflon® should not be used to sample for PFAS.*
- Ensure the flexible tubing (pump head tubing) is compatible with COCs being sampled.
  - The MasterFlex® flexible tubing typically used is compatible with a wide range of COCs (VOCs, SVOCs, metals, and can be compatible with PFAS)

2. Use New or Dedicated Tubing at Each Sample Location

Use of new or dedicated tubing at each sampling location prevents cross-contamination that could occur from reused tubing.

3. Look for off-gassing of sample (bubbles in the sample tubing).

Look for significant bubbles forming in the sample tubing to determine whether off-gassing is occurring due to the use of the peristaltic pump. Off-gassing (methane, CO2, etc.) can cause VOCs to move out of solution and into the entrained bubbles, causing unrepresentative low results. Dissolved VOCs exposed to lower atmospheric pressure of peristaltic pumps can also degas, biasing results low.

Off-gassing of CO2 or other dissolved gasses can alter the geochemical conditions (such as pH) of the water in the tubing, potentially chemically altering metals or other redox-sensitive parameters in the sample.

- If bubble formation in tubing is significant, either:
    - stop sampling with peristaltic and return with alternative method (i.e., bladder pump)
    - if first-time sampling event with additional sampling expected, consider collecting the samples but qualifying the data "J" as estimated low and sample with an alternative method (i.e., bladder pump) during follow-up or confirmation sampling events.
- If no significant bubble formation is observed in the sample tubing, use of the peristaltic pumps is OK.

4. Incompatible flexible tubing considerations. (Rare situation)

If there is a known compatibility issue identified with the flexible tubing, but the sample tubing is compatible, the following alternative sampling methods could be employed to prevent contact with the flexible tubing (i.e., sample collected before the pump head).

- VOCs could be sampled using the "soda straw" method. ***NOTE:*** *When purging low-flow and sampling using the soda straw method, if additional sample volume is needed and the tubing must be replaced in the well, stabilization of that well must start over due to the disturbance of the standing water column in the casing.*
- SVOCs and some metals (e.g., non-VOC samples collected in 1-Liter amber glass jars) could be collected using the "vacuum transfer cap" method.

Peristaltic pumps may not be a preferred sampling method if sufficient dissolved CO_2, dissolved methane, or other dissolved gasses are present in ground water being sampled. Negative pressures created by the pump may cause excessive degassing of dissolved gasses. Degassing of dissolved CO_2 during purging can cause pH changes that may affect dissolved metals concentrations in samples and degassing can create space for volatilization of target VOCs into the entrained gases. If gas bubbles are observed in sample tubing during stabilized pumping rates, then significant degassing may be occurring that could affect sample quality.

If samples are being collected for analyses for low concentrations of organics and there is concern over the potential interference due to contact with the flexible tubing, then they should be collected in-line, ahead of the pump, and a sufficient volume of water should be pumped through the system to account for the initial filling of the containers when a negative head space was present. US EPA provides the following two methods to sample water before the pump-head flexible tubing to collect samples for organics analyses using a peristaltic pump (Striggow et al., 2017):

"Soda straw" method:	Once the well is sufficiently purged, the sample tubing is crimped (typically in a double-z configuration) to prevent the water in the sample tubing from flowing back into the well. The sample tubing is withdrawn from the well and sample containers are filled from the water stored within the tubing by carefully releasing the crimp to allow water to flow. U.S. EPA provides a complete procedure for the soda straw method in Striggow et al., 2017).
Vacuum transfer cap method:	A vacuum transfer cap is added to the sample tubing before the flexible tubing to allow for collection of a sample prior to contact with the flexible tubing. Several vacuum transfer cap devices are commercially available. Due to the potential for degassing of VOCs from samples, this method is only recommended for sampling SVOCs or other sample analyses requiring 1-liter glass containers.

Samples collected for metals and inorganic analyses using peristaltic pumps may be collected through the flexible tubing, provided that a rinse blank of the flexible tubing is also collected. Substantial degassing of CO2 can result in pH shifts that can affect the quality of samples collected for metals and inorganic analyses. (Striggow et al., 2017).

3.2.6 Passive Diffusion Samplers

Passive diffusion bag samplers (PDBs) use a LDPE diffusion membrane filled with deionized water to collect water samples for VOC analysis. The polyethylene acts as a semi-permeable membrane allowing volatile contaminants to diffuse into the deionized water. Once chemical equilibrium is reached, a water sample that is representative of the VOC concentrations may be obtained from the interval at which the sampler is placed.). Use of multiple PDB samplers at different depths within a well screen interval can allow for a vertical profile of the VOC contamination within the well.

Equilibration time for diffusion samplers depends on the time required for the environment disturbed by deployment of the sampler to return to ambient conditions and time required by the sampler to equilibrate with the ambient water. To account for this, PDB samplers are generally deployed a minimum of 14 days prior to sample collection. Some lower conductivity formations may require more than two weeks (Striggow et al., 2017; Vroblesky and Campbell, 2001). Samplers can be left in from one sampling event to another then removed and replaced with a new sampler to minimize mobilization and maximize efficiency. Although the sampler may be deployed for an extended period (e.g., three months or longer); the analytical results will be the average of the sample equilibration time for the analyte of concern (generally the last 1 to 4 days).

Advantages of PDB sampling include its low cost, minimal purging and water disposal, and the ability to monitor a variety of VOCs. A disadvantage is that they are not applicable to inorganics and other contaminants that do not readily diffuse across the semi-permeable membrane. PDB sampling may not be applicable for sites where water in the well casing may not be representative of the saturated zone adjacent to the well screen. This may occur when water in the well casing is stagnant, or when there is a vertical flow within the well. In addition, PDB samplers do not provide a discrete time-interval sample, but rather an average of the concentrations in the well over the equilibrium period.

Passive diffusion bag samplers are appropriate for long-term monitoring at well-characterized sites. The target analytes should be limited to chemicals that have been demonstrated to diffuse well through polyethylene (i.e., most VOCs and limited non-VOCs), as listed in Tables 1-1 and 4-1 of ITRC's PDB sampler guidance document (ITRC, 2004). A combined version of these tables is provided below as a reference (Table 10.2). However, as the compound list may change as further tests are conducted, ITRC ***http://www.itrcweb.org/*** should be referenced for the most recent list of chemicals favorable for sampling with PDB. The site sampled should have sufficient ground water flow to provide equilibrium between the water in the well screen and the surrounding ground water zone. ITRC (2004) suggests that care should be given in interpreting PDB results when the hydraulic conductivity is $<10^{-5}$ cm/s, the hydraulic gradient is <0.001, or the ground water velocity is < 0.5 ft/day. Use of PDBs is not appropriate when a vertical flow in the well exists. A deployment time of at least two weeks is recommended to allow for diffusion of the analytes across the membrane (ITRC, 2004, Vroblesky, 2001; Vroblesky and Hyde, 1997; Yeskis and Zavala, 2002; and USGS, 2014).

3.2.7 Equilibrated Grab Samplers

Equilibrated Grab Samplers are devices that can be used when no purge techniques are acceptable (Section 4.5.4 – Minimum/No Purge Sampling). They are placed in the well before sampling and remain closed. The water is collected when the sampler is activated. Samples are either transferred to containers at the well head or the sampler is shipped to the laboratory for analysis. Examples of equilibrated grab samples include Hydrasleeve™, Snap Sampler™, and Kemmerer Sampler (USGS, 2014; Striggow et al. 2017).

Table 10.2 Compounds tested with PDB in laboratory and field tests.

Favorable laboratory diffusion testing results

Benzene
Bromodichloromethane*
Bromobenzene**
Bromochloromethane**
Bromoform*
_n_-Butylbenzene**
sec-Butylbenzene**
tert-Butylbenzene**
Carbon disulfide**
Carbon tetrachloride
Chlorobenzene
Choroethane
Chloroform*
Chloromethane
2-Chlorovinylether*
Dibromochloromethane
Dibromomethane
1,2-Dichlorobenzene

1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichchloroethane**
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
cis-Dichloropropene*
1,2-Dibromoethane*
trans-1,3-Dichloropropene*
Ethyl benzene
Hexachlorobutadiene**
p-Isopropyltoluene**
1-Methylethylbenzene**

Napthalene*
1,1,2,2-Tetrachloroethane
Tetrachloroethene (PCE)
Toluene
1,2,3-Thrichlorobenzene**
1,2,4-Trichlorobenzene**
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Tricholoroethene (TCE)
Trichlorofluoromethane
1,1,2-Trhichloro-1,2,2-trifluoroethane**
1,2,3-Trichloropropane*
Vinyl chloride
_m,p_-Xylene**
_o_-Xylene**
Xylenes (total)

Unfavorable diffusion testing results

Acetone*
tert-Amyl methyl ether**#
Bromoform**#
Methyl _iso_-butyl ketone*

Methyl tert-butyl ether*
Naphthalene**
n-Propylbenzene**

Styrene*
1,2,4-Trimethylbenzene**
1,3,5-Trimethylbenzene**

* Laboratory results only, (Vroblesky 2001a)
**Results from field tests only, (Parsons 2003)
#The data set for this compound was relatively small (fewer than five instances of comparison), so the power of the classification (i.e., acceptable, or unacceptable) is fairly low.

3.2.8 Other Devices

The ***gas drive sampler*** operates by applying positive gas pressure into a sample chamber to force the water to the ground surface. Water enters through a valve at the bottom of the sampler into the sample chamber. When pressure is applied, the valve closes, and water is forced through a discharge line to the surface. When the pressure is reduced, the valve reopens, allowing water to enter the chamber, and the cycle is repeated.

Gas drive samplers are available with inert components and in a variety of diameters. They can provide continuous flow at acceptable rates for sampling. Their major drawback is that they allow for gas contact with the sample, which can cause the loss of dissolved gasses and VOCs and potentially other chemical alterations. Gas can also mix with the sample, causing further alteration. For these reasons, use of these samplers is generally not recommended. Additionally, mobility is limited by the need to provide compressed gas. When sampling very deep wells, high gas pressures are needed, and the device should be designed to handle this added stress.

Gas lift samplers inject air or gas into the water column to "blow" water to the surface. The gas acts as a carrier fluid; however, the gas (even if inert) causes degassing and volatilization. Additionally, aeration and turbulence can further alter the original water chemistry (Lee and Jones, 1983). Therefore, gas lift systems are unacceptable.

The ***inertial lift pump*** consists of a foot valve at the end of a flexible tube that runs to the surface. At the beginning of sampling, the water column in the sampling tube is equal to that in the well. A levered handle, a gasoline motor drive, or manual operation provides a continuous up-and-down movement of the tubing. An initial rapid upstroke lifts the water column in the tubing a distance equal to the stroke length. At the end of the upstroke, the water continues to move slightly upward by inertia. On the down stroke, the foot valve opens allowing fresh water to enter the tube. Inertial lift pumps can be used for both purging and sampling; however, these devices cause a surging action that may cause increased turbidity, loss of volatiles, aeration, and degassing of samples. These pumps can be used when collecting non-sensitive samples; however, should not be used for VOCs or gas-sensitive samples (Striggow et al., 2017). Table 10.3 summarizes the recommended sampling mechanisms for the targeted analytes.

3.2.9 Use of Packers

Packers are inflatable rubber devices used in a well or open borehole to isolate water-bearing intervals for hydraulic testing or ground water sampling. Packers can be used to minimize purge volumes in wells with long intake columns by isolating the sampled zone from stagnant water above the screen. Both single and double packer assemblies are used. For sampling, a pump is typically installed above or below a single packer or within a double packer assembly with a discharge line extending through the upper packer. Packer assemblies may include a drop tube through which water level tapes, transducers, pump control and discharge lines, and other monitoring and sampling equipment may extend to the isolated interval. Prior to using packer assemblies for sampling, all potential limitations or problems should be carefully evaluated and resolved, and the use of packers should be justified. For example, packer materials selected should not leach or sorb contaminants. In addition, the water level within the packer interval should not be drawn down below the upper packer. The potential for vertical movement of ground water to or from the packer interval outside of the well or borehole should be evaluated, as well as the potential for leakage around the inflated packers. For additional discussion on packers, refer to Oliveros et al. (1988).

3.2.10 Equipment Limitations and Considerations for sampling PFAS

The widespread use of PFAS in materials and manufacturing of ground water sampling equipment creates the potential for cross-contamination that should be considered and minimized to the extent possible. Typical analyses for PFAS are conducted to detect part-per-trillion concentrations, which makes any cross-contamination potential a critical quality assurance issue.

Sampling equipment materials having direct contact with water samples should be both inert and free of PFAS. These can include materials used in sample tubing, pump seals (i.e., o-rings or gaskets), plastic bladders, etc. (KEMI, 2015).

Consideration should also be taken for materials, such as personal protective equipment (PPE), that will not come into direct contact with water samples, but which could create cross-contamination potential. Certain materials that should be avoided may include waterproof textiles (i.e., GoreTex® raingear, sunscreens (KEMI, 2015; Fuji, 2013).

Only certified PFAS-free water supplied by the laboratory should be used for preparation of field reagent blanks and equipment blanks (NGWA, 2018). Certified PFAS-free water may also be needed for equipment decontamination unless any alternative water source used has been adequately tested.

To prevent cross-contamination, PFAS and fluoropolymer-free equipment should be used. If the composition of materials used in sampling equipment is not known, the manufacturer of the equipment should be contacted to determine equipment compatibility with PFAS sampling. The following list of the materials that could be commonly encountered in films, coatings, seals, tube linings, etc. that should not be used when sampling for PFAS (KEMI, 2015) includes, but is not limited to:

- Polytetrafluoroethylene (PTFE / Teflon®)
- Polyvinylidene (PVDF)
- Ethylene-tetrafluoroethylene (ETFE)
- Fluorinated ethylene propylene (FEP)
- Perfluoroalkoxy polymer (PFA)
- Polychlorotrifluoroethylene (PCTFE)
- Fluoroelastomers such as Viton®

As an "emerging contaminant", guidance, recommendations, and operating procedures for sampling may change as more PFAS sampling information and experience is gained. When preparing for PFAS sampling, Ohio EPA recommends consulting the most recent U.S. EPA and Ohio EPA PFAS sampling guidance documents.

Table 10.3 Recommended Ground Water Sampling Techniques for Compliance or Risk Assessment Samples

	Target Analytes			
SAMPLING MECHANISM	**VOC**	**SVOC**	**INORGANIC**	**CONSIDERATIONS FOR USE**
Bladder Pump	X	X	X	overall, most suitable mechanism for most analytes (Pohlmann and Hess, 1988)
Electric Submersible Pumps	X	X	X	potential for alteration by elevated temperature as pump heats up (Imbrigiotta et al., 1988)
Suction Lift Pump (Peristaltic / Centrifugal)	X	X	X	potential for degassing due to negative pressure; must ensure compatible tubing materials; special sampling methods may be needed to prevent interferences (Imbrigiotta et al., 1988; Striggow et al., 2017)
Bailers	X	X	X	potential agitation, degassing, increased turbidity, and surging may affect sample quality and well development; carefully controlled purging and sampling may yield acceptable results (Imbrigiotta et al., 1988; Striggow et al., 2017)
Gas Driven Piston Pumps	X	X	X	may be acceptable if gas is non-contact with sample; valving mechanism may cause pressure drops and degassing (U.S. EPA, 1992)
Syringe Samplers	▨	X	X	potential for degassing; not used for purging; limited sample volume (Imbrigiotta et al., 1988)
Inertial Lift Pumps	▨	X[1]	▨	potential agitation, degassing, increased turbidity, and surging may affect well development; not recommended for VOCs or gas-sensitive samples (Striggow et al., 2017)
Passive Diffusion Bag Sampler	X[1]	X[1]	▨	limited list of acceptable target analytes; may be appropriate for long-term monitoring at well-characterized sites where no-purge is determined to be an acceptable approach (Striggow et al., 2017)
Equilibrated Grab Sampler	X	X	X	option when no-purge is determined to be an acceptable approach at a site (Striggow et al., 2017)

NOTE:

X = may be suitable for listed target analytes
Gray Shaded = not suitable for target analytes
[1] = may not be suitable for all analytes in this category
Table does not address gas lift pumps. These devices are generally not recommended.

4.0 Field Procedures

Prior to the sampling event, all applicable site-specific plans, such as health and safety plans and sampling and analysis plans should be reviewed by the sampling crew. The objective of the sampling event is to collect representative ground water samples. Therefore, the applicable procedures below should be completed and documented to ensure that representative ground water samples can be obtained. (Documentation guidance is provided in subsequent parts of this chapter).

4.1 Field Conditions

Weather and site-specific conditions that could affect sample representativeness should be documented. The approximate ambient air temperature, precipitation, and wind and other field conditions should be noted in a field notebook or field sampling form. In addition, any site-specific conditions or situations that could potentially alter the ground water samples or water level measurements should be recorded. Examples include but should not be limited to excavation or construction activities, accidental spills, and presence of smoke, vapors, or air contaminants from anthropogenic activities.

4.1.1 Operator actions and attire

Activities that are necessary for the sampling crew that may affect the sampling results, such as fueling a vehicle or generator, should be performed taking care that the risk of sample contamination is minimized, such as refueling away from the sample site and re-gloving with new gloves and washing hands after using fuels.

Sampling personnel should not use perfume, hand lotion etc. prior to collecting a ground water sample. If insect repellent is necessary, the repellent should be applied at least one hour before sample collection and care should be taken not to allow the repellent to come into contact with the sampling equipment and it should be recorded that insect repellent was used (Wilson, 1995). Be aware that some personal hygiene products should be avoided when sampling for PFAS compounds (Section 3.2.10). If conducting trace metal analyses, all metal in proximity to sampling should be limited, including apparel.

4.2 Well Inspection and Preparation

Upon arrival, the well protective casing, cap, and lock should be carefully inspected, and observations recorded to document whether damage or tampering has occurred.[5] Cracks in the casing and/or surface concrete seal should be noted, as well as soil washouts and depressions around the casing.

Before taking any measurements, weeds and/or debris that may interfere with the sampling should be cleared from the well area. Equipment that could come into contact with the ground water or contaminated soil should be covered and stored off the ground to avoid potential cross-contamination. If clean plastic sheeting is placed on the ground to help prevent contamination of equipment then care should be taken to prevent slips, trips or falls. Any plastic sheeting should be disposed properly following completion of sampling at each well. A portable field table covered with a new plastic sheet at each well is convenient for preparing equipment and performing field measurements (Wilson, 1995).

4.3 Well Measurements

Appropriate measurements should be made before any water is purged and sampled. These include measuring of static water levels and total well depth, and depending on site-specific conditions or circumstances, detection of gases, organic vapors and immiscible liquids.

4.3.1 Detection of Organic Vapors and Gases

Because VOCs often present health and safety concerns, field screening instruments are often used for field monitoring if ground water is contaminated with VOCs. Field screening instruments include photoionization detectors (PIDs) and flame-ionization detectors.[6] PIDs and FIDs are typically used to provide an estimate of the total volatile organic vapor concentration (e.g., benzene, vinyl chloride, tetrachloroethane), rather than a

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[5] See Chapter 8 (Well Development, Maintenance, and Redevelopment) for additional information on periodic well maintenance checks and well-integrity tests).

[6] For further information on types and uses of these instruments, see Anastas and Belknap (1980), Brown et al. (1980) and DuBose et al. (1981).

quantitative result for individual compounds. FIDs are capable of detecting methane, while PIDs are not. The selection of the correct lamp is important when using a PID meter. Vapor measurements can give useful information about potential ground water quality and allow for sampling personnel to take appropriate safety precautions. It also may be useful to determine the potential for the presence of immiscible layers, which necessitate additional sampling procedures and concerns.

Gases that typically may be of concern include methane, CO_2, and H_2S. Field meters are available for detecting methane, CO_2, and hydrogen sulfide, including combination meters that can be used to screen for two or more of these gases. Generally, methane and CO_2 may occur in monitoring wells at solid waste landfill facilities. Methane may also be present as natural gas in bedrock formations. The presence of methane is significant because it may include trace amounts of VOCs that are too low to be detected with a PID or FID. Additionally, methane is a health and safety concern because it can cause a potentially explosive atmosphere. CO_2 may affect ground water chemistry by altering pH or alkalinity. H_2S, which is typically associated with sewage or decaying vegetation, may affect pH meter performance. H_2S gas can also be naturally occurring in carbonate bedrock aquifers. H_2S presents health and safety concerns at concentrations as low as 1 ppm in air.

4.3.2 Water Level

In addition to providing hydrogeologic information on a continuing basis, measurement of the water level in a well enables determination of the volume of water contained, which may be useful for purging determinations. Measurements should be taken from the entire well network before any water removal to obtain a single "snapshot" of current hydraulic head conditions and to avoid potential effects on the water levels in nearby wells. The measurements should be made within a period of time short enough to avoid temporal variations in ground water flow that could preclude an accurate determination of ground water flow rate and direction. The period of time should not exceed 24 hours.

Measurements can be taken manually or automatically. Table 10.4 summarizes the manual methods. Automatic, continuous recording devices may be useful for collection of long-term data and in pumping tests. Water level measurements are described in more detail by Dalton et al. (1991), Aller et al. (1991), and ASTM D4750. An electronic probe is recommended for taking water level measurements.

Measurements should generally be within ±0.01 ft. There may be instances where this level of accuracy is not necessary (e.g., steep water table, wells are far apart); however, accuracy may be required by rule. All wells should have accurate surveyed reference points[7] for water level determination. Typically, a marked point on the top of the inner riser pipe is used.

Equipment should be properly decontaminated before use in each well to ensure sample integrity and prevent cross-contamination. Techniques are discussed later in this chapter.

LNAPL (see below) may affect the water level measurements in a well. It is important to know the density of the free product because water level measurements in monitoring wells that also contain free product should be corrected to account for the different densities of water and product and the thickness of the product layer. See U.S. EPA (1996a) for procedure to correct for an LNAPL layer.

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[7] Ohio EPA recommends that the reference point be based on the National Geodetic Vertical Datum or local common datum. However, an arbitrary datum common to all wells in the monitoring network may be acceptable if necessary.

4.3.3 Well Depth

Measuring the depth of a well indicates the amount of siltation that has occurred. Natural siltation can block water from entering, which could lead to erroneous water level measurements and bias analytical results by increasing sample turbidity. Checking depth also provides a check on casing integrity.

Depth can be determined with a weighted tape measure or marked cable, each of which should be composed of inert materials. Often, the same device that is used to measure water levels can be used. Heavier weights are necessary as depth increases to effectively "feel" the well bottom. The measurement should be recorded on the field log.

Measuring the well depth every time water levels or samples are obtained is generally not necessary. Obtaining a depth from a well with a dedicated pump may not be possible (and is not advisable) unless the pump is removed. In addition, the logistics of decontaminating the entire length of the measuring tape in contact with contaminated ground water may cause depth measurements to be impractical. At minimum, depth measurements should be taken once a year in wells that do not have dedicated pumps. Measurements in wells with pumps should be taken whenever the pump is removed for maintenance. If siltation is suspected to be a problem (e.g., noted increase in sample turbidity, or decrease in pump efficiency), the pump should be removed, and the well depth checked. Depth measurements should be to the nearest 0.1 foot (U.S. EPA, 2001a). Depth to bottom can be obtained when collecting the round of depth-to-water measurements. Care should be taken to avoid stirring up any accumulated sediments, thus increasing turbidity of the water column. Additional methods for measuring water levels were documented in previous versions of this table but have been removed as the methods are no longer commonly used. The removed methods include weighted steel tape with chalk, airline, float, popper acoustic probe, radar and laser.

Table 10.4 Summary of methods for manual measurement of water levels (based on Dalton et al., 1991, ASTM D4750 and U.S. EPA, 2001a).

MEASUREMENT METHOD	MEASUREMENT ACCURACY (in feet)	DESCRIPTION & ADVANTAGES	MAJOR INTERFERENCES OR DISADVANTAGES
NON-FLOWING WELLS			
Electrical method	0.01 to 0.1	An electronic probe is lowered into the well. When the probe comes into contact with water, the electric circuit in the probe is completed and an audible and/or visible signal is given.	• Errors result from changes in cable length as a function of use, temperature and depth • Reliable contact may be difficult if LNAPLs are present or water has low conductivity
Transducer	0.01 to 0.1	A transducer is lowered a known distance into the well and allowed to equilibrate with fluid temperature. Distance of submergence of the transducer is read on the signal conditioning unit and is subtracted from the cable length referenced at the top of the well.	• Accuracy is dependent upon range and sensitivity of the device.
Ultrasonic	0.02 to 0.1	Water level measurements are determined by an instrument that measures the arrival time of a reflected transmitted sonic or ultrasonic wave pulse.	• Accuracy can be limited by the change of temperature in the path of the sound wave and other reflective surfaces in the well (i.e., casing, pumps, etc.). Greater depth, the less accurate.
FLOWING WELLS			
Casing Extension	0.1	A simple extension is attached to the well casing to allow water level to be measured directly.	• The device is only practical when additional height requirement is only several feet. • Accuracy low because water level in flowing wells tends to fluctuate.
Manometer/ Pressure Gauge	0.1 to 0.5	The pressure of water within a sealed or "shut-in" well is measured.	• Gauge inaccuracies. • Calibration is required.
Pressure Transducers	0.02	Procedures are the same as described above for transducers. The range of a pressure transducer should be carefully matched with shut-in well pressure.	• Changes in temperature in the transducers cause errors.

4.3.4 Detection of Immiscible Liquids

NAPLs are organic liquids that exist as a separate, immiscible phase when in contact with water and/or air. If the presence of NAPLs is suspected, the sampling program should include devices and protocols to detect them. DNAPLs are referred to as "sinkers" because their density (greater than water) causes them to sink. LNAPLs are referred to as "floaters" because their density (less than water) causes them to float on the water table surface. If floaters are of concern, it is important that, upon opening the well cap, the air in the casing is monitored with a PID or an OVA. In addition to providing information on worker health risks, air monitoring can serve as a first indication of the presence of volatile floaters.

Protocol to detect immiscible liquids should always include visual inspection of purged water and any equipment that is removed from the well after use. Additionally, probes and reactive pastes have been developed to determine air/immiscible and water/immiscible interfaces. Indicator pastes are used to coat an interface probe or a weighted tape. An observed reaction indicates the presence of an immiscible liquid. Probes and pastes can be utilized for detecting both floaters and sinkers (U.S. EPA, 1992). Transparent bailers also can be used.

4.4 Sampling Immiscible Liquids

If an LNAPL is found to be present, a bailer or submersible pump can be used to remove it, if necessary (U.S. EPA, 1992). Any LNAPL greater than 2 feet in thickness can be evacuated using a bottom-valved bailer. The bailer should be lowered slowly to a depth less than the product/water interface. A modified, top-filling bailer (bottom valve sealed off with a fluorocarbon resin sheet between the ball and ball seat) can be used to remove immiscible layers less than 2 feet in thickness. In either case, a peristaltic pump also can be utilized if depth to product is less than 25 feet. Any LNAPL less than 2 inches thick can be collected from the top of the water column using a bailer (U.S. EPA, 1992). Samples collected in this manner consist of both an aqueous and non-aqueous phase.

To the extent possible, the sampling and purging method should prevent the disturbance of DNAPL. A sample of the DNAPL should be obtained after the ground water sample has been obtained. Double -check valve bailers, Kemmerer devices and syringe samplers often are used.

When an immiscible layer is to be analyzed, additional sampling equipment (i.e., containers) may be needed to have sufficient volume for laboratory analysis. It is important that appropriate QA/QC procedures be followed when collecting samples of any immiscible liquids. If any immiscible layer is removed, it should be properly collected, containerized, characterized, and managed. The Ohio EPA Division of Environmental Response and Revitalization (DERR) Resource Conservation and Recovery Act (RCRA) Program can be contacted for guidance on these issues.

4.5 Purging & Sampling Procedures

Upon completion of the preliminary procedures, purging and sampling of ground water can generally be accomplished by volumetric or low flow rate methods. However, volumetric purging and low flow rate purging/sampling may not be feasible for wells that produce less than 100 ml/min. Therefore, other approaches should be considered, including minimum/no purge sampling as well as purging to dryness and sampling as soon as the well has recharged sufficiently. These approaches are discussed below, along with methods to determine when purging is complete by measuring indicator parameters.

Where dedicated equipment is not used, sampling should progress from wells least likely to be contaminated to those most likely to be contaminated to minimize the potential for cross-contamination. Decontamination of down-well equipment should be considered as discussed in Section 4.9 below. Care needs to be taken to avoid agitation and temperature increases during sample collection.

4.5.1 Field Measurements of Ground Water Indicator Parameters

Indicator parameters are measured in the field to evaluate well stabilization during purging, provide information on general ground water quality, help evaluate well construction, or indicate when well maintenance is needed. Indicator parameter data also may be helpful in evaluating the presence of ground water contamination. Regulated entities (such as municipal or hazardous waste landfills) may require water quality indicator parameters as part of a sampling program. However, measurement of field parameters is not always required or possible. Indicator parameters to evaluate well stabilization during purging may not be necessary when recovery is slow and the only viable sampling methods are purging to dryness or passive techniques.

Indicator parameters include specific conductance, pH, DO, ORP, temperature, and turbidity. Due to their unstable nature, field measurements of indicator parameters are preferred over laboratory analyses, which may be less representative of in-situ ground water conditions.

Specific conductance measures the ability of water to conduct an electric current. For most circumstances, specific conductance has been demonstrated to be a reliable indicator of the chemical stabilization of purge water (e.g., Barcelona et. al., 1994).[8] For ground water, it is generally reported in micromhos per centimeter (µmhos/cm), as natural waters commonly exhibit specific conductance well above 1 µmhos/cm (Hem, 1992). Specific conductance is a relative measure of the number of ions present in ground water, as the magnitude of the current conducted by a ground water sample is directly proportional to its ionic concentration. Based on this relationship, total dissolved solid concentrations may be approximated from specific conductance data (Hem, 1992). High readings may indicate contamination, especially if the readings are elevated compared to background. Alternatively, elevated specific conductance may indicate grout contamination in a well or an inadequate grout seal that is allowing infiltration of surface water or ground water from overlying saturated zones. Elevated specific conductance readings may also indicate inadequate well development (Garner, 1988).

pH is a measure of the effective concentration (or activity) of hydrogen ions and is expressed as the negative base-10 logarithm of the hydrogen-ion activity in moles per liter (more commonly reported as S.U.). Uncontaminated ground water typically exhibits a pH ranging from 5 S.U. to 9 S.U. (Brownlow, 1979; Ohio EPA, 2003). While pH has commonly been used as a purge water stabilization indicator, it is less sensitive than specific conductance or oxidation-reduction potential in distinguishing stagnant casing water from formation water. However, pH measurements are important for the interpretation of ground water quality data (Puls and Barcelona, 1996), as pH indicates the relative solubility of metals and speciation of many other chemicals (Garner, 1988). First, pH measurements reflect chemical reactions that produce or consume hydrogen ions (Hem, 1992), and therefore, changes in pH from background may indicate the presence of ground water contamination or that existing contamination has spread. Second, pH is useful for identifying well construction or maintenance problems. For example, pH readings that consistently increase (7.8, 8.3, 8.8, 9.4...) during purging may indicate grout contamination in the sand pack and screened interval. pH is also highly dependent on local geology.

***Dissolved oxygen* (DO)** has been demonstrated to be a reliable indicator of the chemical stabilization of purge water under most ground water purging and sampling circumstances (e.g., Barcelona et. al., 1994). DO is a good indicator when sampling for VOCs, because erratic or elevated DO readings may reflect procedures that are causing excessive agitation and aeration of the ground water being drawn from the well and subsequent loss of VOCs (Pennino, 1988). Artificially aerated ground water may also adversely affect dissolved metals analyses.

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[8] Specific conductance should not be used by itself to determine whether adequate purging has been completed. Ohio EPA recommends using multiple indicator parameters to determine when to terminate purging and begin sampling regardless of the assumed reliability of the data.

Concentrations of DO in ground water (1 to 4 milligrams per liter [mg/l]) (Testa and Winegardner, 1991). Ohio EPA recommends measuring DO with a flow-through cell, although in some circumstances a hand-held meter may be acceptable. Natural ground water tends to have low DO conditions (e.g., < 1 mg/L) when there is not a hydraulic connection to the surface. Higher levels can be obtained when the pathways to the surface are short. Accordingly, relatively low DO concentrations (< 1 mg/l) in ground water may indicate the biodegradation of organic contaminants, including VOCs (U.S. EPA, 1997).

Oxidation-reduction potential (ORP), also referred to as redox potential, is a numerical index of the intensity of the oxidizing or reducing conditions within an aqueous solution such as ground water. ORP can be converted to Eh (Striggow et al., 2017; James et al., 2004). Oxidizing conditions are indicated by positive potentials and reducing conditions are indicated by negative potentials. ORP measurements are generally expressed in millivolts (mV). The ORP of natural (uncontaminated) ground water typically ranges from +500 to -100 mV (Brownlow, 1979). Ground water contaminated with organic compounds generally exhibits depressed ORP values compared to background conditions and may exhibit ORP values as low as -400 mV (Wiedemeier et. al., 1997). ORP may not be an appropriate stabilization parameter for some ground water conditions (Yeskis and Zavala, 2002). ORP data is useful for evaluating the expected oxidation state of metals and other chemical species in a general sense, especially when collected with pH data. This can also be used to determine expected solubility, based on oxidation state and specific chemical species present, by using Eh pH diagrams. Such information may be helpful for fate-and-transport modeling. However, aquifers and other saturated zones are open systems that are affected by many variables, and therefore, the actual chemical species present in ground water will not necessarily correspond to measured ORP and pH data (Hem, 1992; Rose and Long, 1988). In addition, ORP values cannot be used to derive or infer DO values, and vice versa (Rose and Long, 1988).

Temperature is not necessarily an indicator of ground water chemical stabilization and is generally not very sensitive in distinguishing between stagnant casing water and formation water (Puls and Barcelona, 1996). Nevertheless, temperature is important for data interpretation. Eh, pH, and other parameters are temperature dependent. For example, stabilized temperature readings that are representative of typical ground water conditions help demonstrate that the sample was collected in a manner that minimized exposure to elevated temperature variations, e.g., heating from the electric motor of a submersible pump. Elevating the temperature of a sample may result in loss of VOCs or the progression of chemical reactions that may alter the sample quality in an undesirable manner. Ground water temperatures in Ohio typically range from 9 to 13 degrees Celsius (˚C) (Heath, 1987).

Turbidity, which is the visible presence of suspended mineral and organic particles in a ground water sample, can be useful to measure during purging. Relatively high or erratic measurements may indicate inadequate well construction, well development or improper sampling procedures, such as purging at an excessive rate that exceeds the well yield (Puls and Powell, 1992; Paul *et. al.*, 1988), or redox reactions occurring/changing oxidation state. Purging and sampling in a manner that produces low-turbidity water is particularly important when analyzing for total metals, which may exhibit artificially elevated concentrations in high-turbidity samples (Gibbons and Sara, 1993). Generally, the turbidity of *in-situ* ground water is very low (Nightingale and Bianchi, 1977). When sampling for contaminants or parameters that may be biased by turbidity, Ohio EPA recommends stabilizing the turbidity readings at or below 10 nephelometric turbidity units (NTUs) (Yeskis and Zavala, 2002). It is recognized that some ground water zones may have natural turbidity higher than 10 NTUs. If turbidity is being used as a stabilization parameter, it may be necessary to evaluate the stabilization criteria on a site-by-site basis. The recommended stabilization criteria for NTUs is 10 percent. In addition, turbidity can be used if high anomalous levels of Fe, Mn, or other metals are detected due to sample acidification and dissolution of solid constituents.

Table 10.5 provides stabilization criteria for each parameter discussed above. Ohio EPA recommends that specific conductance plus two additional parameters should be selected[9]. **A parameter can be considered stable when at least three consecutive readings have all stabilized within the stabilization criteria**

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[9] Regulatory program rules should be checked to determine whether the rules require specific indicator parameters.

range when compared to one another. For example, three pH readings of 6.80, 6.90 and 7.00 S.U. indicate stabilization because all three values are within +/-0.2 S.U. of one another. However, three pH measurements of 6.60, 6.80 and 7.00 S.U. do not indicate stabilization because two values (6.60 and 7.00) are greater than +/-0.2 S.U. of each other. The interval between measurements is discussed in the particular purging/sampling methodology section.

Field measurements performed to fulfill regulatory requirements, beyond those used to measure for stabilization, should be obtained after purging and before samples are collected for analysis. Portable field instruments should be used. Probes enabling down-hole measurement can be used and may increase data representativeness. All in-well instruments and probes should be appropriately decontaminated before use to prevent contamination of the well water. Flow-through cells can be used when sampling with pumps.

Table 10.5. Stabilization Criteria with References for Water-Quality Indicator Parameters (Yeskis and Zavala, 2002).

Parameter	Stabilization Criteria
pH	± 0.2 standard units
specific conductance	± 3%
oxidation-reduction potential (ORP)	± 20 millivolts
turbidity	less than or equal to 10 NTUs, or ± 10% if turbidity is > 10 NTUs
dissolved oxygen (DO)	± 10% of reading value or ± 0.2 mg/L, whichever is greater
temperature	± 0.5 º Celsius

Calibration of instruments should be performed in accordance with the manufacturer's instructions during each day of ground water sampling. A pH meter should be periodically calibrated with a two-to three -point calibration by using two to three buffer solutions that bracket the expected pH range of the ground water, including acidic, neutral and basic solutions. If field measurements fall outside the calibrated range, then the meter may need to be recalibrated with appropriate solutions. Calibration of DO meters should be performed at least once daily and at a greater frequency if significant changes in elevation or atmospheric pressure occur. All calibration and recalibration checks should be recorded in a field notebook or on field forms (Wilson, 1995).

4.5.2 Volumetric Purging & Sampling

Removal of sitting well water via purging is an important step in well sampling. Water remaining in the pump and tubes are likely stagnant prior to purging, and need to be replaced with fresh, representative ground water. Additionally, drawing water through the purging equipment prior to taking stabilization measurements tends to condition the equipment (i.e., remove entrained gas bubbles).

Traditionally, a sample has been collected after purging of a specified volume of water. The various types of sampling and purging equipment, pros and cons, and recommended uses are described in detail in the section on types of equipment (Section 3.2, Types of Equipment). It is recommended that sampling equipment be dedicated to specific wells to eliminate the need for decontamination. This is most important when pumps are used because their intricate design can often make adequate cleaning difficult.

The amount of water purged is usually three to five well volumes. One well volume can be calculated as follows:

V = H x F where:

V = one well volume.
H = difference between depth of well and depth to water (ft).
F = factor for volume of 1-foot section of casing (gallons).

Table 10.6 provides F for various casing diameters. Multiplying the computed volume (V) times the number of desired volumes to be purged will give the volume of water in gallons to be evacuated.

Field stabilization parameters, as discussed above, should be monitored for stability to determine if additional purging is necessary.

At a minimum, at least 3 well volumes should be removed, and the indicator parameters have stabilized. For volumetric purging, it is suggested that stabilization parameters be collected every ½ well volume after an initial 1 to 1½ well volumes are purged (Yeskis and Zavala, 2002). The volume removed between readings can be adjusted as well-specific information demonstrates that the well stabilizes with less volume removed. However, the volume removed must be more than the volume of the pump and sampling tube capacity or the flow through cell (if used), whichever is greater.

Purging should be at or below rates used for development and those observed for well recovery. Excessive rates may result in the introduction of ground water from zones above or below the well screen, which could dilute or increase contaminant concentration in samples. Overpurging also may cause formation water to cascade down the screen, enhance the loss of VOCs, and introduce oxygen into the subsurface, which may alter water geochemistry and affect chemical analysis. As indicated by Puls and Powell (1992), excessive rates may also lead to increased sample turbidity and the exposure of fresh surfaces capable of adsorbing dissolved metals. If bailers are used for purging, entry and withdrawal to and from the water column should be as slow as possible. Water entrance velocities into bailers may have the same undesirable effects as unacceptably high purging rates (Puls and Powell, 1992).

Monitoring wells should be sampled immediately after purging, unless site-specific conditions preclude it (e.g., if some wells are too low yielding). This minimizes the time for physical and chemical alteration of water in the well casing. Where immediate sampling is precluded, sample collection should begin no later than 24 hours after purging.

Table 10.6 Volume of water in one-foot section of well casing.

Radius (½ Diameter)		F[1]
inches	feet*	gallons
0.75	0.625	0.09
1	0.083	0.16
1.5	0.125	0.37
2	0.1.67	0.65
3	0.25	1.47

[1] F is the volume (in gallons) in a 1-foot section of the well and is computed using:

$$F = 3.14r^2 \text{ x } 7.48\, gal/ft^3 \qquad \text{Equation 1}$$

* Where: r = the inside radius (½ inside diameter) of the well casing (ft).

4.5.3 Low-Flow Purging & Sampling

Low-flow purging, also referred to as low-stress purging, low-impact purging, minimal drawdown purging, or Micropurging®, is a method of well purging that does not require large volumes of water to be withdrawn. The term low-flow refers to the fact that water enters the pump intake with a low velocity. The objective is to minimize drawdown of the water column in the well, avoid disturbance of the stagnant water above the well screen, and draw fresh water through the screen. Purging rates are dependent on stabilizing drawdown. Usually, this will be a rate less than 500 ml/min and may be as low as 100 ml/min; however, the rate should not be based on an arbitrary value

The method is based on the principle that water within the screened zone passes through continuously and does not mix with water above the screen. After drawdown has stabilized and indicator parameters have stabilized, water in the screen can be considered representative of water in the formation. Given this, purging of multiple well volumes is not necessary (Kearl et al., 1994; Powell and Puls, 1992; Nielsen and Nielsen, 2002, ASTM Method D6771). A packer assembly may be necessary in fractured bedrock.

Low-flow sampling offers several advantages. It lessens the volume of water to be purged and disposed, reduces aeration or degassing, maintains the integrity of the filter pack, and minimizes disturbance within the well water column and surrounding materials, thus reducing turbidity. Accordingly, filtering of samples may be avoided, and low-flow sampling may allow for the quantification of the total mobile dissolved phase and the contaminants adsorbed to mobile particles. Disadvantages include higher initial setup costs, need for greater setup time in the field, and increased training needs. In addition, this procedure cannot be sued to sample wells with LNAPL or DNAPL.

When performing low-flow purging and sampling, it is recommended that the pump be set in the center of the well screen interval to help prevent disturbance of any sediments at the bottom of the well. If known, the pump can be placed adjacent to the areas with the highest hydraulic conductivity or highest level of contaminants. However, empirical studies and modeling simulations show that the entire well screen contributes to the sample. Flow into the screen is controlled by the geology near the well, regardless of pump position; higher permeability zones contribute more water (Varljen et al., 2006).

The use of dedicated pumps is preferred to minimize disturbance of the water column. If a portable pump is used, the placement of the pump can increase turbidity and displace water into the formation. Therefore, the pump must be placed far enough ahead of the time of sampling so that the effect of the pump installation has completely dissipated. The time between pump placement and sampling may vary from site to site and may be in excess of 48 hours (Kearl, et al., 1992; Puls and Barcelona, 1996; Nielsen and Nielsen, 2002). Use a submersible pump with an adjustable rate, such as a low-flow centrifugal or bladder pump. The pump should be capable of reducing the flow to 100 ml/min. If using a bladder pump, follow the manufacturer's recommendations for adjusting the emptying/filling cycle to minimize the potential for turbid flow. During subsequent sampling events, try to duplicate as closely as possible the intake depth and the stabilized extraction rate from the previous events.

Because the objective during low-flow purging and sampling is to minimize drawdown, it is important to measure the water level in the well before pumping. To begin purging, the pump should be started at the lowest speed setting and then the speed can be slowly increased until water begins discharging. Check the water level and slowly adjust the pump speed until there is little or no drawdown or drawdown has stabilized. Water level should be monitored and documented frequently during purging; every three to five minutes is recommended. In certain hydrogeologic settings, a well may initially drawdown several feet before it stabilizes. Drawdown can be considered to be stable when it is at or near the asymptotic part of the drawdown curve. Evidence that drawdown is at or near the asymptotic part of the drawdown curve would include less than a total of 0.3 feet difference between at minimum of three consecutive drawdown measurements (Puls and Barcelona, 1996 Reinhart and Smaldone, 2017). The water level should not be allowed to fall to the pump intake level. If the static water level is above the well screen, drawing the water below the top of the well screen should be avoided or minimized as much as possible. To minimize disturbance, pumping rate adjustments are best made within the first fifteen minutes of purging.

A representative sample can be collected when both drawdown and water quality indicators have stabilized. Depending on the well yield, the time to reach stabilization may vary from 15 minutes to over an hour. At least three to five minutes should be allowed to elapse between drawdown and indicator parameter measurements. Otherwise, the ground water sample may be collected before adequate stabilization has occurred. In addition, at least one sampling equipment volume (pump, discharge line and flow-through cell) should be purged before sampling.

Stabilization parameters (see Table 10.5) should be monitored frequently. It is recommended that specific conductance plus two additional parameters be selected. The measurements should be with a hand-held meter or a flow-through-cell and be at least three minutes apart. Measurements should be spaced apart so that the volume of water in the flow through cell or pump and sampling tubes, whichever is greater, is completely replaced.

An indicator parameter can be considered stable when at least three consecutive readings have stabilized. When all selected parameters have stabilized the well may be considered purged and sampling may commence. A turbidity level of less than 10 NTUs is desirable. If the recharge rate of the well is less than the lowest achievable pumping rate, and the well is essentially dewatered during purging, a sample should be taken as soon as the water level has recovered sufficiently to collect the sample, even if the parameters have not stabilized.

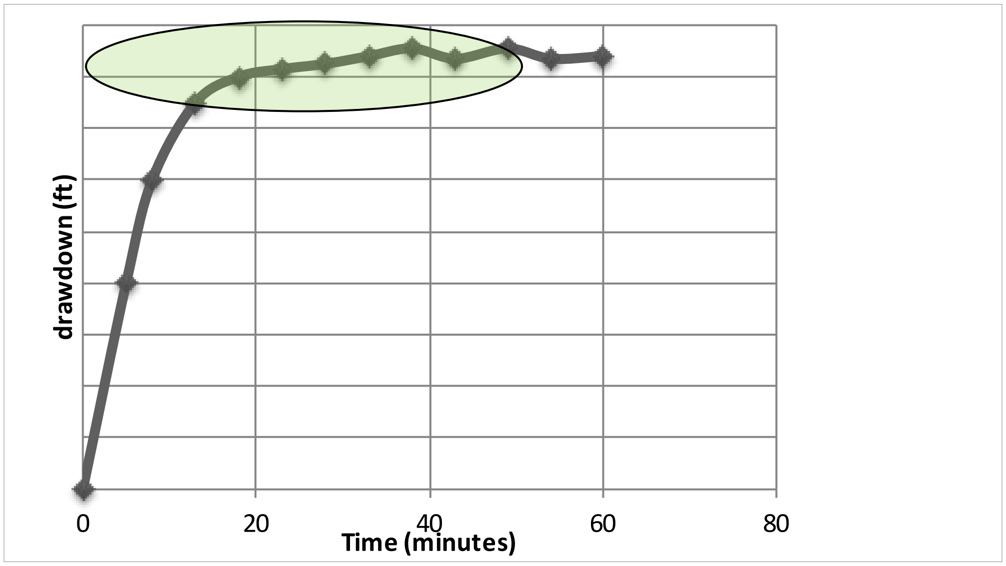

Figure 10.1 Stabilization of drawdown. Shaded area represents area where indicator parameters should be collected to document adequacy of purging.

When conducting low flow sampling at new wells or established wells being sampled for the first time by low flow procedure, it is recommended the purging process be verified by continuing to purge 9 to 15 minutes, then retaking the stabilization parameters. If the parameters remained stable, then the purging procedure can be established for that well based on pump location, rate of purging, and frequency of obtaining the three sets of stabilization parameters. This will help support whether an appropriate amount of water has been purged from the system.

4.5.4 Minimum/No Purge Sampling[10]

Minimum/no purge sampling may be necessary when wells tend to go dry when using other purging and sampling techniques. It involves either pumping just the equipment volume (i.e., pump and discharge tube) prior to obtaining a sample or deployment of a passive sampling device. Minimum/no purge sampling should only be conducted when volumetric or low-flow sampling is not feasible (e.g., well yields less than 100 ml/min). The methodology assumes that the ambient ground water flow through the well screen approximates the ground water chemical conditions within the saturated zone. For low-yielding wells where the flow-through assumption appears to be true, passive sampling techniques are generally considered less disruptive than sampling by purging.

4.5.4.1 Minimum/No Purge by Pumping

This method obtains the sample from within the well screen above the pump intake and removes the least possible volume of water prior to sample collection, which is generally limited to the volume of the sampling system, i.e., pump and discharge tubing. A sample is collected immediately after this volume is withdrawn and is presumed to represent formation water. Very low flow rates are used for minimum/no purge sampling, generally 100 mL/min or less. With minimum/no purge sampling, indicator parameters for chemical stabilization are not monitored. However, indicator measurements may still be needed for other purposes (e.g., regulatory requirements, evaluation of general quality of the ground water).

The volume of water available for sampling within the well screen located above the pump intake should be determined before purging and sampling to avoid drawing stagnant water from the overlying water column into the sample pump and compromising the sample. Drawdown should be measured during pumping to ensure that the water above the screened interval is not drawn into the pump. If possible, the amount of drawdown should be no more than the distance from the top of the screen to the position of the pump intake within the screen, minus a 2-foot safety margin (Figure 10.2) (Nielsen and Nielsen, 2002). In

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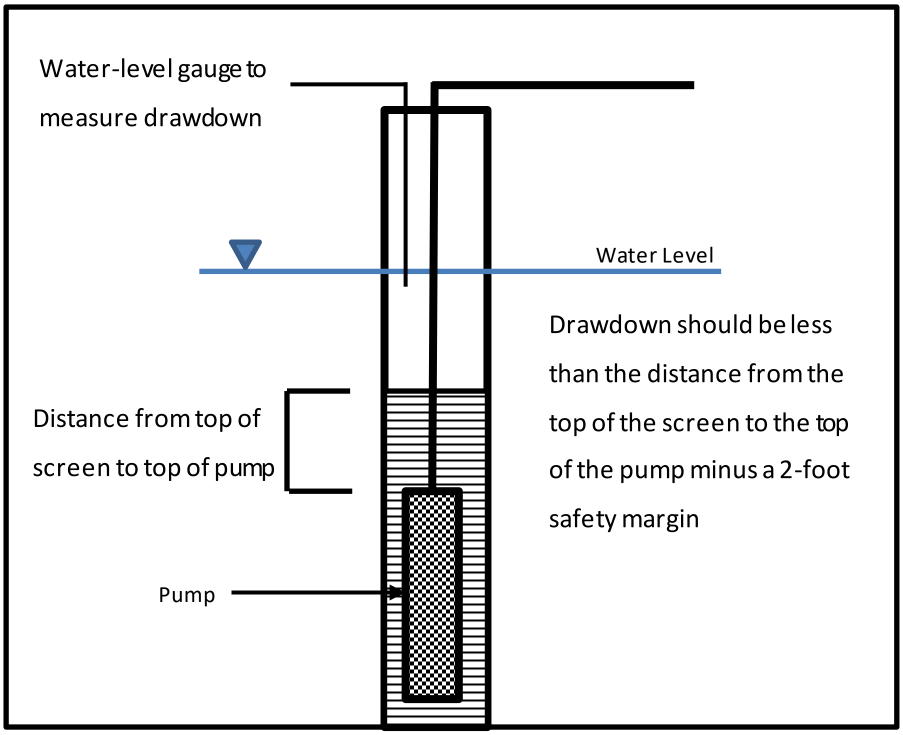
[10] Referred to in some literature as passive sampling.

situations where the 2-foot safety margin above the pump intake cannot be obtained, the volume of water in the pump and discharge tubing at the time the overlying casing water reaches the pump may provide a safety margin.

If available water is insufficient to meet the sample volume requirements, it may be necessary to discontinue the sampling once allowable drawdown is reached. Sample collection should proceed when the well has recharged sufficiently to meet the remaining sampling requirements.

Figure 10.2. Recommended maximum drawdown for minimum/no purge sampling and purging with a pump.



Bladder and low-flow submersible pumps are recommended for minimum/no purge sampling. Pumps should be placed within the well screen, but not too close to the bottom to avoid drawing in any sediments that may have settled, or too close to the top to avoid incorporating stagnant water that is above the well screen. One to two feet above the bottom is generally sufficient. As with low-flow purging and sampling, lowering a pump into the well can increase turbidity and displace water into the formation. Therefore, the pump must be placed far enough ahead of the time of sampling so that the effect of the pump installation has completely dissipated. Though the time between placement and sampling can vary from well to well, it may be in excess of 48 hours (Kearl, et al., 1992; Puls and Barcelona, 1996; Nielsen and Nielsen, 2002).

4.5.4.2 Minimum/No Purge with Passive Sampling Device

Several passive no purge samplers exist. These samplers obtain discrete samples within the well screen where the samplers are placed or activated, rather than a flow-weighted average of the screen zone (unless ambient mixing occurs). Therefore, several samplers may need to be deployed at various depths in the well intake to identify the water quality and any contaminant stratification within the water column. Types of minimum/no purge samplers include the following: diffusion samplers, equilibrated grab samplers and accumulation samplers.

A Passive Diffusion Sampler can be used to sample for a variety of VOCs. As described in Section 3.2-Types of Equipment, the passive diffusion bag is suspended in the well at the target horizon by a weighted line and allowed to equilibrate with the surrounding water (typically 2 weeks). The sampler bags are retrieved from the well and the enclosed water is immediately transferred to the sample container. Passive diffusion sampling is recommended only for long term ground water monitoring of VOCs at well-characterized sites (ITRC, 2004). PDS is not applicable for inorganics, where there is vertical flow. See Section 3.2.6 – Passive Diffusion Samplers for more description of the applicability of PDS.

Equilibrated Grab Samplers are deployed into the well in a closed position. The sampler allows the well to return to equilibrium, then the sampler is opened to collect the water. Samples are either transferred to containers at the well head or the sampler is shipped to the laboratory for analysis. Examples of equilibrated grab samples include Hydrasleeve™®, Snap Sampler™, and Kemmerer Sampler (U.S.G.S., 2014).

Accumulation Samplers are deployed over a long period of time and use a medium to capture specific COCs. These types of samplers are generally cost prohibitive and specialty or supplier (few) labs are the only ones that can run the samples for analyses. Some of these samplers only gives mass flux results. Examples of accumulation samplers include AGI Sample Module®, Semi-Permeable Membrane Device, diffusion gradient in thin-film, and ceramic dosimeter (U.S.G.S., 2000).

4.5.5 Purge to Dryness & Sampling

Traditionally, low-yielding wells have been sampled by purging a well dry and obtaining a sample upon sufficient recovery of the well. However, there are concerns when a well is purged dry (Nielsen and Nielsen, 2002; U.S. EPA 2001a), including:

- Cascading water as the well recovers may result in a change of dissolved gases and redox state, thus affecting the concentration of the analytes of interest through oxidation of dissolved metals. In addition, the cascading water can strip VOCs that may be present;
- Stressing the formation may increase sample turbidity by inducing soil fines into the well or stirring up any sediments that may have accumulated at the bottom of the well;
- Draining the water from the filter pack may result in air being trapped in the pore spaces, with lingering effects on dissolved gas levels and redox states; and
- The time required for sufficient recovery of the well may be excessive, affecting sample chemistry through prolonged exposure to atmospheric conditions.

Attempts should be made to avoid purging to dryness; however, in some situations it may be the only feasible method (e.g., low yielding wells, insufficient water column to use minimum/no purge). If an operating facility monitoring program has been historically established on purging to dryness, then for consistency, it may be necessary to continue this practice.

If purging to dryness is unavoidable or inadvertent, then samples should be taken when there is a sufficient amount of water to collect a sample that best represents the ground water quality. Extended recovery times after purging (hours) allow the ground water to equilibrate to atmospheric conditions. In the case of a well with very slow recharge, sample collection may continue for several days. However, sample collection should be attempted at least every 24 hours. Herzog et al. (1988) concluded that the common practice of next day sampling for low yield, slow recovery wells is adequate. The intervening time should be consistent from event to event. In addition, it is important to evaluate all data from slowly recovering wells based on the possibility that it may be unrepresentative of actual conditions.

4.6 Filtration[11]

Ground water samples collected from monitoring wells may contain noticeable amounts of sediment. This sample "turbidity" is an important field concern for samples to be analyzed for metals (e.g., cadmium, nickel, zinc) or metalloids (e.g., arsenic, selenium). If large, immobile particles to which metals are bound

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[11] Filtration is banned at RCRA subtitle D facilities (Municipal Solid Waste Facilities) CFR 40 258.53(b).

are allowed to remain in field-acidified samples, laboratory "total" analyses will overestimate the true concentration of mobile species because acidification dissolves precipitates or causes adsorbed metals to desorb. Additionally, changes in the relative degree of sedimentation over time (due to changes in well performance, sampling device, or sampling personnel) and space (due to natural hydrogeologic variations) can result in data interpretation difficulties.

Removal of sediment by filtration prior to containerization and acidification also presents problems. The potential for filter clogging, variable particle size retention, filter media leaching, and aeration is well documented (Puls and Powell, 1992; Striggow et al., 2017). Filtration of water samples to be analyzed for VOCs should be avoided as the filtration process may lead to VOC loss (Connecticut DEEP, 2012; Striggow et al., 2017). Also, filtration has the potential to remove particles that may be mobile in certain hydrogeologic environments. As described by McCarthy and Zachara (1989) and Puls et al. (1990), colloidal material (particles less than 10 micron) may be transported large distances. Because of these difficulties, some investigators (Puls and Barcelona, 1989a & b; Kearl et al., 1992; Puls and Powell, 1992; Striggow et al., 2017) have recommended against field-filtering. Further, federal regulations [40 CFR 258.53(b)] for ground water monitoring at municipal solid waste landfills specify that analyses for metals be performed on unfiltered samples.

For sampling at sites that are not municipal solid waste landfills, filtration may be appropriate in some instances, provided it is done properly (Nielson and Nielson; 2006, Striggow et al., 2017). Significant turbidity is sometimes unavoidable, and filtration may be necessary to remove immobile particles. For example, reducing turbidity may be difficult when a clay-rich glacial deposit is monitored. Clay and natural organic matter can attract contaminants and physically retard particle movement. Therefore, particles in ground water may be presumed to be immobile in formations primarily containing natural organic material and clays. Additionally, while unfiltered data generally would be preferred for a risk assessment of the drinking water pathway, filtered data may be used if there is an obvious discrepancy between filtered and unfiltered data or if secondary maximum contaminant levels MCLs are exceeded (U.S. EPA, 1991). In this case, unfiltered samples might be too turbid to represent drinking water. It is recommended that entities work closely with the Agency to define project requirements. The following sections provide Ohio EPA's general recommendations on whether and how to filter.

4.6.1 Deciding When to Filter

Ohio EPA recommends a general framework (Figure 10.3) for making decisions as to whether filtering is appropriate. Adequate monitoring wells and sampling techniques that minimize disturbance should be confirmed before any decision is made. Filtration generally should occur only when <u>all</u> of the following conditions are present:

- ***The samples have been collected from monitoring wells that are properly designed, installed, and developed.*** Adequate wells are essential to minimizing turbidity and obtaining representative samples. When turbidity is an issue at an existing well, the well should be redeveloped using appropriate well development techniques outlined in Chapter 8 prior to sampling.
- ***The samples have been collected using procedures that minimize disturbance.*** Low-flow purging and sampling procedures are recommended to minimize agitation of the water column and minimize turbidity. Achieve stabilization of indicator parameters prior to sampling to ensure that the sample is representative of natural ground water conditions.
- ***Turbidity has been demonstrated to stabilize above 10 NTU***. (See Section 4.5 – Purging and Sampling Procedure)
- ***Professional judgment indicates that the formation sampled does <u>not</u> exhibit a high degree of particle mobility, and therefore it is reasonable to assume that a portion of the sediment in the samples is likely attributable to immobile particles.*** In general, this judgment can be based on the geology of the ground water zone. For example, clays, because the size of the pores, would prevent particle mobility. Examples of formations that <u>do</u> show significant particle mobility include, but are not limited to, karst; bedrock with open, interconnected fractures, and clean, highly porous gravel-to-boulder sized deposits.

Note that one should exercise professional judgment when applying this approach. Deviations may be necessary if the practices would cause undesirable problems in data interpretation. For example, if a site is underlain by karst bedrock and the historical data for metals has been based on analyses of filtered samples, filtration could be continued to ensure data consistency and comparability. If a single zone is monitored both by wells that are capable of providing samples that meet the turbidity criterion and wells that are not capable of meeting it, it may be prudent to filter all of the samples to ensure spatial consistency and valid statistical comparisons.

Some may wish to collect both filtered and unfiltered samples. The advantage of having both is that a comparison can help determine the form in which a chemical exists (e.g., primarily adsorbed to particulate matter or dissolved) (Puls and Barcelona, 1989b). For example, if the concentration of a chemical is much greater in unfiltered samples compared to filtered samples, it is likely that the majority of the chemical is adsorbed onto particulate matter and not dissolved in the ground water. The comparative data may help justify which data set is more appropriate.

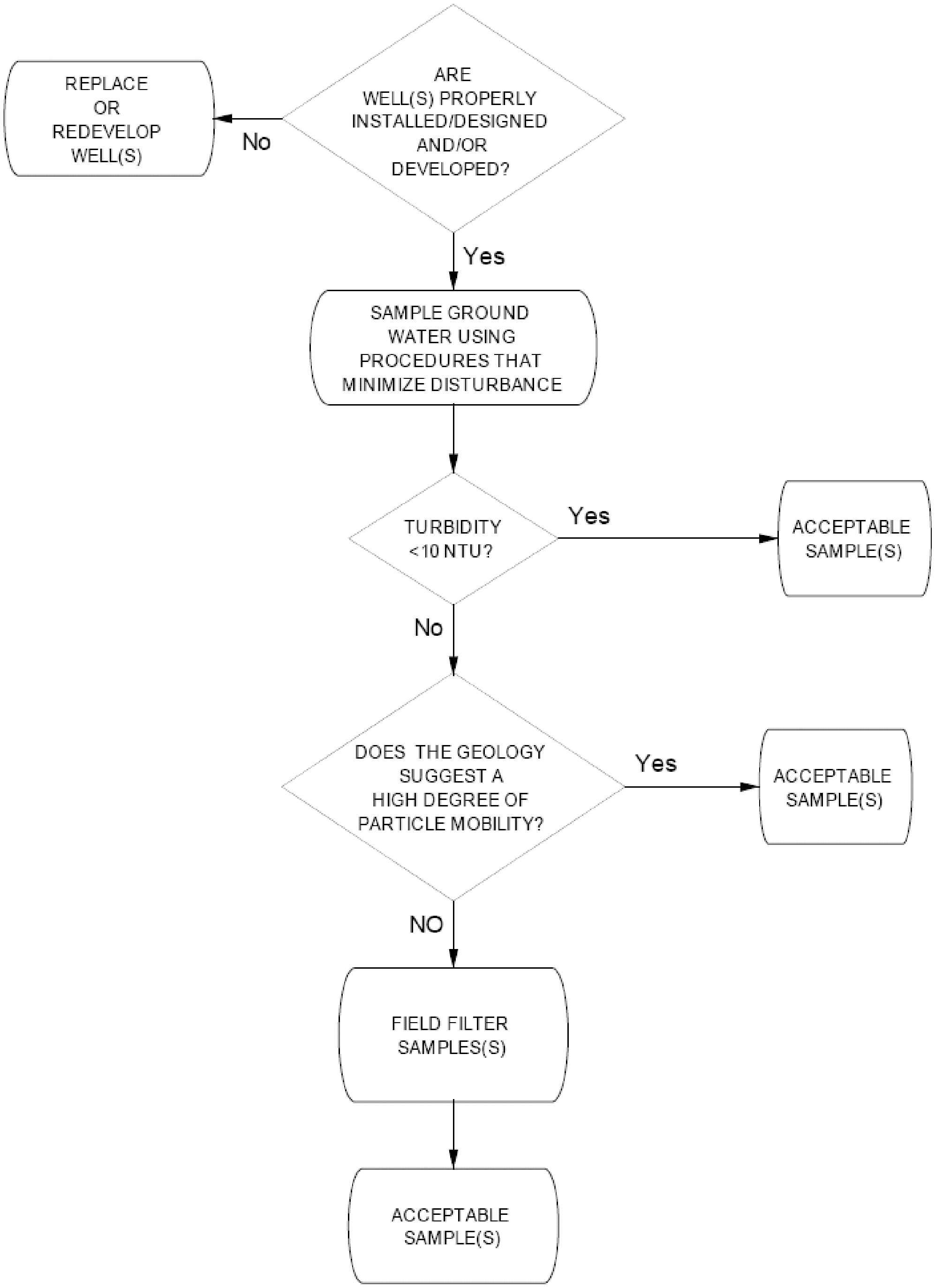

Figure 10.3 Ground water field filtration decision tree

4.6.2. Recommended Procedure/Equipment When Filtering is Necessary

If filtration is necessary, the following are recommended:

- ***Use "in-line" filtering whenever possible.*** In-line methods use positive pressure provided by a sampling pump to force the sample through an attached filter. The advantage is that samples remain isolated prior to atmospheric exposure. Stolzenburg and Nichols (1986) compared different filtering methods and found in-line to provide the best results. If bailers are used for sampling, in-line filters cannot be used unless a pressure or vacuum hand pump (i.e., peristaltic) is utilized to force the sample through.

- If it is not possible to filter in-line, “open system" techniques may be used. These techniques require a transfer of the sample before filtration, thus allowing for additional exposure and agitation. Open system filtration should be conducted immediately in the field, at the wellhead, and prior to sample acidification and containerization. If filtration does not occur immediately, metals can begin to precipitate and, upon filtration, be removed, causing laboratories to underestimate actual concentrations. Agitation should be kept to a minimum, and the use of "double" filtration is not recommended. "Double" refers to filtering a sample twice using filters with progressively smaller pore sizes. This has been used to speed up filtration; however, it can cause excessive agitation.
- Open system techniques offer varying degrees of portability and ease of decontamination. In addition, changes in pressure and aeration/oxygenation can alter sample representativeness. Open system filtration is primarily driven by either pressure or vacuum mechanisms. For pressure, only pure, inert gas should be used (i.e., nitrogen). If a pump is used, the peristaltic is commonly employed. Whereas pressure "pushes" the sample using compressed gas or a pump, vacuum "pulls" the sample through the filter. Vacuum can cause extensive degassing, which can seriously alter metals concentrations (U.S. EPA, 1986a; EPRI, 1987; and Barcelona et al., 1985); therefore, vacuum is not recommended. The extensive alteration is due to an exacerbation of the pressure decrease inherent with bringing a sample to the surface.
- ***Filter samples using a polycarbonate or cellulose acetate filter.*** Filtration media should be inert and selected to minimize bias. Polycarbonate membrane filters are recommended. Puls and Barcelona (1989b) have stated that this material should be used due to its more uniform pore size, ease of cleaning, and minimization of adsorptive losses. The NCASI (1982) found polycarbonate to be most appropriate. Cellulose membranes and glass microfiber filters have been used commonly.
- ***Prepare the filter prior to collecting the sample.*** Filters must be pre-rinsed following manufacturer’s recommendations to remove the residue from the manufacturing, packing, or handling. In-line filters should be flushed with sample water before collection to create a uniform wetting front.
- ***Use of a 5-micron filter is recommended to ensure that the mobile fraction of turbidity is sampled.*** While a 5-micron size filter is recommended, a filter with a different pore size may be used based upon site conditions. Theoretically, the filter pore size should equal the size of the largest mobile particles in the formation, although differences in particles passing different sizes may be lessened significantly by clogging. Traditionally, 0.45-micron filters have been used; however, different pore sizes can be used in specific instances if justified. Puls and Powell (1992) suggested a coarse filter size such as 5-micron. If estimates of dissolved metal concentrations are desired, use of 0.1-micron filters is recommended (Puls and Powell, 1992). Samples filtered with a medium with a small pore size (e.g., 0.1 micron for dissolved concentrations) may be appropriate for geochemical modeling (Puls and Powell, 1992).
- ***The filtration medium should be disposed between wells, including filter and syringe.***
- ***If the ground water is highly turbid, periodic filter changes may be necessary (e.g., for the same sample)***
- ***The filtration device, tubing, etc. should be appropriately decontaminated as sample-contacting equipment (see Section 4.10 - Decontamination)***

4.7 Sample Handling, Preservation, Containers, and Shipping

Once a sample has been removed from a well, appropriate procedures should be utilized to containerize, preserve, and transport it to the laboratory. This ensures that an in-situ state is maintained as much as possible prior to analysis. Issues that should be considered include preservation, containers and labels, holding times, and shipping. Examples of these for some chemicals are listed in Table 10.7. Deviating from Table 10.7 does not necessarily mean that a sample is invalid. Deviations should be recorded on the data reports and should be evaluated on a case-by-case basis, with appropriate reasoning. Appropriate preservation and handling should be coordinated with the laboratory prior to each particular sampling event.

4.7.1 Sample Acquisition and Transfer

Transfer to a container or filtration device should be conducted in a way that minimizes agitation and aeration. Samples should be transferred directly to the final container for laboratory submittal and not collected in a larger container with subsequent transfer to smaller containers. (Exceptions for filtration are allowable.) Care should be taken to prevent overfilling so that the preservative, if used, is not overly diluted. If no preservative is used, the containers should be rinsed with sample water prior to collecting the sample. After sealing, containers should not be opened in the field for any reason.

Special considerations are needed when sampling for VOCs. Collection, handling, and containerization should not take place near a running motor or any type of exhaust system. Sample vials should be filled and capped in a manner that minimize bubbles and does not agitate or aerate the sample. Samples should be placed in 40 ml glass vials until a meniscus is formed. Flow rate into the vials should be between 100 and 500 ml/min. The vials should be sealed with a fluorocarbon-lined cap.

The presence of air bubbles in a vial may indicate either improper sampling technique or a source of gas evolution with the sample. Check for air by inverting the vial and tapping. If any bubbles are present greater than 0.25 inches (6 mm) in diameter, the sample should be discarded and a new sample taken (U.S. EPA, 1996b; Yeskis and Zavala, 2002). The container should not be opened and "topped-off" to fill the additional head space (U.S. EPA, 1992). If a sample cannot be obtained without air bubbles due to off-gassing, then the presence of air bubbles should be noted on the field log or field data sheet. Also, air bubbles may form during shipment to the laboratory. These bubbles do not necessarily invalidate the sample[12].

Sampling flow rates “less than 500ml/min are appropriate.” (Puls and Barcelona, 1996). Use rates at or below the purging flow rate for metals and other inorganic parameters, lower rates (100 ml/min.) for VOCs and filtered samples. The sample order is dependent on the method of sampling. When volumetric purging/sampling, sampling with bailers, purging to dryness, or no purge sampling is conducted, samples should be collected and containerized in the following order of volatilization sensitivity (U.S. EPA, 1986a):

1. Volatile organic compounds (VOCs).
2. Purgeable organic carbon.
3. Purgeable organic halogens.
4. Total organic halogens (TOX).
5. Total organic carbon (TOC).
6. Extractable organics.
7. Total metals.
8. Dissolved metals.
9. Phenols.
10. Cyanide.
11. Sulfate and chloride.
12. Nitrate and ammonia.
13. Radionuclides.

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[12] Studies conducted by U.S. EPA indicate that “pea-sized” bubbles (1/4 inch or less in diameter) did not adversely affect data. These bubbles were generally encountered in wastewater samples.

When samples are collected by low flow methods, larger bottles can be filled first, then reduce the flow rate for VOCs and any filtered parameters to 100 to 500 ml/min. The bottles should be filled in a manner that minimizes agitation/aeration.

In addition to the sensitivity, the relative importance of each parameter should be evaluated on a site-by-site basis to establish sampling order protocol. Therefore, when a low-yielding well is being sampled, it may be necessary to change the order of sampling to ensure that a representative sample is collected for the most important constituents for a particular site.

4.7.2 Sample Splitting

Samples are often split into two separate portions and submitted to different laboratories to determine the accuracy of lab results. The proper procedure is to fill the two containers alternately until both are filled. However, if samples for VOC analysis are being collected, the first container should be completely filled, followed by filling of the split container.

4.7.3 Sample Preservation

Preservation is an important step that should be conducted to stabilize the collected sample and prevent physical and chemical changes from occurring during transport to the laboratory and storage before analysis. Preservation is intended to retard biological action, prevent hydrolysis of chemical compounds and complexes, and reduce volatility of constituents (U.S. EPA, 1982). Preservation methods generally are limited to pH control, chemical addition, refrigeration, and protection from light. Appropriate techniques (see Table 10.7), should be implemented immediately upon collection (and after filtration) to minimize changes that begin when a sample is exposed to the atmosphere. Any preservation used should be reported to the appropriate regulatory agency when submitting analytical results.

Sample preservation usually involves reducing or increasing the pH by adding an acid or a base. For example, acids are added to samples submitted for dissolved metals analysis because most metals exist in the dissolved state at low pH. If not preserved, most metals will oxidize and precipitate, which prevents representative analysis. If preserved in the field, the chemical preservative should be obtained from the laboratory contracted to analyze the sample and the appropriate aliquot placed in the sample container, preferably before entering the field. Many laboratories will provide sample bottles containing the appropriate amount and type of preservative. Sampling personnel may want to carry limited amounts of some preservatives in the event that additional preservation is needed for a particular sample. However, if previous samples indicate that a sample may be acidic or alkaline, the amount of preservative should be discussed with the laboratory prior to sample collection.

Samples for temperature-sensitive parameters should be preserved immediately after collection by placement into an insulated cooler maintained at a temperature of approximately 4 - 6° C with ice. Ice substitutes should be avoided. Any deviation in temperature should be noted and assessed as to its impact on sample quality. Care should be taken to ensure that the paperwork and samples are not damaged by ice water. The laboratory should record whether or not the cooler contains any amount of visible ice. The presence of ice is sufficient to demonstrate that the samples are adequately preserved. If no ice is present, the laboratory should obtain a measure or estimate of the sample temperature upon receipt of the samples.[13] This can be accomplished by either a temperature blank or measuring the internal temperature of the cooler.

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[13] Some regulatory programs may require that the temperature of the cooler/sample be recorded regardless of whether there is visible ice.

Table 10.7 Common Examples of Containers, preservation, and holding times.

PARAMETER	CONTAINER	PRESERVATIVE[2]	MAXIMUM HOLDING TIME
INORGANIC TESTS			
Acidity	P,G	Cool, ≤6 °C	14 days
Alkalinity	P,G	Cool, ≤6 °C	14 days
Ammonia	P,G	None	7days
		Cool, ≤6 °C; H_2SO_4 to pH<2	28 days
Bromide	P,G	None required	28 days
Chloride	PG,	None required	28 days
Chlorine, residual	P,G	None required	Analyze immediately (within 15 minutes)
Cyanide, total	P,G	Cool ≤6 °C; NaOH to pH>12 ascorbic acid if oxidants (e.g., Chlorine is present.)	14 days
Hardness	P,G	HNO3 to pH<2; H_2SO_4 to pH<2	6 months
Kjeldahl and organic nitrogen	P,G	none	7 days
		Cool, ≤6 °C; H_2SO_4 to pH<2	28 days
Nitrate	P,G	Cool, ≤6 °C	48 hours
Nitrate-nitrite	P,G	Cool, ≤6 °C; H_2SO_4 to pH<2	28 days
Sulfate	P,G	Cool, ≤6 °C	28 days
Sulfide	P,G	Cool, ≤6 °C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulfite	P,G	None required	Analyze within 15 minutes
Metals, except Cr(VI) & Hg	P,G	HNO_3 to pH<2 at least 24 hours prior to analysis	6 months
Chromium (Cr) VI	P,G	Cool, ≤6 °C	24 hours
Chromium (Cr) VI	P,G	use sodium hydroxide and ammonium sulfate buffer solution to pH 9.3 to 9.7 to extend holding time to 28 days	28 days
Mercury (Hg)	P,G	HNO_3 to pH<2	28 days
ORGANIC TESTS			
Volatiles	G, Teflon-lined cap	Cool, ≤6 °C; 0.008% $Na_2S_2O_3$[3] ; HCl to pH<2 No head space	14 days
(Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, ≤6 °C; 0.008% $Na_2S_2O_3$[3], adjust pH to 4-5	14 days
Dioxins and Furans	G, Teflon-lined cap	Cool, ≤6 °C	30 days until extraction, 45 days after extraction
Oil and grease	G	Cool, ≤6 °C; H_2SO_4 or HCl to pH<2	28 days
Phenols	G, Teflon-lined cap	$Na_2S_2O_3$	7 days until extraction, 40 days after extraction
PCBs	G, Teflon-lined cap	Cool, ≤6 °C	1 year
Pesticides	G, Teflon-lined cap	Cool, ≤6 °C; pH 5-9	1 year
Per- and Polyfluorinated Alkyl Substances (PFAS)	250 ml polypropylene bottle	Cool, ≤10 °C; 5.0 g/L Trizma to pH = 7.0	14 days until extraction, 28 days after extraction
RADIOLOGICAL Alpha, beta, and radium	P,G	HNO_3 to pH<2	6 months

[1] Polyethylene (P), Glass (G)

[2] For some constituents the free chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.
Note: The preservative and holding times may vary with sampling procedures, method analysis and selected laboratory. The table is partially based on U.S. EPA, Federal Register, 40 CFR Volume-72, No-47, March 12, 2007 and U.S. EPA Region 3, Sample Submission Procedures for the Office of Analytical Services and Quality Assurance, January 2014.

4.7.4 Containers and Sample Labels

Upon collection, samples should be contained properly to maintain integrity. Specifications on container design, including shape, volume, gas tightness, material construction, and use of cap liners, are defined for specific parameters or suites of parameters. For example, various fluorocarbons (i.e., Teflon®), polyethylene plastic, or glass bottles with Teflon-lined lids are recommended for metals analysis. Samples to be analyzed for VOCs should be containerized in 40 ml glass vials. Specifications on containers are documented in parameter-specific analytical methods (e.g., SW-846). Clean containers can usually be obtained from the contracted laboratory. Note that analytical laboratories may not accept samples for analysis if the bottles have not been cleaned by their own laboratory. If cleaning is necessary, decontamination should be performed, and appropriate blanks collected to verify cleanliness.

Samples should be properly identified with labels. The labels should be permanent and remain legible when wet. When sampling for VOCs the pen’s ink may cause false positives, so labels should be completed and the ink allowed to dry before being affixed to the bottles (Wilson, 1995). The following information should be included:

- Sample field identification number (e.g., well location).
- Name or initials of collector.
- Date and time of collection.
- Place of collection.
- Parameters and method requested for analysis.
- Chemical preservatives used.

4.7.5 Shipping

When samples are to be shipped to a laboratory, an appropriate container should be used to protect and preserve them. Coolers are typically used for containing samples and providing temperature preservation. “Wet” ice should always be used for temperature preservation unless otherwise instructed by the laboratory. Ice substitutes such as “blue” ice may cause potential cross contamination issues for some constituents and are not as effective as wet ice for temperature control, especially under warm weather conditions. During warm weather, copious amounts of ice are recommended to avoid having a sample cooler arrive at a laboratory outside of the acceptable temperature range.

Forms such as a sampling request sheet and/or chain-of-custody containing pertinent information should be included (See Section 4.10 Decontamination). Plastic shipping tape should be used to seal sample coolers; do not use duct tape, as commercial shippers cannot accept duct-taped containers due to homeland security concerns. Evidence tape also should be placed around the shipping container (and around each container, if desired), to guard against disturbance or tampering. Special federal requirements apply to hazardous or potentially hazardous samples. For example, flammable, explosive or reactive samples (e.g., LNAPL) cannot be shipped via air carrier (these must be shipped via ground). Always check with the shipping company for packaging, labeling and other requirements or important guidelines. In addition, contact Ohio Department of Transportation (ODOT) and the Public Utilities Commission of Ohio (PUCO) may be contacted for information.

Not all samples will maintain complete stability, regardless of the preservation technique. Therefore, a limit on when analysis should take place has been set for most parameters (see Table 10.7). These "holding times" specify the maximum allowable time between sample collection and laboratory analysis. Depending on the specific circumstances, if one is exceeded, the sample may need to be discarded and a new sample obtained. Therefore, it is important that the time of sampling and transportation to the lab be documented to ensure that the limits are met. Be aware of analytical holding times and minimize the time between sampling and delivery to the laboratory.

4.8 Disposal of Purged Water

Though it is not the intent of this document to define/determine Ohio EPA's policy on disposal of purged water, the following guidance is provided. If routine sampling shows that the ground water is free from contaminants (e.g., constituent concentrations are not above ambient/natural levels), then it may be acceptable to discharge the purged water onto the ground away from the wellhead but within the limits of the site/facility.[14] Otherwise, the purged water should be containerized until the ground water samples are analyzed. If the water has been contaminated by a listed hazardous waste constituent or exhibits a characteristic of hazardous waste as specified in 3745-51 of the Ohio Administrative Code, it will need to be managed as a hazardous waste. However, if the ground water is treated such that it no longer contains hazardous waste, the ground water would no longer be subject to regulation. Information on this subject can be found at ***epa.gov/correctiveaction/resource/guidance/remwaste/refrnces/12cntdin.pdf***.

If the ground water is known or suspected to contain VOCs, air-monitoring equipment may be needed to determine potential exposure and the level of protection for the sampling team. This should be addressed in a site-specific Health and Safety Plan.

4.9 Decontamination Procedures

If non-dedicated sampling equipment is used, it should be cleaned between wells to prevent cross-contamination. This includes all non-dedicated equipment that is submerged in a monitoring well or otherwise contacts a ground water sample. The level of decontamination is dependent on the level and type of suspected or known contaminants. A sampling event where high levels of contaminants are known or suspected would require the most intensive decontamination procedure., However, acid and solvent rinses are not necessary and should not be used, as these procedures create added health and safety concerns for the samplers, may damage sampling equipment, generate hazardous waste and significantly increase the time and level of effort for equipment decontamination. If sampling equipment is contaminated so badly that it cannot be decontaminated using the procedures in Table 10.8 (e.g., a PVC bailer contaminated with LNAPL, Ohio EPA recommends that the equipment be discarded or used only for sampling or removing highly contaminated media (e.g., designating the contaminated PVC bailer for only purging LNAPL from monitoring wells). To help avoid significant contamination of non-disposable sampling equipment, Ohio EPA recommends the use of disposable sampling equipment in highly contaminated monitoring wells. The decontamination area should be upwind of activities that may contribute dust or other contaminants to the solutions used. The process should occur on a layer of polyethylene sheeting to prevent surface soils from coming into contact with the equipment. The effects of cross-contamination can also be minimized by sampling the least contaminated wells first and then progressing to the more contaminated wells, in addition to cleaning equipment between wells.

Table 10.8 outlines sequences and procedures that should be used (modified from ASTM D5088 and Yeskis and Zavala, 2002). The procedures are based on equipment contact with collected samples. Sample-contacting equipment includes non-dedicated bailers and pumps (i.e., devices used for purging and sampling), sample containers, tubing, downhole field parameter probes, water level probes, non-dedicated filtration equipment, etc. In most instances, a distilled water rinse should be sufficient for field parameter measurement probes that are not lowered into wells. Many items are inexpensive and disposable (i.e., gloves, rope, tubing). Items dedicated to a well or disposed of after each well (i.e., gloves, cord, plastic sheet, bailer) would not need to be decontaminated. These items should be properly discarded[15] and new materials provided for the next well.

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[14] Under detection monitoring, it may be possible to discharge the purged water without containerizing if historical ground water records indicate that ground water quality beneath the site is similar to the ambient quality. The Division with authority over the site/facility should be contacted for approval of this disposal method.

[15] As discussed in the applicable sampling and analysis plan or equivalent protocol, e.g., a standard operation procedure.

Table 10.8 Decontamination procedure for ground water sampling equipment*.

- Wash with non-phosphate detergent and potable water. Using a pressure washer sprayer filled with soapy water and bristle brush is recommended.
- Rinse liberally with potable water.
- Rinse liberally with deionized/distilled water. For containers, this includes 3+ rinses.
- Air-dry thoroughly before use.
- Return equipment to its clean container or wrap with inert material if equipment is not to be used promptly.

4.10 Documentation

4.10.1 Field Sampling Logbook

A field logbook or field sampling forms should be completed and maintained for all sampling events. It should document the following for each well sampled[16].

- Identification of well
- Well depth
- Static water level depth.
- Presence of immiscible layers and detection method
- Thickness of immiscible layers, if applicable
- Well yield estimate
- Purging device, purge volume and pumping rate
- Time well purged
- Measured field parameters
- Collection method for immiscible layers (if applicable) and identification numbers
- Sampling device used
- Well sampling sequence
- Sample appearance
- Sample odor if present
- Types of sample containers and sample identification numbers
- Preservative(s) used
- Parameters requested for analysis
- Field analysis data and method(s)
- Sample distribution and transporter
- Field observations on sampling event
- Name of sampler(s)
- Climatic conditions (e.g., air temperature, precipitation, and wind conditions)
- Problems encountered and deviations made from the established sampling protocol

4.10.2 Chain-Of-Custody

A chain-of-custody record (Figure 10.4) should be established to provide the documentation necessary to trace sample possession from time of collection to final laboratory analysis. The record should account for each sample and provide the following information (U.S. EPA, 1992):

- Sample identification number
- Printed name and signature of sampler
- Date and time of sample collection
- Sample media (e.g., ground water)
- Identification of well
- Number and types of containers
- Constituents and parameters to be analyzed
- Analytical methods
- Preservatives used
- Field QA/QC samples
- Commercial carrier or courier used to deliver samples to the laboratory
- Printed name and signature of person(s) involved in the chain of possession[17]
- Dates/times samples were relinquished by sampler and received by the laboratory
- Internal temperature of shipping container upon opening at laboratory, if applicable
- Presence/absence of ice (when samples are received at the laboratory)
- Special handling instructions (if any)
- Name of person receiving the sample

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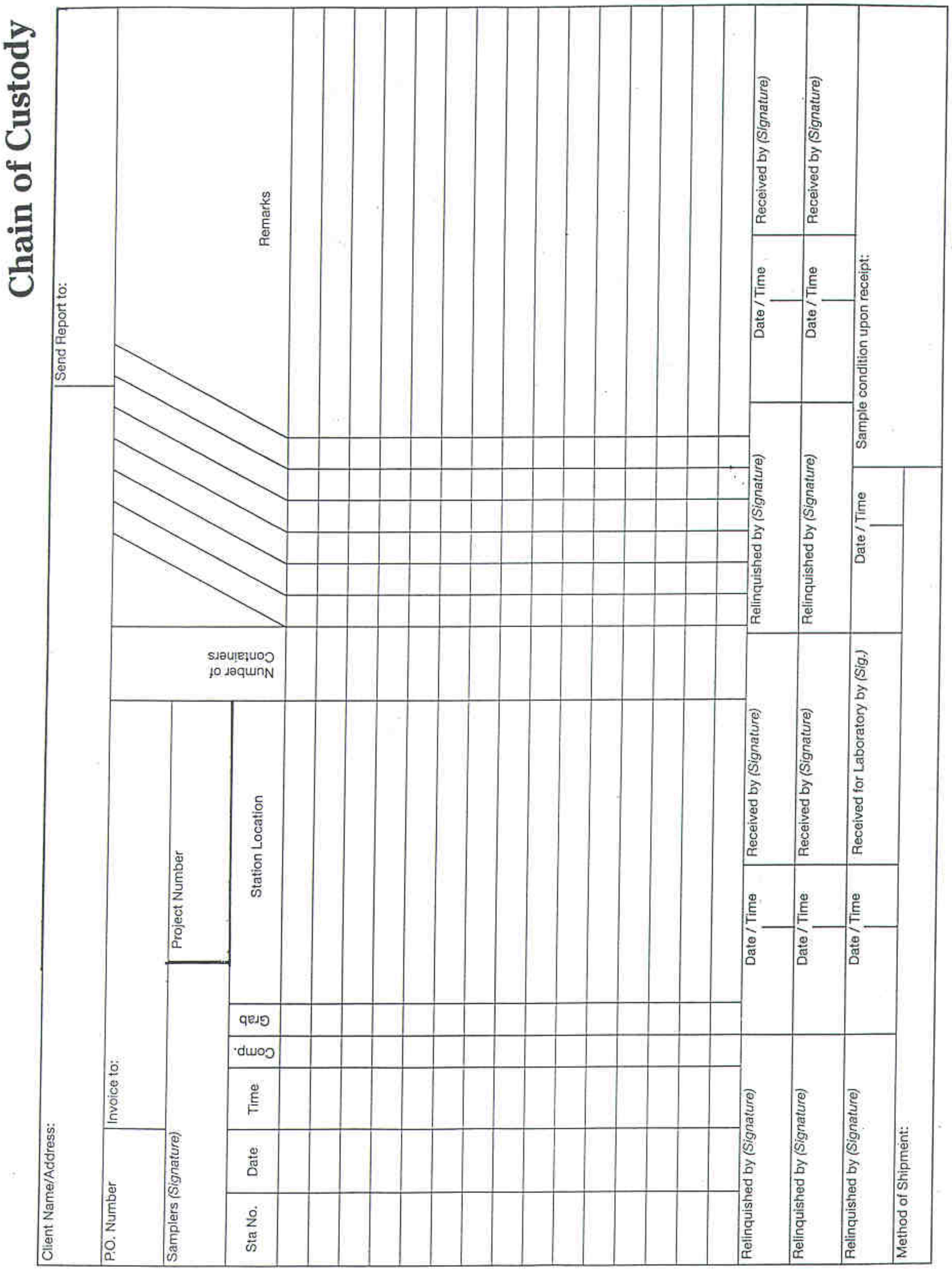
[16] Items documented on the chain-of-custody do not need to be repeated in the field log.

[17] Including all persons relinquishing the samples and all persons receiving the samples, but excluding the U.S. Postal Service, courier services, or commercial shipping companies.



Chain of Custody

Client Name/Address:

Send Report to:

P.O. Number

Invoice to:

Samplers *(Signature)*

Project Number

Sta No.	Date	Time	Comp.	Grab	Station Location	Number of Containers								Remarks

Relinquished by *(Signature)*	Date / Time	Received by *(Signature)*	Relinquished by *(Signature)*	Date / Time	Received by *(Signature)*
Relinquished by *(Signature)*	Date / Time	Received by *(Signature)*	Relinquished by *(Signature)*	Date / Time	Received by *(Signature)*
Relinquished by *(Signature)*	Date / Time	Received for Laboratory by *(Sig.)*	Date / Time	Sample condition upon receipt:	
Method of Shipment:					

Figure 10.4 Example Chain of Custody Form

4.11 Field Quality Assurance/Quality Control (QA/QC)

To assure adequate QA/QC in the field, the sampling plan should be followed consistently. To verify if procedures are contaminating ground water samples, a variety of samples and blanks need to be collected and analyzed. If re-sampling is triggered, best professional judgment should be used to decide what type of QA/QC sampling is needed. The following are typical checks:

- **Field Duplicates -** Field duplicates are samples collected as close to each other in time and space as practical at a specific location. Ultimately, upon analysis, both should yield the same results within an acceptable range. Excessive variation could indicate problems with the sampling procedures or analysis. At a minimum, duplicates should be collected at a frequency of one per twenty samples (Yeskis and Zavala, 2002), one per week, and one per sampling event.
- **Trip Blanks -** Trip blanks are generally prepared by the laboratory before entering the field. Containers are filled with analyte-free, distilled, deionized water and sealed. These blanks are taken to the field and handled along with the collected samples, thereby acting as a control sample to determine potential VOC contamination from the containers themselves. Trip blanks should be included in each cooler containing VOC samples. At a minimum, at least one trip blank should accompany each sampling event. Trip blanks are never opened in the field.
- **Equipment Rinsate Blanks -** Whenever non-dedicated sampling equipment is used, equipment rinsate blanks should be collected. An equipment blank is obtained by passing analyte-free, distilled, deionized water through a cleaned sampling apparatus (pump, bailer, filtration gear, etc.) and collecting it in a clean container. This blank is used to assess the effectiveness of the decontamination procedures implemented between sampling locations. Ideally, equipment blanks should be collected after sampling the well(s) that historically show(s) the highest levels of contamination. They should be collected at a frequency of one blank per 20 samples (Yeskis and Zavala, 2002), one per week, and one per sampling event.
- **Field Blanks -** Field blanks are samples of analyte free water poured into the container in the field, preserved and shipped to the laboratory. They are used to assess whether there is a potential for sample contamination from field conditions. Analysis from field blanks cannot be used to adjust sample results.
- Matrix Spike and Matrix Spike Duplicates - **Matrix Spikes and Matrix Spike Duplicates** – A sufficient volume of sample (typically two or three times the volume of a normal bottle set, depending on the laboratory) shall be collected at a frequency of one in every twenty wells sampled for the laboratory to conduct matrix spike (MS) and matrix spike duplicate (MSD) analyses. A MS is a sample that is spiked by the laboratory with known concentrations of known compounds and subjected to the entire analytical procedure. It is used to indicate the appropriateness of the method for the matrix by measuring recovery and accuracy. A MSD is a duplicate of the MS sample. The purpose of the MSD, when compared to the MS, is to determine method precision. The results of the MS/MSD analysis are to be reviewed to assess sampling and analysis precision and accuracy.
- **Temperature Blank -** A temperature blank may be used to estimate the sample temperature at the time the sample is received by the laboratory (ASTM, D6517).

All duplicates and blanks should be subjected to the same analysis as the ground water samples. The results are used to determine if proper procedures were followed. Blank contamination can result from improper decontamination of sampling equipment, poor sampling and handling procedures, contaminated rinse water or preservatives, or the interaction between sample and container. The concentration levels of any contaminants found should ***not*** be used to correct the ground water data. Blank contamination should trigger a re-evaluation of procedures to determine the source of the problem. Sample results should be normalized/adjusted per control results as part of lab results data sheets.

5.0 Ground Water Sample Analysis

5.1 Selection of Analytical Method

The selection of the method for ground water analysis is determined by the parameters of interest and the purpose of the investigation. Several methods may exist for the same parameter. The selected analytical method should be capable of accurately measuring the constituent of concern in the sample. Some regulatory programs may mandate that the analytical method be U.S. EPA-approved or may suggest a preferred method. Therefore, it is recommended that one check with the regulatory program Ohio EPA staff prior to specifying an analytical method.

There are different methods that are approved by U.S. EPA. The following web sites may be helpful in choosing an appropriate method:

> ***epa.gov/osw/hazard/testmethods/*** - This web site provides resources relating to "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", also known as SW-846. This site contains updates about SW-846 and information about the development and approval process of SW-846 methods.
>
> ***epa.gov/fem/methcollectns.htm*** - Test Method Collections. This site is maintained by EPA's ***Forum on Environmental Measurements*** as a service to the environmental analytical community

Environmental data may be reported with a variety of detection or quantitation limits. Detection and quantitation limits are not the same. The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated as an exact value. The detection limit is based more upon the sensitivity of an analytical instrument and will only rarely account for the full range of matrix effects that are normally encountered with environmental samples. The appropriate detection and/or quantitation limit should be discussed with the regulatory program and generally will need to be below a human health and/or environmental standard. Various detection limits associated with environmental samples are discussed in the following Ohio EPA documents:

- Tier I Data Validation Manual for the Ohio EPA, Division of Hazardous Waste Management June 13, 2011
- Practical Quantitation Limits. Division of Solid and Infectious Waste Management. April 24, 2007
- Laboratory and Field Screening Data Review. Division of Emergency and Remedial Response. August 19, 2005

5.2 Laboratory Quality Assurance/Quality Control (QA/QC)

Procedures, methods, and levels of quality control are discussed in various U.S. EPA publications (1979a, 1983, and 1986b). Laboratory QA/QC may include, but may not be limited to, qualifications, performance, matrix effects (e.g., blanks and matrix spikes), documentation, and record reporting. For sites under the CERCLA process, Ohio EPA-DERR (1998) has established set guidelines and specifications for preparing quality assurance project plans. Also, information on QA/QC can be found in DHWM Tier I Data Validation Manual (Ohio EPA, 2011).

To obtain reliable results, appropriate laboratory procedures and methods should be followed. An extensive laboratory QA/QC program ensures the production of scientifically sound, defensible results that can be documented and verified. Whether Ohio EPA review is required depends on the regulatory program involved. For example, submittal of a laboratory QA/QC plan is not required for sites undergoing RCRA closure (Ohio EPA, DERR RCRA Program); however, the owner/operator should demonstrate that the laboratory has a plan that contains the elements listed by U.S. EPA (1986b). A laboratory QA/QC plan should be approved for sites remediated under the CERCLA process (Ohio EPA, DERR program).

An appropriate level of laboratory QA/QC data should be submitted with sample results to allow verification that the samples were properly handled and analyzed. A particular regulatory program may dictate the amount and type of data. All QA/QC data should be kept and made available upon request.

This data may be valuable for explaining outliers and questionable results. However, the laboratory QC results should not be used to alter the sample analytical data. A report on analytical data is incomplete without some verification of laboratory QA/QC.

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Appendix A
Additional Information for Sampling Water Supply Wells

Water supply wells are often sampled as part of characterizing a potential pollutant source. This information is helpful for characterizing the extent of a plume and to ensure that the public has a safe source of water.

Many of the same techniques and protocol for sampling monitoring wells also apply to collecting a representative sample from a water supply. This includes the following: planning and preparation; sample preservation, sample containers, handling and shipping; and documentation. These are discussed in other sections of this document. However, there are additional conditions/procedures that must be considered when selecting the sampling point and the actual sample. These additional considerations are summarized below.

Selecting the Sampling Point

The following should be considered when choosing the location to collect a water sample:

- Prior to sampling, existing information such as well construction, yield and depth should be obtained. The Ohio Department of Natural Resources, Division of Water keeps records of all well logs. Well log records can be searched online at ***http://water.ohiodnr.gov/***. If a well log record does not exist, then the local health department should be contacted to see if they have any records. Also, if no log exists, the depth of the well should be measured, if possible, and compared to the ODNR Ground Water Resource maps. These maps can be obtained at the above cited web link.

- The intake of the water supply well should be screened/opened to the targeted ground water zone of interest.

- The tap selected for sample collection should be the closest to the water source and prior to any treatment system. Also, if possible, the sampling point should be prior to entering the residence, office, building, or holding tanks etc. It is noted that for some small systems the first tap downstream from the pressure tank and upstream from any water treatment may be the best tap available.

- The sampling tap should be protected from exterior contamination associated with being too close to a sink bottom or to the ground. Contaminated water or soil from the faucet exterior may enter the bottle during the collection procedure since it is difficult to place a bottle under a low tap without grazing the neck interior against the outside faucet surface. If the tap is too close to the ground for direct collection into the appropriate container, it is acceptable to use a smaller (clean) container to transfer the sample to a larger container. The smaller container should be made of glass or stainless steel, or of the same composition of the sample bottles. Also, if samples are to be collected for bacteria, then the tap needs to be disinfected prior to sampling. The laboratory should provide you with their tap disinfection procedures.

- Leaking taps that allow water to discharge from around the valve stem handle and down the outside of the faucet, or taps in which water tends to run up on the outside of the lip, should be avoided as sampling locations.

- Disconnect any hoses, filters, or aerators attached to the tap before sampling. These devices can harbor a bacterial population if they are not routinely cleaned or replaced when worn or cracked. If disconnection from an aerator, or treatment system, is required, permission should be obtained from the well owner.

- Taps where the water flow is not constant should be avoided because temporary fluctuation in line pressure may cause clumps of microbial growth that are lodged in a pipe section or faucet connection to break loose. A smooth flowing water stream at moderate pressure without splashing should be used. The sample should be collected without changing the water flow. It may be appropriate to reduce the flow for the volatile organic compounds aliquot to minimize sample agitation.
- When sampling for bacterial content, the sample container should not be rinsed before use due to possible contamination of the sample container or removal of the thiosulphate dechlorinating agent (if used). When filling any sample container, care should be taken that no splashing drops of water from the ground or sink enter either the bottle or cap.

Sampling Technique

The following procedures should be followed when collecting samples from water supplies:

1. Ideally, the sample should be collected from a tap or spigot located at or near the well head or pump house and before the water supply is introduced into any storage tanks or treatment units. If the sample must be collected at a point in the water line beyond a pressurization or holding tank, a sufficient volume of water should be purged to provide a complete exchange of fresh water into the tank and at the location where the sample is collected. If the sample is collected from a tap or spigot located just before a storage tank, spigots located inside the building or structure should be turned on to prevent any backflow from the storage tank to the sample tap or spigot. It is generally advisable to open several taps during the purge to ensure a rapid and complete exchange of water in the tanks.
2. If the water system is not actively running, purge the system for at least 15 minutes. Systems that are actively pumped may require less purging (e.g., 3-5 minutes). After purging for several minutes, measure the stabilization parameters (See Section 4.5.1 – Field Measurements of Ground Water Indicator Parameters). Continue to monitor these parameters until three consistent readings are obtained.
3. After three consistent readings have been obtained, samples may be collected. Samples collected from potable water supplies should not be filtered.

A detailed operation/procedural process for sampling water supplies can be found in the following references:

Wilde, F.D., D.B. Radtke, J. Gibs, and R.T. Iwatsubo. 2006. Collection of Water Samples: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, Chap. A4. Version 2.0. 231 p. ***http://pubs.water.usgs.gov/twri9A4/***

U.S. EPA, 2001. Environmental Investigations Standards Operating Procedures and Quality Assurance Manual. U.S. EPA. Region 4. Athens, Georgia. 414 p. ***http://www.epa.gov/region4/sesd/eisopqam/eisopqam.html***

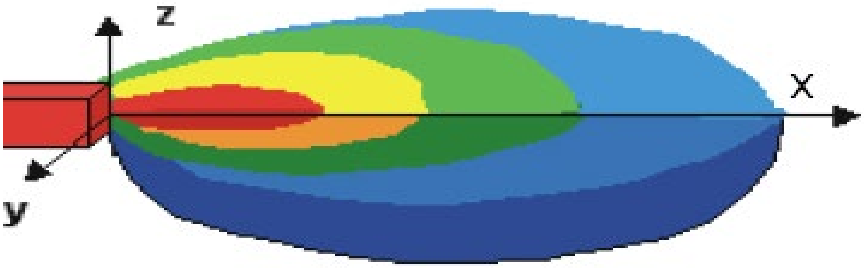
State of Ohio
Environmental Protection Agency

Division of Drinking and Ground Waters

Technical Guidance Manual for Ground Water Investigations

Chapter 14

Ground Water Flow and Fate and Transport Modeling



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Governor : Ted Strickland
Director : Chris Korleski

TECHNICAL GUIDANCE
MANUAL FOR
GROUND WATER INVESTIGATIONS

CHAPTER 14

Ground Water Flow and Fate and Transport Modeling

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Revision 1

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PREFACE

This document is part of a series of chapters incorporated in Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM), which was originally published in 1995. DDAGW now maintains this technical guidance as a series of chapters rather than as an individual manual. These chapters can be obtained at http://www.epa.state.oh.us/ddagw/tgmweb.aspx.

The TGM identifies technical considerations for performing hydrogeologic investigations and ground water monitoring at potential or known ground water pollution sources. The purpose of the guidance is to enhance consistency within the Agency and inform the regulated community of the Agency's technical recommendations and the basis for them. In Ohio, the authority over pollution sources is shared among various Ohio EPA divisions, including the Emergency and Remedial Response (DERR), Hazardous Waste Management (DHWM), Solid and Infectious Waste (DSIWM), and Surface Water (DSW), as well as other state and local agencies. DDAGW provides technical support to these divisions.

Ohio EPA utilizes ***guidance*** to aid regulators and the regulated community in meeting laws, rules, regulations, and policy. Guidance outlines recommended practices and explains their rationale. The Agency may not require an entity to follow methods recommended by this or any other guidance document. It may, however, require an entity to demonstrate that an alternate method produces data and information that meet the pertinent requirements. The procedures used usually should be tailored to the specific needs and circumstances of the individual site, project, and applicable regulatory program, and should not comprise a rigid step-by-step approach that is utilized in all situations.

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ACKNOWLEDGMENTS

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TECHNICAL CHANGES FROM THE FEBRUARY 1995 TGM

The Ohio EPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) was finalized in 1995. This guidance document represents an update to Chapter 14(Ground Water Modeling). Listed below are the major technical changes from 1995.

1. Additional introductory language, including more detailed discussion on types of models that may be used at Ohio EPA regulated sites has been added.
2. Web sources are provided that may aid in model selection.
3. Some common input parameters were identified. Information is provided on whether the inputs should be based on site-specific data collection or whether there are any acceptable default values (Appendix A).

CHAPTER 14

GROUND WATER FLOW AND FATE AND TRANSPORT MODELING

Ground water flow and contaminant fate and transport models are used to help understand and evaluate hydrogeologic systems. Models are simplified representations or approximations of real hydrogeologic systems and may incorporate a number of processes operating within ground water and/or unsaturated zones. The purpose of modeling can vary widely, and the approach used may depend on site-specific needs, current understanding of the hydrogeologic system, availability of input data, and expectation and use of the model results. Models are typically used to:

- Evaluate ground water movement, flow direction, velocity, and discharge rates.
- Evaluate the interaction between hydrogeologic systems.
- Interpolate between known measurement points.
- Identify data gaps during site characterization.
- Aid in the development and management of ground water supply systems.
- Simulate changes in flow conditions resulting from stresses to a ground water zone.
- Determine potential impacts of contamination to nearby wells or surface water.
- Aid in the design and/or performance of remedial systems.
- Estimate leachability from soil sources to ground water.
- Demonstrate compliance with regulatory requirements.
- Estimate vapor intrusion from ground water and soils into buildings.
- Estimate capture zones and drinking water source protection areas.

Models are not a substitute for field investigations, but should be used as supplementary tools. They produce estimates, not a absolute answers. Results depend on the quality and quantity of the field data available to define input parameters and boundary conditions (Wang and Anderson, 1982). Results should always be evaluated in context with the fundamental assumptions of the model and the adequacy of the input data. Modeling may be of limited value when: a remedy can be readily identified, available data indicate there is not an environmental problem, or the site is too complex to model realistically. If a site is poorly characterized or poorly understood, any simulation of the transport and impacts of contaminants using models could be misleading. The use of models under such circumstances can help to support only limited types of decisions, such as planning and prioritizing activities. As a general rule, it is prudent to continually question the results of modeling and the potential consequences of decisions based on misleading results, and consider what can be done to verify results (U.S. EPA, 1996c).

Because major decisions frequently are based on modeling results, it is essential that modeling be conducted in a manner that provides confidence that the results portray field conditions. Thus, the effort must be documented in detail. This chapter identifies types and uses of models and the necessary documentation. It is not intended to provide approval/authorization for particular models. Internet addresses are provided that discuss various public domain and, in some cases, proprietary models. This does not represent an Ohio EPA endorsement of any model.

GROUND WATER FLOW MODELS

Ground water flow models are used to simulate the rate and direction of movement through the subsurface. This simulation requires a thorough understanding of the hydrogeologic system. Hydrogeologic investigations should include a complete characterization of:

- Subsurface extent and thickness of aquifers and confining units (hydrogeologic framework).
- Hydrologic boundaries (also referred to as boundary conditions), that control flow.
- Hydraulic properties of the ground water zone and confining units.
- Horizontal and vertical distribution of hydraulic head throughout the modeled area for beginning (initial conditions), equilibrium (steady-state conditions) and transitional conditions when hydraulic head may vary with time (transient conditions).
- Distribution and magnitude of groundwater recharge, pumping or injection of ground water, leakage to or from surface-water bodies, etc. (sources or sinks, also referred to as stresses). These stresses conditions may be constant or transient.

The outputs from model simulations are the hydraulic heads and groundwater flow rates, which are in equilibrium with hydrogeologic conditions (framework, boundaries, initial and transient conditions, hydraulic properties, and sources or sinks) for the modeled area. Models can also be used to simulate possible future changes to hydraulic head or ground water flow rates as a result of future changes in stresses on a ground water zone.

FATE AND TRANSPORT MODELS

Fate and transport models simulate the movement and chemical alteration of contaminants as they move through the subsurface. They may be used to model contaminants in both the ground water and vadose (unsaturated) zone.

Fate and transport models used to model transport within a ground water zone require the development of a calibrated flow model or, at a minimum, an accurate determination of the flow velocity, which has been based on field data. The model simulates the following:

- Movement of contaminants by advection, diffusion, and dispersion.
- Removal or release of contaminants by sorption or desorption from soil or rock.
- Alteration of contaminants by biological or physical processes, or by chemical reactions.

In addition to a thorough hydrogeological investigation, the simulation of fate and transport processes may require characterization of:

- Horizontal and vertical distribution of average linear ground water velocity (direction and magnitude) determined by a calibrated flow model or through accurate determination from field data.

- Initial distribution of solute.
- Location, history and mass loading rate of chemical sources or sinks.
- Effective porosity.
- Soil bulk density.
- Cation exchange capacity.
- Fraction of organic carbon in soils.
- Octanol-water partition coefficient for chemicals of concern.
- Density and viscosity of non-aqueous fluid.
- Longitudinal and transverse dispersivity.
- Diffusion coefficient.
- Chemical decay rate or degradation constant.
- Equations describing chemical transformation processes, if applicable.
- Initial distribution of electron acceptors, if applicable.

The outputs from model simulations are contaminant concentrations that are in equilibrium with the groundwater flow system and geochemical conditions (described above) for the modeled area.

As with flow models, fate and transport models should be calibrated and verified by adjusting values of the different hydrogeologic or geochemical properties to reduce any disparity between the simulations and field data. This process may result in a re-evaluation of the model used for simulating flow if the adjustment of values of geochemical data does not result in an acceptable simulation. Predictive simulations may be made with a fate and transport model to predict the expected concentrations of contaminants as a result of implementation of a remedial action. Monitoring of hydraulic heads and groundwater chemistry may be required to support predictive simulations.

TYPES OF MODELS

Models use a single equation or a set of governing equations that represent the process(es) occurring (e.g., ground water flow, solute transport, etc.). They can be analytical or numerical; deterministic or stochastic; or steady state or transient. In addition, models can be one-, two-, or three-dimensional. The various types are discussed below. Table 14.1 provides guidance on one-, two-, and three-dimensional models.

Table 14.1 Use of One-, Two-, and Three-Dimensional Models.

DIMENSION	USES
One-Dimensional	• Initial assessments where the degree of the ground water zone heterogeneity or anisotropy is not known. • Sites where a potential receptor is immediately downgradient of a contaminant source. • Model inputs are conservative.
Two-Dimensional	• Problems that include one or more ground water sources/sinks (e.g. pumping or injection wells, drains, rivers, etc.). • Sites where the direction of ground water flow is obviously in two dimensions (e.g. radial flow to a well or single ground water zone with relatively small vertical hydraulic head or contaminant concentration gradients). • Sites at which the ground water zone has distinct variations in hydraulic properties. • Contaminant migration problems where the impacts of transverse dispersion are important and the lateral, or vertical, spread of the contaminant plume must be approximated. • Large ratio between horizontal length and ground water zone thickness. • Thin ground water zones. • Model inputs are conservative.
Three-Dimensional	• The hydrogeologic conditions are well known. • Multiple ground water zones are present. • The vertical movement of ground water or contaminants is important. • Large vertical components exist (e.g., near springs, rivers). • Objectives require detail modeling. Extremely detailed and accurate results that closely match site conditions are needed.

ANALYTICAL MODEL

Analytical models are based on exact solutions to one- or two-dimensional ground water flow or transport equations. These equations are simplifications of more complex three-dimensional ground water flow and solute transport equations used in numerical modeling. Analytical models require a simplification of the flow system, including a horizontal aquifer base, uniform hydraulic and chemical reaction properties, and simple flow or chemical reaction boundaries. In addition, analytical models are typically steady-state and one-dimensional, although selected ground water flow models are two-dimensional (e.g. analytical element models) and some contaminant transport models assume one-dimensional ground water flow conditions and one-, two- or three-dimensional transport conditions. Analytical models are best used:

- When designing data collection plans prior to beginning field activities.
- As an independent check of numerical model results.
- When field conditions support the simplifying assumptions embedded in the model.
- When field data shows that flow or transport processes are relatively simple.
- As an initial assessment of conditions or screening of remedial alternatives is needed.

Analytic element models (AEMs) have been developed that are capable of solving more complex regional flow problems through the superposition of hundreds of individual analytical solutions (or analytic elements) within one model. These analytic elements can represent complexities such as hydraulic conductivity inhomogeneities, streams, lakes, wells, variable recharge areas, etc. Another feature of AEMs is their lack of a model grid, which allows the user to extend the model indefinitely to incorporate regional features without sacrificing accuracy in the area of interest. For more information, see *Analytic Element Modeling of Groundwater Flow* (Haitjema, H.M. 1995).

NUMERICAL MODELS

Numerical models (e.g., finite difference or finite element) solve the partial differential flow or solute transport equations through numerical approximations using matrix algebra and discretization of the modeled domain. In discretization, the model domain is represented by a network of grid cells or elements and the time of the simulation is presented by time steps. The accuracy of numerical models depends on the model input data, the size of the space and time discretizations, and the numerical method used to solve the model equations.

Where the ground water system is very complex, and where sufficient data exist to simulate the complexities in detail, a numerical model may be able to simulate the system with greater accuracy. Generally, they can model irregular boundaries, variations in input parameters such as hydraulic conductivity and recharge, vertical flow gradients at recharge and discharge areas, transient flow conditions, complex multilayered hydrogeologic framework, and other complexities.

Numerical models are best used when:

- Field data shows that ground water flow or transport processes are relatively complex.

- Ground water flow direction, hydrogeologic or geochemical conditions, and hydraulic or chemical sources are sinks that vary with time and space.

- Appropriate input data is available for the model.

Numerical models may be of limited value when there are limited data and in simple hydrogeologic settings where the cost of creating such a model outweighs the information.

DETERMINISTIC VERSUS STOCHASTIC

Most computer models utilize a deterministic approach where all data are input as single, "best estimate" values. Single value inputs result in single value outputs. When modeling on a site-specific scale, where extensive data has been collected and spatial characterization is well established, a deterministic approach is generally appropriate. Simulations with appropriate calibration, sensitivity analysis, and history matching can produce an adequate representation of the real hydrogeologic system. If the modeling effort utilizes very limited data or where a larger, regional scale is involved, a stochastic (statistical) approach may be acceptable (e.g., Monte Carlo simulations). This approach utilizes hydraulic parameters having a probability distribution that results in all output having the same probability distribution. A stochastic approach to modeling would characterize parameter uncertainty by incorporating a measure of uncertainty into the parameters and database utilized in the simulations.

When a lack of data and a high degree of data uncertainty exists, calibration and additional history matching can be long, tedious, or impossible. The stochastic approach allows the uncertainty factor to be maintained throughout the modeling process, allowing for potentially more realistic interpretations of the results by providing ranges of scenarios applicable to the real system. Too often, the data uncertainty factor is lost when deterministic approaches are utilized at sites for which limited data are available. The results become "fact" without acknowledgment of the limitations dictated by the input parameters and the underlying assumptions.

SIMULATION-OPTIMIZATION

Simulation-optimization couples mathematical optimization algorithms with ground water flow or contaminant transport models to determine the optimal solution when many solutions exist. It may help identify pumping solutions that:

- Minimize life-cycle cost, annual cost, or cleanup time while assuring protectiveness.
- Maximize mass removal.
- Minimize pumping rate required for plume capture.

There are two general subclasses of simulation-optimization, hydraulic optimization and transport optimization. Hydraulic optimization is based on ground water flow modeling and is used when containment is the primary concern. Transport optimization is based on both ground water flow and transport modeling and is appropriate when ground water restoration is the primary concern. Additional information can be found at the Federal Remediation Technology Web Site and U.S. EPA, 2004.

STEADY STATE VERSUS TRANSIENT

Ground water flow and fate and transport models simulate either steady state or transient flow. In steady-state systems, inputs and outputs are in equilibrium so that there is no net change in the system with time. In transient simulations, the inputs and outputs are not in equilibrium so there is a net change in the system with time. Steady state models provide average, long-term results. Transient models should be used when the ground water regime varies over time.

GENERAL PROTOCOL

The following paragraphs outline the general protocol that should be used to ensure that modeling is conducted and documented appropriately.

DEFINE THE PURPOSE/OBJECTIVES

The purpose/objectives of modeling should be clearly defined and understood because it dictates the selection and development of the model. Additional factors that should be considered are regulatory requirements, potential risk to human health and the environment, site complexity, and economic constraints.

Note that models are tools only and are not a substitute for field data. For example, an evaluation of the effectiveness of a proposed ground water remedial system may be based on modeling. However, a verification that the existing remedial system is adequately cleaning up the ground water needs to be based on field data.

QUALITY ASSURANCE PLANS

Quality assurance is a component of site investigations to ensure that data collection and interpretations have been appropriate. Quality assurance may need to be considered during the development, application, and verification. Development of a quality assurance plan at the beginning of modeling will help ensure more reliable results. The following may need to be addressed (California EPA, 1995):

- Protocols for field data collection, verification, and processing.

- Narrative and graphical presentation of a conceptual model, including description of processes to be considered.

- Criteria for model selection.

- Documentation and retesting when changes are made to a model code.

- Protocols to be followed in model formulation.
- Protocols to be followed in model calibration, including, limits on parameter adjustments, and identification of calibration goals.

- Protocols for sensitivity analysis.

- Procedures for analysis of error.

- Level of information to be included in computer output.

- Applicability of the specific modeling program and mathematical formulas.
- Assumptions made and their potential influence on model output.

- Establishment of record keeping procedures to document the model application process.

- Format for presentation of results.

CONCEPTUAL MODEL DEVELOPMENT

A conceptual model should be developed. This is critical in any modeling project (Bear et al., 1992). A conceptual model is a simplified description and schematic that outlines the components of the system to be modeled. The model must be based on a thorough understanding of site hydrogeologic conditions derived from field investigations and regional data obtained from academic or government studies (see Chapter 3). At a minimum, the conceptual model should include the geologic and hydrologic framework, hydraulic properties, areas of recharge and discharge (sources and sinks), boundary and initial conditions, transport processes, and spatial and temporal dimensionality (U.S. EPA 1996a & b). For contaminant transport modeling, additional factors should be incorporated, including (but not limited to), contaminant sources when released (if known), media affected, and concentration distributions. In addition, the physical and chemical properties of the contaminants that may affect their movement should be evaluated. Conceptual models should be continually refined as more data are obtained. ASTM E1689 provides additional guidance on the development of a conceptual model. (Note: the ASTM guidance is for a *site conceptual model* for all pathways, not just ground water.)

MODEL SELECTION

A model should be chosen based on its applicability to the conceptual model, availability of the required input data, and the defined purpose/objective of the modeling effort. It is important to choose a model that simulates the natural system as accurately as possible. The model should satisfy fundamental assumptions and the boundary and initial conditions of the area to be modeled. The user will need to decide whether it is more appropriate to use an analytical model versus numerical and also whether to use a one-, two- or three dimensional model (See section on Types of Models, page 14-4). In addition, it is important that any model selected be code-verified, peer-reviewed, and documented.

- **Code verification** is a process of checking the accuracy of the algorithms used to solve the governing equations, thereby demonstrating that the model actually approximates the process equations for which it is being applied. This can be accomplished by solving a problem with the model and comparing the results to those obtained from an analytical solution or to another model that has been verified. *(Note: Code verification does not ensure that the model can solve important problems, or correctly reflects the real world process.)*

  The publication of a model or its availability for sale does not necessarily mean that the model has been code-verified. If the model has been code-verified in the literature or user's manual, evidence of this information can be used to document that the model has been verified. The results of the code-verification should be included in reports summarizing the model results.

- It is important that the chosen model has been **peer-reviewed**. Modelers often choose to employ a general but widely used model rather than one that is specialized and less well known because the widely used model's code has been widely tested in numerous settings and should be relatively free of "bugs."

- The model should be well **documented.** The fundamental assumptions and limitations of the model, the mathematical solution techniques, and the code structure should be documented. In addition, documentation should include instructions on how to use the model, input data requirements, and an explanation of the output. ASTM D6171-97(2004) provides additional information on documenting a ground water modeling code.

Contaminant transport modeling should include simulation of advective flow, which is typically the major component of contaminant transport. Mechanical dispersion and diffusion also can play a role, and these parameters are often lumped into a single dispersion value (Faust and Mercer, 1980). Sorption and transformation processes (e.g. biodegradation, hydrolysis, etc.) can change the physical or chemical state of contaminant(s). When modeling contaminant movement, all applicable transport processes should be considered. Excluding or combining any of the processes must be justifiable.

The following Web sites may aid in the selection of a model.

International Ground Water Modeling Center, Colorado School of Mines (IGWMC).
Can purchase models and download demos or free software. Provide technical support.

Ground Water and Ecosystem Restoration Research. U.S. Environmental Protection Agency. (Formerly Kerr Labs: Center for Subsurface Modeling Support (CSMoS)). Access to EPA public domain models and other technical support information.

NTIS, National Technical Information Service. Source for the sale of scientific, technical and engineering products produced by or for the U.S. government.

U.S. Geological Survey. The software and related documentation on these Web pages were developed by the U.S. Geological Survey (USGS) for use by the USGS in fulfilling its mission. The software can be used, copied, modified, and distributed without any fee or cost. Use of appropriate credit is requested. The software is provided as a minimum in source code form as used on USGS computers.

Center for Exposure Assessment Modeling (CEAM). CEAM was established in 1987 to meet the scientific and technical exposure assessment needs of the United States Environmental Protection Agency (U.S. EPA) as well as state environmental and resource management agencies. CEAM offers exposure assessment techniques for aquatic, terrestrial, and multimedia pathways for organic chemicals and metals.

U.S. EPA OnSite OnLine Tools for Site Assessment: Contains a suite of calculators for assessing subsurface contaminant transport.

Army Corps of Engineers. The Department of Defense, in partnership with the Department of Energy, the U.S. Environmental Protection Agency, the U.S. Nuclear Regulatory Commission and 20 academic partners, has developed the DoD Groundwater Modeling System. The

GMS provides an integrated and comprehensive computational environment for simulating subsurface flow, contaminant fate/transport, and design of remediation systems.

The Geotechnical and Geoenvironmental Software Directory (GGSD). Catalogues 1679 programs in the fields of Geotechnical Engineering, Soil Mechanics, Rock Mechanics, Engineering Geology, Foundation Engineering, Hydrogeology, Geoenvironmental Engineering, Environmental Engineering, Data Analysis and Data Visualization and lists 828 worldwide suppliers and publishers of these programs.

DEVELOP MODEL

Input Parameters

Inputs should be based on field data and, in some cases, literature values. The use of literature values may depend on how sensitive the model is to the particular parameter whether the approach is conservative, and in some cases, whether there are field methods to reliably obtain the data. Appendix A identifies common modeling input parameters and a discussion on whether site-specific or default values are appropriate. Chapter 3 (Hydrogeologic Characterization), provides additional guidance on determining site-specific values for many parameters that are needed for modeling. Inputs may need to be adjusted to calibrate the model. The modeler should demonstrate that final values lie within a reasonable range (e.g., physically realistic for the conditions).

The values of all inputs for each model node or cell should be specified in tabular or graphical form. The source of the values should be specified. Any methods used to process field-measured data to obtain model input should be specified and discussed in a report

Boundary Conditions

Types of boundaries include constant head, impermeable, constant flow, and variable head. Examples of boundaries are surface water bodies, rivers, geologic structures, injection barriers, and ground water divides. Boundary conditions are represented by mathematical expressions of a state of the physical system that refine the equations of the mathematical model. Selection of boundary conditions may have profound effects on model simulations. A model may yield biased or erroneous results if wrong boundary conditions are used.

It is desirable to represent only existing natural hydrogeologic boundaries in a model. This is possible in analytic element models and large regional numerical models that incorporate distant flow boundaries. However, many smaller site-specific numerical models employ grid systems that require an artificial boundary be specified at the edge of the grid system. In these instances, the grid boundaries should be sufficiently remote from the area of interest so that the artificial boundary does not significantly impact the predictive capabilities of the model.

Another technique for selecting appropriate boundary conditions for numerical models is to employ a stepwise or telescopic refinement modeling approach (Anderson and Woessner 1992; Feinstein et. al. 2003; Hunt et. al. 1998). In these approaches either a coarser regional numerical model or a regional analytic element model is developed, based on natural hydrogeologic boundaries, and the results from the model are used to define appropriate boundary conditions for a smaller-scale more detailed numerical model. In some cases multiple precursor models will be developed with varying degrees of complexity, with the final result being a detailed small-scale fine-grid numerical model with boundaries based on the conditions specified from the coarser precursor models. Detailed small-scale numerical models developed using this approach will usually be more easily calibrated and provide better results than those developed with arbitrary model boundaries.

Various scenarios can be evaluated during calibration by modifying the boundaries and comparing the effects. However, once a model grid size is selected for most numerical models, it is not possible to expand the grid without creating a new model. If a numerical model was developed and there is concern that the artificial boundaries are impacting the predictive capabilities of the model, a larger scale but more simplistic analytic element model can be developed to test the influence of various boundary conditions. This approach may be simpler than developing a larger numerical model. For further information on boundary conditions, see Franke et al. (1987), Franke and Reilly (1987) and Anderson and Woessner (1992), and ASTM D5609-94(2002). A more simplistic analytic element model can also be developed to test the influence of boundary conditions on the area of interest prior to developing a more complex numerical model.

Network/Areal Grid Design

Most numerical methods require the development of an areal grid overlay. The input parameters and grid form the database on which the ground water system is defined. The formation and input of this database is specific to the computer code chosen. Fine, closely spaced grid patterns produce more accurate results. On the other hand, the finer the grid pattern, the longer the computer run time. With more recent advances in personal computers, however, computational time has become less of an issue. If computational time is not a factor and regional data is available, having a larger model area with boundaries based on actual hydrologic boundaries will be more appropriate than assigning artificial boundaries Faust and Mercer (1980) and U.S. EPA (1996a & b) provided the following general guidelines:

- Locate "well" nodes near pumping wells or near the center of a well field.

- Locate boundaries accurately. For distant boundaries, the grid may be expanded, but large spacing next to smaller ones should be avoided.

- Grid spacing should be an appropriate scale for the problem. Grid spacing should be closer together in areas where there are large spatial changes in transmissivity or hydraulic head. Large changes in hydraulic head typically occur in recharge and discharge areas, and may be especially significant near pumping wells.

- Align axes of the grid with the major directions of anisotropy (i.e., orient grid with major trends).

- Strong vertical gradients within a single saturated zone should be accommodated by multiple planes or layers or nodules.

In addition, when expanding finite difference grids beyond the interior nodes (area of modeling interest) to the boundaries, as a rule of thumb, grid spacing should not be more than 1.5 times the previous nodal spacing (Anderson and Woessner, 1992). It may be helpful to develop an analytic element model first, determine appropriate boundary conditions, and then develop a numerical model based on the information gained from the analytic element model.

Calibration

Calibration consists of changing values of input parameters in an attempt to match field conditions within acceptable criteria. Calibration requires that field conditions be properly characterized. Lack of proper characterization may result in a calibration to a set of conditions that do not represent actual field conditions. Calibration comparisons may include, but are not limited to:

- Ground water flow direction.
- Hydraulic heads and/or gradient.
- Water balance.
- Infiltration rates.
- Soil moisture content.
- Contaminant migration rates and direction (if appropriate).
- Contaminant concentrations (if appropriate).

Since some inputs (e.g., hydraulic conductivity, transmissivity, dispersivity, etc.) are highly variable, sometimes suspect, and the data is limited, these values are typically adjusted and extrapolated through an iterative process until an acceptable "match" is made. As calibration proceeds, data gaps often become evident. The modeler may have to redefine the conceptual model and collect more data. When the best calibrated match is achieved, a final input data set should be established and demonstrated to be reasonable and realistic. The degree of accuracy and how precise the match should be is governed by the defined purpose of the modeling. Each modeler and reviewer will need to use professional judgment in evaluating the results. There are no universally accepted "goodness-of-fit" criteria that apply in all cases. However, it is important that the modeler make every attempt to minimize the difference between model-simulated and field conditions. Additional information for calibrating a ground water model can be found in ASTM D5981-96(2002).

Documenting the degree of model calibration is important since it helps demonstrate how well the model estimates reality. Documentation can be in two forms: qualitative and quantitative. Qualitative is the simpler of the two, and involves using words, maps, tables and graphs to demonstrate that the model-derived predictions are consistent with the behavior that is expected based on field data. Quantitative analysis involves a statistical comparison of modeled results to values measured in the field. Many model post-processors include statistical packages that can provide an efficient tool for quantifying a model's degree of accuracy (Randazzo, 2005, ASTM D5981-02).

For initial assessments, it is possible to obtain useful results from models that are not calibrated. Potential applications include screening and guiding data collection activities.

Field-Verified

The model should be field-verified, if possible, to ensure that favorable comparisons exist between the modeled results and observed field data for the area being modeled Field verification is the process in which the calibrated model is shown to be capable of reproducing a set of field observations independent of that used in the model calibration (e.g., historical matching). The degree of verification necessary is dependent on the purpose of the modeling, type of model, results of the sensitivity analysis, and the site complexity. [Note: If the model cannot be adequately field-verified, then more emphasis should be placed on the sensitivity and uncertainty analyses.]

Sensitivity Analysis

A sensitivity analysis is the process of varying inputs over a reasonable range (range of uncertainty in the value of the parameter) and observing the relative change in model response. The sensitivity of one parameter versus others is also evaluated. Typically, the observed changes in hydraulic head, flow rate, or contaminant transport are noted. The purpose of the sensitivity analysis is to demonstrate the sensitivity of the simulations by varying input values. If some change in a parameter or boundary condition causes significant changes in output, then the model is sensitive to that parameter or boundary. For example, the modeled hydraulic conductivity is varied between 100 and 500 feet/day and the heads in the model do not vary significantly, it could be interpreted that the particular model is not sensitive to K. However, if riverbed conductance is varied from 1 to 100 days and the modeled heads vary significantly, then the model could be interpreted to be sensitive to river conductance.

Sensitivity analyses are also beneficial in determining the direction of future data collection activities. Data for which a model is relatively sensitive would require future characterization, as opposed to data for which the model is relatively insensitive, which would not require further field characterization. For additional information, see Anderson and Woessner (1992); Zheng and Bennett (1995), and ASTM D5611-94(2002).

Uncertainty Analysis

An uncertainty analysis is conducted by assigning distributions to parameters that are demonstrated to have the most variability in the field and are demonstrated to be the most sensitive to the model output. Various methods for introducing uncertainty into the models and the modeling process have been proposed. For example, one approach is to employ Monte Carlo methods in which the various possibilities are represented in a large number of simulated realizations. Another approach is to construct stochastic models in which the various coefficients are represented as probability distributions rather than deterministic values (Bear et al., 1992).

PREDICTION

Upon completing calibration, sensitivity analysis, and field-verification, the model can be used to predict future scenarios. Such simulations may be used to estimate the hydraulic response of a zone, the possible migration pathway of a contaminant, the contaminant mass removal rate, or concentrations of a contaminant at a point of compliance at some future point in time.

Predictive simulations can also be used to predict responses to the system as natural- or man-induced stresses are applied. For example, a model may be used to predict the pumping rate needed to capture a contaminant plume and to estimate the contaminant concentration of the extracted ground water. Monitoring of hydraulic heads and contamination concentrations should be used to verify hydraulic containment and remediation.

The predictive simulations should be viewed as estimates and not as a certainty. There is always some uncertainty in predictive models. The simulations are based on the conceptual model, the hydrogeological and geochemical input parameters, and the model algorithms. The model's limitations and assumptions, as well as the differences between field conditions and the conceptual model will result in errors in simulations. In an attempt to minimize these errors, models are calibrated by adjusting inputs until the model closely reproduces field conditions within some acceptable criteria. However, the time period over which a model is calibrated is typically small compared to the length of time used for predictive simulations. Relatively small errors observed during the time period over the model calibration or history matching may be greatly magnified during predictive simulations because of the larger time period typically used in predictive simulations. The growth in errors resulting from projecting model simulation into the future may need to be evaluated by monitoring field conditions over the time period of the simulation or until appropriate cleanup criteria have been achieved.

Predictive simulations are often conservative. That is, given the uncertainty in model input parameters and the corresponding uncertainty, model input values are selected that result in a "worst-case" simulation. Site-specific data may be used to support a more reasonable worst-case scenario. Or stated another way, site-specific data should be collected to limit the range of uncertainty in predictive models. If long-term action is necessary, it may be necessary to refine and update the model as additional data are collected and future stresses are observed (see Performance Monitoring section).

PERFORMANCE MONITORING ("Validation")

A sufficiently calibrated and field-validated model uses historical data to predict the future; however, it is difficult to predict the magnitude, location, and duration of future stresses. As a result, performance monitoring (validation) of predictive simulations often show the flow system did not behave as predicted. Post-audits utilize the additional field data collected after the model study is completed to evaluate the accuracy of the prediction. The new data should be used to recalibrate the model to update and improve the simulation. These periodic updates allow appropriate "corrective actions" to be made (e.g., modifications to an extraction well system). Anderson and Woessner (1992) and Konikow (1986) provided discussions on post-audit methods that can be utilized to re-calibrate a model. Many investigators have suggested not extending transient predictive simulations for more than twice the number of years for which there is transient calibration and verification data (Faust et al., 1981).

DOCUMENTATION OF MODEL RESULTS

Documentation of a model is important to show that the interpretations made reasonably represent site conclusions. This will facilitate peer review and also enable further scientific verification by allowing the model to be reproduced by future modelers. Results should be presented clearly and concisely and include appropriate documentation. Model documentation includes written and graphical presentation of the assumptions and objectives, the conceptual model, code description, model construction, calibration, predictive simulations, and conclusions. The following provides an outline of components that should be incorporated into a report (ASTM D5718-95 (2006), Anderson and Woessner (1992), Mandle (2002)):

- ***Purpose*** - The purpose and specific goals or objectives of the modeling should be clearly stated. It should be documented that the objectives of the simulation correspond to the decision-making needs.

- ***Hydrogeologic Setting*** - A narrative, with appropriate cross-sections and maps of the hydrogeologic system, should be provided. The data used (e.g., borings, well logs) should be provided or referenced to where the data can be obtained.

- ***Data Collection*** - Methods and techniques for collecting, analyzing and interpreting data should be explained. Levels of confidence for system parameters should be discussed. Any data gaps and simplifying assumptions should be discussed. Data set strengths and deficiencies should be noted.

- ***Detailed Conceptual Model*** - It should be documented that the conceptual model is consistent with the site's physical and chemical processes. Any uncertainties and simplifying assumptions should be justified.

- ***Model Description*** - The rationale for the choice of a particular model should be documented. Simplifying assumptions and limitations of the model should be discussed and related to the problem to be simulated, along with the impact these assumptions may have on the results. A description of where assumptions and actual field conditions do not coincide should be presented. It should be shown that the model chosen is appropriate for the system. Any modifications to the code should also be discussed.

- ***Model Construction -*** The layering and gridding of the model should be described. This would include describing how pumping wells and natural boundary conditions are represented. Document whether the grid selection was appropriate for the scale of the problem.

- ***Assignment of Model Parameters*** - It should be shown that there are sufficient data to characterize the site and satisfy the data needs of the model. All input data, including initial conditions, boundary conditions, and hydraulic and transport parameters, should be defined. The reasons for selecting initial and boundary conditions should be justified. Assigned values throughout the modeled area should be presented. Data can be presented on cross-sections and maps showing flow boundaries, topography and surface water features, water-table/potentiometric surfaces, bedrock configuration, saturated thickness, transmissivity/hydraulic conductivity, specific storage, cross sections, etc. All sources of data used, whether derived from published sources, measured, or calculated from field data or laboratory testing should be documented.

- ***Model Calibration*** - Specific goals and procedures of calibration, results of the final calibrated model, departure from the calibration targets, the effects of the departure on the model results, and the overall water and/or chemical balance of the model should be presented and discussed.

- ***Sensitivity Analysis*** - All sensitivity analyses should be presented and interpreted. Input parameters that have the greatest impact on results should be described.

- ***Field Verification***- Goals and procedures of any field verification should be presented and discussed. Additional sensitivity analyses on these new comparisons should be documented.

- ***Data Pre- and Post-Processing*** - All pre- and post-processing of model input and output data should be described and any computer codes utilized should be documented. The modeler(s) should describe the data manipulation process and why it was conducted.

- ***Model Prediction-*** All output from predictive simulations should be presented and interpreted in detail. The modeler(s) should cover model water balance, highlighting salient features such as pumpage, recharge, leakage, etc. All predictions should be presented in the context of the fundamental assumptions of the model. Limitations of and confidence in predictions should also be stated.

- ***Sources of Error-*** Known problems and errors may need to be evaluated and discussed by utilizing ranges and expressing levels of confidence for predictions made. Konikow (1988) identified several common types of predictive errors. Sources of error are also discussed in ASTM D5880-95(2006).
- ***Summary and Conclusion*** – Summarize the modeling effort and draw conclusions related to the study objectives. The limitations of the modeling and all assumptions should be discussed. Also, discuss uncertainties inherent to the model and their effects on conclusions.

- ***Model Records*** - The entity should keep on file, and be able to provide upon request, input and output data sets for model runs (in digital form or hard copy), including final calibration, additional history matching, and all predictions. The original model documentation and a copy of the source code used should also be available upon request.

- ***Post Audit*** - If a model will be used to make decisions that extend beyond its predictive limit, the report should include a plan for future ~~post-audits~~ evaluations to check the model in time and space to be certain that past decisions are still appropriate.

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APPENDIX A
COMMON MODELING INPUTS

HYDROGEOLOGIC INPUTS

Hydraulic Conductivity

Hydraulic conductivity **(**K) is a coefficient of proportionality describing the ease at which fluid can move through a permeable medium and is expressed in units of length per time. It is a function of properties of both the porous medium and the fluid. In most cases, site-specific values should be used for both vertical and horizontal K. It is generally a sensitive modeling input parameter. Methods to determine K are described in Chapter 3.

If an insufficient amount of site-specific data exists or the site is more complex than the model can handle, then literature values are often used to support the model. However, models relying on literature data would need to rely on good sensitivity and uncertainty analysis.

Intrinsic Permeability

Site-specific hydraulic conductivity is generally determined in a site investigation. However, some models use intrinsic permeability instead of hydraulic conductivity. Intrinsic permeability describes the ease with which a porous medium can transmit a liquid under a hydraulic or potential gradient. It differs from hydraulic conductivity in that it is a property of the porous media only and is independent of the nature of the liquid. For water, it is related to hydraulic conductivity by

$$\mathrm{k} = \frac{\mathrm{K} \times \mu}{\rho \times \mathrm{g}} = 10^{-5}\mathrm{m} \cdot \mathrm{s}$$

k = intrinsic permeability cm^2
K = hydraulic conductivity cm/sec
μ= dynamic viscosity g/cm-sec (0.01 g/cm sec)
ρ = density of fluid g/cm^3 (0.99821 g/cm^3)
g = acceleration of gravity cm/sec (980 cm/sec^2)

Hydraulic Gradient

Hydraulic gradient is the total change in head with change in distance in the direction of flow. The gradient generally is analogous to the slope of the potentiometric or water table surface. It is generally a sensitive input. Hydraulic gradient is generally entered as a value in analytical model, while hydraulic heads are generally input into numerical models. Methods to determine hydraulic gradient can be found in Chapter 3.

Bulk Density

Bulk density (also called dry bulk density) is the ratio of the mass of dry solids to the bulk volume of a soil. The bulk density is therefore less than the density of particles that make up the soil, because it also includes the volume of pore space. It is used by geotechnical engineers to estimate compaction of the soils. Bulk density is used in modeling to calculate between the volumetric water content and the gravimetric water content, to calculate retardation factors, and is coupled with the particle density to calculate the porosity of a soil.

There is no standard method for measuring of bulk density. Most commonly, dry bulk density is measured by taking a sample of known volume, drying it at 105°C for 24 hours or until a constant weight is obtained, then weighing the dried soil sample. The dry weight divided by the volume is the bulk density (Ohio EPA, 2003b). Other methods to measure bulk density include radiation techniques (Blake and Hartge,1986). Site-specific bulk density also can be determined by ASTM D2167-94 (2001), D2922-05, and D2937-04.

The dry bulk density will vary within certain limits for different soil types. Range of default values for various media can be found in Table A14.1. In most cases, bulk density is not a sensitive parameter and these values may be used as defaults in models. A sensitivity analysis should be provided unless the model documentation indicates the bulk density is not sensitive.

Table A14.1 Bulk Density (Jury,1986).

Soil Type	Bulk Density (g/cm3)
Sand	1.59 - 1.65
Sandy Loam	1.2 - 1.49
Silt loam	1.47
Clay Loam	1.2-1.36
Silty clay	1.26

Porosity/Effective Porosity

Porosity is the ratio of openings to the total volume of rock and soil. The pore space and the arrangement of pore spaces within a soil sample are very complex and difficult to measure. This is because the arrangement of soil particles influences the shape, size and orientation of pores within the soil matrix. The porosity of a soil will vary with the arrangement of particles or texture. In general, finer grained soils, rich in clay, will have the highest porosity, and coarser textured soils, rich in sand, will have lower porosity.

Porosity (n) can be calculated by a variety of means. The most common is to calculate the percentage of total soil volume occupied by pores. This is done by calculating a soil's bulk and particle density (Blake and Heritage, 1986) and using:

$$\text{porosity (n)}=[1-\frac{\text{bulk density}}{\text{particle density}})]$$

Typical porosities are listed in Table 14.2 and in TGM Chapter 3, Table 3.9. On average, particle densities of 2.65 g/cm3 are typical of sandy soils but decrease as the clay and organic matter content rise.

Another method is to use pycnometry as described by Danielson and Sutherland (1983). Porosity measurements are important and are used in most ground water and fate and transport models. These measurements serve as a basis for determining the water-filled porosity, air-filled porosity and in calculations to determine the total mass of contaminants.

Not all of the porosity is available for flow. Part will be occupied by static fluids being held to the soil/rock by surface tension or contained in dead end pore spaces. The porosity available for fluid flow is the effective porosity. It is also a function of the size of the molecules that are being transported to the relative size of the passageways that connect the pores. Therefore, the effective porosity for solute transport may differ from that of water for the same material.

Effective porosity is difficult to measure and is typically selected by experience and intuition. Effective porosity is generally estimated based on the description and classification of subsurface materials and by total porosity, determined from lab tests or estimated from the literature. Tables A14.2 and A14.3 provide data that might be useful to this estimation. Peyton et al. (1986) found that even in lacustrine clay, water molecules could pass through all pore throats, so that effective porosity was essentially the same as porosity (Fetter, 2001). This suggests that, for at least water, effective porosity may be considered equal to total porosity.

For unfractured glacial till, it is recommended that 30 percent be used for n_e in velocity calculations[7]. While a default value of one percent has been cited for clay (U.S. EPA, 1986), this results in high rates that are intuitively incorrect. Primary flow through clay is known to be very low. This 30% compares favorably with the value for clays reported by Rawls et al. (1983) (Table A14.2). Ohio EPA's experience is that use of 30 percent results in very conservative estimates of ground water movement through unfractured glacial till.

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[7] It should be noted that the applicability of Darcy's law to calculating primary flow velocity in fine-grained material is questionable. However, this currently is one of the best available tools to assist professionals in evaluating whether a confining unit provides protection to the underlying ground water. To further demonstrate that ground water has not/will not be affected by a potential contaminant source, other methods such as tracers may be helpful.

Table A14.2 Porosity and Effective Porosity of Common Soils (Rawls et al., 1983).

Texture	Mean Total Porosity	Mean Effective Porosity
Sand	0.437	0.417
Loamy Sand	0.437	0.401
Sandy Loam	0.453	0.412
Loam	0.463	0.434
Silt Loam	0.501	0.486
Sandy Clay Loam	0.398	0.330
Clay Loam	0.464	0.309
Silty Clay Loam	0.471	0.432
Sandy Clay	0.430	0.321
Silty Clay	0.479	0.423
Clay	0.475	0.385

Table A14.3 Range of percentage of porosity for various geologic materials.

GEOLOGIC MATERIALS	BOUWER (1978)	TODD AND Mays (2004)	FETTER (2001)	FREEZE AND CHERRY (1979)	SEVEE (2006)
gravel, mixed	20-30			25-40	25-40
gravel, coarse		28			
gravel, medium		32			
gravel, fine		34			
sand, mixed	25-50			25-50	15-48
sand, coarse	25-35	39			
sand, medium	35-40	39			
sand, fine	40-50	42			
sand & gravel	10-30		25-50		
silt	50-60	46	35-50	35-50	35-50
clay	50-60	42	33-60	40-70	40-70
glacial till	25-40	31-34	10-20		
limestone	10-20	30		0-20	0-20
shale		6		0-10	0-10
sandstone	5-30	33-37		5-30	5-40

Water Content

Water content indicates the amount of water in a soil sample. In the vadose zone, this value will change over time as the soil water budget changes. Most vadose zone models require some measure of water content. However, there is some confusion about the basis for water content measurement and the use of the data. The most common measurement is the percent moisture content of a soil sample. The measurement is made by weighing a soil sample, drying it at 105 ℃ until a constant weight is obtained, then weighing the dried soil sample. The percent moisture content is then:

$$\%\,\text{moisture} = \frac{\text{wet weight -dry weight}}{\text{dry weight}} \times 100 \qquad (1)$$

The ratio of dry weight to wet weight of a soil sample represents the gravimetric water content or water content on a mass basis (θ_m). Unfortunately, most vadose zone models require that water content of a soil be expressed in terms of volumetric water content (θ_V). The conversion from water content based upon mass to that of a volumetric basis can be made with the following relationships:

$$\frac{\text{volume of water (ml)}}{\text{volume of soil (ml)}} = \theta_m \left(\frac{g}{g}\right) \times \frac{\text{bulk density } \left({}^{g}/_{cm^3}\right)}{\text{density of water } \left({}^{g}/_{cm^3}\right)} \qquad (2)$$

where the bulk density is defined previously and density of water is usually assumed to be 1.0 g/cm3.

In many applications, the model prompts the user for neither the volumetric nor mass water content. Instead, it requires water-filled porosity or the percentage that the average pore-space is filled with water. This value can be determined by first noting that:

$$\text{volume of pore space (mL)} = \text{porosity } \times \text{volume of Soil (mL)} \qquad (3)$$

Rearranging equation 3 in terms of volume of soil and substituting this relation in equation 2, the following relationship is found:

$$\frac{\text{volume of water (mL)}}{\text{volume of soil (mL)}} \times \frac{\theta_m \left(\frac{g}{g}\right)}{\text{porosity}} \times \frac{\text{bulk density} \left(\frac{g}{cm3}\right)}{\text{density of water } \left(\frac{g}{cm3}\right)} \qquad (4)$$

This ratio is then multiplied by 100 to determine the percentage of water in the pore space of a soil sample. For example, if a sample is determined to have 20% moisture content (determined on a mass basis), a dry bulk density of 1.5 g/cm3 , a total porosity of 0.5 (i.e. 50%) and the density of water is 1.0 g/cm3, then:

$$\% \text{ of pore filled with water} = \frac{0.2}{0.5} \times \frac{1.5(\frac{g}{cm3})}{1.0(\frac{g}{cm3})} \times 100 = 60\%$$

FATE AND TRANSPORT INPUTS

Dispersion Coefficients

Dispersion (or dispersvity) is the spreading of a solute caused by mechanical dispersion and molecular diffusion:

- Mechanical dispersion results from ground water moving at rates both greater and less than the average linear velocity. This is due to: 1) fluids moving faster through the center of the pores than along the edges, 2) fluids traveling shorter pathways and/or splitting or branching to the sides, and 3) fluids traveling faster through larger pores than through smaller pores (Fetter, 2001). Because the invading solute-containing water does not travel at the same velocity, mixing occurs along flow paths. This mixing is called mechanical dispersion and results in distribution of the solute at the advancing edge of flow (Fetter, 1993). The mixing that occurs in the direction of flow is called longitudinal dispersion. Spreading normal to the direction of flow from splitting and branching out to the sides is called transverse dispersion.

- Molecular diffusion is the process by which ionic and molecular species dissolved in the water move from areas of higher concentration (i.e., chemical activity) to areas of lower concentration. Diffusion is an important process influencing contaminant migration in unfractured clayey aquitards.

Mechanical dispersion and molecular diffusion cannot be distinguished in a ground water flow system and often are referred to collectively as hydrodynamic dispersion (Fetter, 2001). Depending on the degree of dispersion, a contaminant may form a wide or a narrow plume. Hydrodynamic dispersion phenomena also may cause contaminants to arrive at a given location significantly ahead of the arrival time expected solely from an average flow rate. General textbooks by Freeze and Cherry (1979), Fetter (2001), Luckner and Schestakow (1991), Domenico and Schwartz (1990), and Fetter (1993) should be consulted for additional information on hydrodynamic dispersion.

Many models require a dispersivity term to account for both mechanical dispersion and diffusion. Due to the impracticability of measuring dispersion in the field, dispersivity values are often estimated based on plume length or distance to receptors. Gelhar et al. (1992) cautions that dispersivity values vary between 2-3 orders of magnitude for a given scale due to natural variation in hydraulic conductivity. Therefore dispersivity values can be manipulated within a large range and still be within the range of values observed at field test sites.

Longitudinal dispersivity (a_L), which is a measure of the "spread" of the plume in the direction of flow, can be estimated based on a formula developed by using a weighted best fit of field data (Xu and Eckstein,1995). This equation is provided below and can also be found on

U.S. EPA On-Line Tools for assessing longitudinal dispersivity. (Note: Equation is specific to units (e.g., metric)).

$\alpha_L = 0.83 \times (\log L_p)^{2.312}$ α_L = Longitudinal dispersivity (m)
L_p = Plume length (m)

Other commonly used relationships for dispersivity include:

$\alpha_L = 0.1L_p$ (U.S. EPA 1996)

$\alpha_v = 0.0056L_p$ (Gelhar and Axness, 1981)

$\alpha_T = 0.10\ a_L$ (Gelhar and Axness, 1981)

Where: α_L = Longitudinal dispersivity (m)
α_v = vertical dispersivity (m)
α_T = transverse dispersivity (m)
L_p = Plume length (m)

Fraction of Organic Carbon

The fraction of organic carbon (f_{oc}) is the carbon in the soil that is made up of decaying plant and animal matter, humus, *etc.* It is differentiated from inorganic carbon (typically in calcium or magnesium carbonates), which does not have the same effect on contaminant movement. The fraction of organic carbon is generally the dominant retarding mechanism for contaminant movement in the vadose zone.

Organic carbon and matter contents of soils can have a significant effect on fate and transport; therefore, accurate determination is important and sampling and analysis should be performed with great care. For site-specific modeling, the practitioner should collect a representative number of samples, both horizontally and vertically, over the affected area. Analytical methods to determine organic matter can be found in ASTM D2974-00 or Soil Science Society of America Methods (Nelson and Sommers, 1996). Commonly, modified ground water methods for total organic carbon are used by commercial laboratories and, in general, these methods can overestimate the amount organic carbon in soils. This is because inorganic carbon is not distinguished by the analytical method. The practitioner is directed to the methods of analysis outlined by Nelson and Sommers (1996), which will give an accurate account of soil organic carbon content. Methods such as SW-846 Method 9060A (U.S.EPA, 2004) should not be used to determine the organic carbon content of soils without modification. Additional information can found in VAP TDC document VA30007.03.019 (Ohio EPA,2003a).

If site-specific values are not determined, acceptable defaults for sand, silt, and clay are 0.2, 0.25 and 0.3, respectively.

Partitioning

Partitioning is a process in which chemicals are distributed between solid, liquid, and gas phases, depending upon solubility, sorption, and vapor pressure characteristics.

Soil Organic Carbon-Water Partitioning Coefficient

The soil organic carbon-water partitioning coefficient (Koc) is the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution. Koc values are useful in predicting the mobility of organic soil contaminants; higher Koc values correlate to less mobility chemicals, while lower Koc values correlate to more mobility. Koc values can vary greatly in the literature, and a sensitivity analysis may be needed. However, depending on the regulated program, Ohio EPA will generally accept the values listed in Table 3 of the Division of Hazardous Waste Management, Closure Review Guidance (2006), or the Division of Emergency and Remedial Response, Voluntary Action Program, Support Document for Development of Generic Numeric Standards and Risk Assessment (Ohio EPA, 2002).

The coefficients presented in these papers are not applicable for situations where mobilization is from enhanced solvation. The Kd values presented assume that relatively dilute solution conditions are present, that a narrow range of soil moisture content is applicable and that a consistent range of soil organic matter is present. If these basic assumptions are not met, site-specific determination of the leaching of inorganic substances is warranted.

Distribution Coefficient

Distribution coefficient (Kd) is the ratio of a chemical's sorbed concentration (mg/kg) to the dissolved concentration (mg/L) at equilibrium. For organics, Kd may be calculated by multiplying Koc (the soil organic carbon-water partitioning coefficient) by the fraction of organic carbon (foc):

$$Kd = Koc \times foc$$

For metals, acceptable values for several metals can be found in Table 3 of Ohio EPA’s, Division of Hazardous Waste Management, Vadose Zone Modeling for RCRA Closure (Ohio EPA, 2003b).

Relative Solubility

Relative solubility controls whether a contaminant exists in ground water primarily as a dissolved (soluble) or free liquid phase (insoluble). Movement of the dissolved phase is generally in the direction of flow and is governed primarily by the processes of advection-dispersion and biological/chemical attenuation. Literature values are generally acceptable for solubility and the values provided in guidance listed under the Koc section are acceptable.

Henry’s Law Constant

At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. Note that care should be taken to determine the units of Henry’s Law constant. Some models require the term to be in m^3-atm/mol while other models require it to be dimensionless.

Variation of Henry's Law constant can affect model results. The high Henry's Law constant of some volatile organics controls volatilization in the subsurface, dominating other pollutant loss mechanisms. Hence, a slight change may affect the model. However, Henry's Law constants do not vary to a great degree as reported in literature. For ground water and subsurface fate and transport models, acceptable default values are listed in Table 3 of the Division of Hazardous Waste Closure Review Guidance (Ohio EPA, 2006), or the Division of Emergency and Remedial Response, Voluntary Action Program, Support Document for Development of Generic Numeric Standards and Risk Assessment (Ohio EPA, 2002).

Degradation

Degradation of contaminants in the environment can be biotic (biologically mediated) or abiotic (chemical reaction). It accounts for the loss of a pollutant and the formation of daughter products. If the degradation process is accounted for, but not properly justified, predicted concentrations of a pollutant could be underestimated. Likewise, if degradation is occurring, but not accounted for, daughter products, which may be more toxic than the parent compound, may not be properly addressed.

Many models incorporate degradation as a first order decay rate. The user is responsible for demonstrating whether degradation is occurring, what degradation products will form, and the significance of the degradation products

Literature values for biodegradation rates are highly variable and are often based on laboratory testing or in field conditions where the factors affecting biodegradation can be controlled. The *Committee on In Situ Bioremediation*[1] recommends that the effectiveness of intrinsic bioremediation should be continually monitored by analyzing the fate of the contaminants and other reactants and products indicative of bioremediation. This monitoring includes three types of information: documented loss of contaminants from a site, laboratory assays showing that the microorganisms from site samples have the potential to transform contaminants under the expected site conditions, and confirming evidence that the biodegradation potential is actually realized in the field. Additional information on biodegradation can be found in ASTM E1943-98 (2004), US EPA, (1998), ITRC (1999), and

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[1] The Committee on In Situ Bioremediation was established in 1992 with the specific task of developing guidelines for evaluating in situ bioremediation projects and determining whether they are or will meet clean-up goals. It represents the span of groups involved in bioremediation: buyers of bioremediation services, bioremediation contractors, environmental regulators, and academic researchers.

NRC (2000). The user should consult with the regulatory program to determine whether literature values of degradation are acceptable and if so, how they can be applied.[1]

Source Size

Sufficient data needs to be collected to adequately determine or estimate the source or plume size both vertically and spatially.

Initial (concentration) Inputs

Initializing the plume concentration needs to be assessed. Whether to use the maximum or average may be dependent on the purpose of the model, amount of data, and the complexity of the chosen model. It is recommended that the user consult with the regulatory program to develop an acceptable approach.

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[1] For RCRA Closures, the Division of Hazardous Waste Management will not accept literature values for biodegradation of organic chemicals. If biodegradation rates are included in a model, site-specific data, including the methods used, number of samples, and laboratory data reports must be supplied to verify these inputs. For DERR/VAP properties see TDC document VA 30007.97.004 (Ohio EPA, 1997).

APPENDIX A
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APPENDIX C
PADEP TECHNICAL GUIDANCE MANUAL (PADEP TGM): SECTION III AND APPENDIX A

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SECTION III: TECHNICAL AND PROCEDURAL GUIDANCE

A. Fate and Transport Analysis

Fate and transport analyses required under Act 2 may involve a wide spectrum of predictive assumptions, calculations and simulations, ranging from the simple to the complex, depending on the hydrogeologic characteristics of a site, future use scenarios, and the selection/applicability of a particular cleanup standard.

Fate and transport analysis or modeling is a necessary part of site characterization and demonstrating attainment of an Act 2 standard. However, the Chapter 250 regulations governing Act 2 use the term "fate and transport analysis" as opposed to "fate and transport model." This particular distinction was made because it will not always be necessary to run an analytical or numerical quantitative "fate and transport model" to achieve a standard.

Whether simple or complex, any fate and transport analysis must rely on having and/or obtaining valid data. Reliable field data will be critical in supporting the professional conclusions regarding any predictions of contaminant fate and transport and needs to be considered during the site characterization.

Fate and transport analysis will be used in the Act 2 process to predict contaminant concentrations migrating through the unsaturated zone and the saturated zone, including the impact of soil contamination on groundwater. It will also include an analysis of diffuse groundwater flow into surface water (e.g., a stream) for purposes of determining compliance with surface water quality standards.

Generally, fate and transport analyses under Act 2 may be used for the following purposes:

- To predict the concentrations of one or more contaminants at one or more locations in the future, often at a specific time (e.g., 30 years).
- To assess potential remediation alternatives.
- To evaluate natural attenuation remedies and associated monitoring requirements.
- To assure continued attainment of the relevant standard.
- To estimate groundwater chemical flux used in mass balance calculations for attainment of surface water standards.
- To assess postremediation care requirements and termination.

Furthermore, fate and transport analysis is used in specific ways under the three remediation standards.

BACKGROUND STANDARD

- To justify reduced duration for monitoring of upgradient release.

- To combine the background groundwater standard with non-background soil standards.

- To assess the impact of transformations in the upgradient plume.

STATEWIDE HEALTH STANDARD

- To justify reduced duration of attainment monitoring at the point of compliance.

- To complete the equivalency demonstration for soil-to-groundwater attainment.

- To predict the extent of contamination above the standard in off-property nonuse aquifers.

- To demonstrate attainment of the used aquifer standard at a point 1,000 feet downgradient from the point of compliance (POC) for the nonuse aquifer standard.

- To demonstrate compliance with surface water standards where there is diffuse groundwater flow to surface water.

SITE-SPECIFIC STANDARD

- To identify current completed pathways and related exposures.

- To predict future completed pathways and related exposures.

- To demonstrate pathway elimination.

- To establish numerical site-specific risk-based standards.

- To demonstrate compliance with surface water standards where there is diffuse groundwater flow to surface water.

When applicable, the fate and transport analysis should also consider the degradation of a particular chemical compound(s) into one or several “breakdown” compounds. This can occur in the unsaturated or saturated zone at or below the point of release of a particular compound of concern, or downgradient in the chemical plume. An example may include a scenario involving a release of trichloroethylene from an upgradient source which has entered the saturated zone and migrated downgradient under a site seeking a release under the background standard. The site in question may exhibit dichloroethylene and vinyl chloride in wells on its property, but it also may have never used chlorinated compounds. In this case, the remediator may be able to demonstrate that there was no release of the regulated substance on the property and use fate and transport analysis to demonstrate that the constituents result from breakdown of compounds from the upgradient release.

1. Fate and Transport Analysis in the Unsaturated Zone

a) General

In lieu of using the soil-to-groundwater medium-specific concentrations (MSCs) from Tables 3 and4 in Appendix A of Chapter 250 as the Statewide health standards (SHS), a person may also perform a site-specific demonstration. The site-specific demonstration can be used to show that contaminant levels in soil exceeding the SHS for one or more contaminants at that site are protective of groundwater. Such a demonstration requires the use of fate and transport models, equations, algorithms, or methods (hereafter "analytical tools") applied to contaminants in the soil of the unsaturated zone and may also include the use of groundwater fate and transport analytical tools (e.g., using the results of an unsaturated zone transport demonstration as input into a groundwater fate and transport analysis).

The unsaturated zone fate and transport analytical tools may be very simple equations requiring minimal input or may be more complex models requiring much more detailed input. The choice of the analytical tool or tools used in making site-specific demonstrations for contaminants in unsaturated zone soil should be appropriate to the circumstances of the site. At a minimum, the analytical tools used in making demonstrations in the unsaturated zone should include certain contaminant-specific and site-specific parameters. Other parameters may also be necessary depending on the analytical tools being used and the overall goal of the demonstration. In addition, the analytical tools and parameter input values themselves are subject to certain conditions.

b) Minimum Contaminant-Specific and Site-Specific Requirements

With very few exceptions, the analytical tools currently available for unsaturated zone contaminant fate and transport demonstrations are based on equilibrium partitioning equations. The equations that have been used in estimating the soil-to-groundwater MSCs and the soil buffer distances in Tables 3 and 4 in Appendix A of the regulations are equilibrium partitioning equations. These equations can be used in a variety of different types of analytical tools. Depending on the analytical tool being used, other parameter input values may be necessary. At a minimum, input values are needed for each of the following parameters for any unsaturated zone analytical tool:

i) Contaminant-Specific Requirements for All Analytical Tools

- K_{oc} in L/kg or mL/g (for organic compounds only): this is the organic carbon partition coefficient. Values for this parameter for listed organic regulated substances can be found in Table 5A in Appendix A of the regulations or in scientific literature. For organic compounds not listed in Appendix A of the regulations, values can be found in literature. K_{oc} estimation methods (based on other parameters such as aqueous solubility, octanol-water partition coefficient, bioconcentration factor, and molecular structure) are also available in literature.

- K_d in L/kg or mL/g (primarily for inorganic contaminants and, in some instances, organic compounds): this is the soil-to-water partition coefficient. Values for this parameter for listed inorganic regulated substances can be found in Table 5B in Appendix A of Chapter 250. Some K_d values for inorganic contaminants can also be found in scientific literature. In many instances, it may be necessary to estimate K_d values based on soil analytical data at a particular site. This can be done by using total contaminant concentrations in soil in conjunction with leachable concentrations. Generally, the K_d values for organic compounds are estimated from K_{oc} values and the fraction of organic carbon in soil (f_{oc} - which is discussed later) or by using total contaminant concentrations in soil in conjunction with leachable concentrations. If K_d values are estimated in this manner, it is not necessary to include or use a K_{oc} value for the organic compound.

- C_{soil} in mg/kg: This is the dry weight concentration of a regulated substance or contaminant in soil which is determined through use of the site characterization data (if the demonstration is being done to show that groundwater is protected under current site conditions) or which is used as input (on a trial-and-error basis) to estimate a concentration in soil that would be protective of groundwater.

ii) Site-Specific Requirements for All Analytical Tools

- **θ_w** (dimensionless): This is the water-filled porosity of the unsaturated zone soil. Appropriate values for this parameter generally range from 0.05 to 0.15 for sandy soils to 0.26 to 0.45 for clays. A default value of 0.2 has been used in the estimation of the soil to groundwater MSCs in Tables 3 and 4 in Appendix A of the Chapter 250 regulations.

- **ρ_b** in kg/L or g/mL: This is dry bulk density of unsaturated zone soil. Appropriate values for this parameter generally range from 1.3 to 2.0 for silts and clays to 1.6 to 2.2 for sandy soils to 1.8 to 2.3 for gravelly soils. A default value of 1.8 has been used in the estimation of the soil to groundwater MSCs in Tables 3 and 4 in Appendix A of the regulations.

- **f_{oc}** (dimensionless): This is the fraction of organic carbon in unsaturated zone soil. This parameter applies only to demonstrations being done for organic compounds where the K_{oc} values for the compounds are being used. For demonstrations for organic compounds where K_d is being estimated or determined by a means other than use of K_{oc}, this parameter is not needed.

Typical values for this parameter range from 0.001 to 0.006 for subsurface soils to 0.01 to 0.03 for topsoil. A default value of 0.0025 has been used in the estimation of the soil to groundwater MSCs in Table 3b in Appendix A of the regulations. A value of 0.005 has been used in estimation of the soil to groundwater buffer distances in Table 3B in Appendix A of the regulations.

iii) Additional Requirements

The simplest unsaturated zone analytical tools are those that estimate contaminant concentrations in unsaturated zone soil pore water from equilibrium partitioning equations and utilize these aqueous concentrations as source input into a groundwater fate and transport analysis. Actual transport through the unsaturated zone is not estimated with this type of analytical tool. This type of unsaturated zone analytical tool would require input data for only those parameters discussed above.

Another type of unsaturated zone analytical tool that is commonly used and is more complex is one that estimates the migration of contaminants through the unsaturated zone. These are generally either infinite source or finite source analytical tools. Both are more complicated than the one previously discussed and, as such, require additional parameter input values. Both of these analytical tools require the vertical depth to groundwater or bedrock from the contaminated soil as well as a water recharge rate so that pore water velocity can be estimated. An unsaturated zone finite source analytical tool is particularly useful in demonstrating how long it will take a contaminant to migrate from unsaturated zone soils to groundwater (if at all) and what the contaminant concentration (including the maximum concentration) will be in soil or soil pore water at various depths and at various times as migration occurs. Finite source models generally require input values for additional parameters such as values for C_{soil} at different depths from the surface of the unsaturated zone. This can ensure that mass balance constraints are met, i.e., the analytical tool will not estimate migration of a greater mass of contaminant than the amount that was originally in the source soil. The **BUFFER1.XLS** spreadsheet model is available on the DEP website to assist in performing this modeling.

In addition, more complex unsaturated zone analytical tools can take into account other mechanisms that would affect the vertical migration of contaminants toward groundwater. These mechanisms are generally ones that result in loss of the contaminant through time, meaning that additional input values are required. Two loss mechanisms are biodegradation and volatilization. Analytical tools that consider biodegradation require either a degradation rate constant (in units of reciprocal time) or a half-life value (in units of time). In rare circumstances, an analytical tool may consider loss from volatilization. This would require a volatilization rate constant which can be calculated from several other parameters (such as Henry's constant, vapor pressure, aqueous solubility, other partition coefficients as well as soil property data) or can be estimated using onsite analytical data.

c) Conditions for Use of Analytical Tools and Parameter Input Values

Dozens of unsaturated zone analytical tools exist in the public domain, most of which are based on equilibrium partitioning between the solid soil matrix and the soil pore water. As such, most of these analytical tools are very similar with respect to the parameters that require input values. In order to ensure validity of the results of all unsaturated zone demonstrations submitted to the Department, the following conditions should be met:

- Analytical tools used for unsaturated zone transport demonstrations should be based on equilibrium partitioning concepts when possible. Although analytical tools based on other concepts (such as metal speciation and non-equilibrium desorption) exist and may be technically valid, their use could cause significant delays in Department review time.

- The source of all values for all required input parameters (K_{oc}, K_d, C_{soil}, θ_w, ρ_b, f_{oc}) should be provided. All data used as input for C_{soil} should be representative of the area for which the demonstration is being made and should meet all site characterization requirements.

- If analytical tools require input values for water recharge rate and vertical depth to groundwater, the sources of those values should be provided.

- Any degradation rate constant or half-life used in any unsaturated zone analytical tool should be based on site-specific data. Well-documented degradation constants and half-life values may be used from the literature or other studies only when it can be shown that the conditions at the site are clearly similar to those from which the degradation rate constant or half-life came. In addition, degradation products which may be toxic (such as those from chlorinated alkenes) should be considered in the demonstration. If these conditions are not met, the degradation rate constant should be assumed to be zero.

- Any unsaturated zone analytical tool that incorporates loss of contaminant from volatilization processes should base the volatilization rate constant on volatilization data for soils existing at the site. Otherwise, loss due to volatilization should be assumed to be zero.

- Any unsaturated zone analytical tool should be used only for soils in the unsaturated zone and should not be used for saturated zone soils or bedrock.

- For any unsaturated zone analytical tool that links to groundwater by means of dilution directly under the area of contaminated soil, the entire aquifer depth directly under the soil should not be used in dilution calculations, i.e., as a mixing zone. The mixing zone should be calculated based on specific site parameters such as pore water velocity, groundwater velocity and direction, depth of the entire aquifer under the site, and areal extent of soil contamination.

d) Conclusion

This guidance is being provided to aid any person who is submitting results of a fate and transport analysis for the unsaturated zone to do so in a manner that will ensure validity of the analysis as well as timely and efficient review by the Department. There are many unsaturated zone analytical tools available in the public and private domains. Some of these are extremely complex, difficult to use, and not readily available to Department staff while others are fairly simple, easy to use, and are readily available to the Department. For unsaturated zone fate and transport analysis submissions that rely on concepts other than equilibrium partitioning (such as metal speciation and non-equilibrium desorption), adequate supporting documentation must be submitted to the Department.

2. Fate and Transport Analysis in the Saturated Zone

This section provides guidelines for the application of fate and transport analysis in the saturated zone. As stated above, a “fate and transport analysis” is not necessarily a highly complex computer simulation. It can be a range of analyses, based on physical, structural, chemical and hydraulic factors. It is based on professional judgment and may need to include the use of simulations.

Elements of fate and transport analysis include:

GROUNDWATER FLOW

- Direction
- Velocity
- Boundaries

CHEMICAL FATE AND TRANSPORT MECHANISIMS

- Leaching/dissolving
- Adsorption/desorption
- Matrix diffusion
- Degradation/transformations/reactions
- Volatilization
- Precipitation

- Phase behavior

Depending on the characteristics of the site and the type of standard/remediation selected, the fate and transport analysis can range from the simple to the complex, which can span from qualitative “empirical” or simple conceptual models, up to quantitative simulation (analytical and numerical) models.

Simple descriptive or conceptual models may be either qualitative or quantitative. A particular example under this scenario might be a facility seeking a release of liability under the background standard. This facility (facility “A”) is downgradient from facility “B,” which has caused a release of a contaminant to groundwater. The fate and transport analysis required under Section 250.204(f)(5) of the regulations could conceivably be a simple qualitative demonstration of a conceptual site model which employs the use of monitoring well data/measurements to clearly establish that facility “A” is hydraulically downgradient of facility “B.” Data requirements would include water level measurements from a sufficient number of properly located monitoring wells and establishing the hydraulic gradient. Note, however, that simple scenarios such as this can easily become more complicated by other factors including water level fluctuations, pumping influences of wells, etc., which could require a more detailed quantitative fate and transport analysis.

Another scenario could involve the use of simple extrapolation in predicting groundwater plume movement or its relative stability over time. If groundwater monitoring samples have been collected over a sufficiently long period of time, and the information consists of reliable data, then certain predictions can be made using professional judgment as to aspects of plume behavior. For example, monitoring over a number of years may indicate that the contaminant plume has exhibited no movement over that time. In this case, the use of professional judgment involving simple extrapolation of the data may be a sufficient fate and transport analysis. The conclusion could be made, based on the above merits, that the plume has reached a steady-state condition and would not migrate further downgradient. In this case it may also be possible to determine that downgradient surface water quality criteria may be met even though the concentrations in the groundwater plume exceed the MSCs.

Quantitative fate and transport analysis may be needed in more complex situations, where a demonstration of attainment would require additional data and calculations.
One example might be a facility seeking to demonstrate that very low groundwater velocities in bedrock would preclude contaminated groundwater from the facility from reaching the property boundary/POC. Data requirements in this case would need to include calculation of hydraulic gradient, determination of hydraulic conductivity, estimation/measurement of effective porosity, and calculation of groundwater velocity. Note that this somewhat simple example could evolve into a more detailed quantitative or simulated model given a variety of complicating factors, such as saturated flow in soil, preferential fracture flow, etc. Another example of this type may be a demonstration of groundwater discharge into a natural flow boundary, as in the case of a facility located adjacent to a large river sustained by regional groundwater discharge. While in some cases this might be a qualitative analysis, in other cases there would be a need to

determine both vertical and horizontal gradients to demonstrate the stream is in fact a discharge feature and not losing flow to the surrounding terrain.

Quantitative analysis may involve the use of more complicated fate and transport tools involving various analytical equations up to the more complex numerical simulations of groundwater flow, which collectively can help determine the spread of contamination in a plume and predict its fate and concentration at specific future times and locations. The simpler analytical equations are more appropriate where more uniform aquifer conditions exist and there are no complex boundary conditions. An example might be a facility seeking a release under Act 2 which is underlain by alluvium near a stream. Analytical fate and transport equations can be used to help determine the concentration of a groundwater contaminant at a downgradient location. In many cases the simple empirical examples mentioned above may need to employ analytical equations, as conditions warrant, to account for dilution, attenuation, degradation, and other physical and chemical factors in contaminant fate and transport.

Numerical simulations are the most complex models used under the provisions of fate and transport analysis under Act 2. They generally require use of a computer software model due to the number of simultaneous equations to be solved. They are most applicable where predictions of groundwater contamination need to be made at certain locations in the future (e.g., property boundary, 1,000 feet downgradient from property boundary, etc.), at sites which exhibit more heterogeneous geologic/hydrogeologic characteristics and more complex boundary conditions (which are common in Pennsylvania). As such, they will be useful tools for a variety of sites where such predictions are required to demonstrate attainment of an Act 2 standard.

a) Groundwater Solute Fate and Transport Modeling (General)

The Department recommends that those with appropriate academic training and practical experience in the field conduct fate and transport analysis, especially if it involves more complex numerical models.

Except in cases where it is unnecessary to project or predict contaminant concentrations in groundwater at various locations into the future, some sort of quantitative fate and transport analysis such as groundwater modeling will very likely be needed.

Some considerations:

- All models rely on input parameters that vary because of inherent heterogeneity and anisotropy of the aquifer.

- Some of the required input parameters such as dispersivity are not measured and need to be determined by model calibration to accurate isoconcentration contour maps.

- Some important information such as the date of the release and mass involved is often difficult to pin down.

All of the above creates uncertainty that needs to be considered in how the results of any model are used and their reliability. The uncertainty associated with models can and should be reduced by collecting site-specific data for certain input parameters that are representative of subsurface conditions.

Accurate isoconcentration contour maps of each parameter of concern, which are constructed from data collected during the site characterization phase of the remedial action, are especially important. These maps are the calibration targets of the model. Adequate data to determine if a plume exhibits a centerline, and, if so, its location and associated concentrations is fundamental to a fate and transport analysis. It is good practice to install several transects (lines of wells) downgradient from the source and perpendicular to the direction of groundwater flow to accurately find and define any plume centerline and the spread of contamination away from the centerline.

The following data are the minimum input requirements of many models, both analytical and numerical. The following data should be derived from measurements made at the site:

- Source Geometry and Concentration
- Hydraulic conductivity
- Hydraulic gradient
- Natural fraction of organic carbon in the aquifer
- Porosity

The following additional parameters are also often involved:

- Time source active – this is a very important parameter in calibrating any model if transient plume conditions are suspected or involved and can be one of the hardest to pin down unless good historical records are available.
- K_{oc} – this value can be obtained from Appendix A-Table 5A of Chapter 250.
- Lambda – this measure of biodegradation (as first order decay) varies from site to site for each compound and is usually determined by model calibration, or sometimes calculated from plume centerline data. Published values such those in Appendix A, Table 5A of Chapter 250 should not be relied on as default values for site-specific modeling.
- Soil Bulk Density – often estimated as (2.65 g/cm^3)(1-porosity).
- Dispersion – this parameter is used to simulate the spread of contaminants in one, two, or three dimensions. Values are often initially derived using

several published “rules of thumb” and then adjusted during model calibration to fit plume isoconcentration contours.

After selection of the best values for input parameters, the model is run and compared to the plume geometry portrayed by isoconcentration maps of each parameter of concern. Adjustments may be needed for certain parameters such as lambda, dispersion or others within reasonable ranges to obtain a better match to site data. Measured site data should be utilized in conjunction with initial modeling results to further calibrate the model using to ensure the most accurate predictive results. Modeling efforts associated with a postremediation care plan under an Act 2 standard should include a test of the predictive accuracy of the model by comparing predictions to a future data set sometimes referred to as a “post-audit,” followed by recalibration and retesting, if needed.

Readers are referred to ASTM Standard Guide D 5447-04 (2010) for an overview of the basic elements involved in groundwater flow modeling effort. The same general principles apply to fate and transport modeling. Since the ASTM Standard Guide 5447-04 (2010) is intended as a general guide, covering both analytical and numerical models, all elements discussed may not be applicable to every modeling situation.

b) Define Study Objectives

In all cases the site characterization should be conducted with the objective of providing the data necessary to demonstrate attainment of an Act 2 standard. Prior to any computer modeling, an initial conceptual model of local hydrogeologic conditions should be developed. The results of the characterization/initial conceptual site model will influence what kind of fate and transport model, if any, should be used, as well as many of the values for the input parameters to that model. Some models require certain kinds or quantities of data which is good to know ahead of time. To some extent this will be an iterative process. As data are collected and evaluated, the selected Act 2 remediation standard may change, and areas where additional data are needed may be identified.

The acceptable tolerances for model calibration should also be defined in the study objectives.

c) Data Collection

The data used for groundwater fate and transport modeling will come from the site characterization, attainment monitoring, and in some cases, values published in scientific literature or Table 5 in Appendix A to the regulations. Examples of data that may need to be obtained from published values include first-order decay coefficients and equilibrium partitioning coefficients. Once obtained, these values may need to be adjusted within reasonable ranges to calibrate a model to site conditions. Examples of data which should be obtained from the site characterization, to name a few, include hydraulic conductivity, gradients, porosity, organic carbon content and chemical concentrations. Some parameters such as dispersion coefficients, which are not available from the literature or site characterization work, initially need to be estimated according to basic assumptions and then adjusted during model calibration to match actual plume shape and concentration data.

d) Conceptual Model

As stated in ASTM D 5447, “the purpose of the conceptual model is to consolidate site and regional hydrogeologic and hydrologic data into a set of assumptions and concepts that can be evaluated quantitatively.” The conceptual model of the site will emerge from the data collected during the site characterization. The site characterization work should be designed to assure that the quantity and kind of data collected will, in the end, be sufficient for justifying and completing the fate and transport analysis. Elements important to developing the conceptual model of the site for any fate and transport analysis include geologic, hydrologic, hydraulic and contaminant data (note that these are common elements of some of the non-numerical conceptual models discussed above). Data collection should be concentrated on the site, but offsite features that influence contaminant fate and transport on the site should not be overlooked.

i) Geologic Data

- Thickness, continuity, lithology, and structural features of consolidated geologic formations underlying the site.
- Thickness, texture, density, and organic carbon content of soil and unconsolidated units.
- Information from review of published reports on the geology and soils of the site and nearby areas, or previous work at the site.
- Information from any additional investigation needed to confirm or refine existing data such as wells, borings, and backhoe pits, and possibly geophysical methods.

ii) Hydrologic Data

- Water levels, hydraulic gradients and groundwater flow directions, including seasonal variations; determining seasonal variations in hydrologic data are extremely important for conceptual site model development. Seasonal variations in hydrologic data are site dependent and may not exist at every Act 2 site. Conceptual site model development as well as fate and transport analysis should take into account any seasonal variations that may exist at an Act 2 site.
- The presence and magnitude of vertical gradients at the site.

- Recharge and discharge boundaries relevant to the site including groundwater divides, streams, and drains.

- Sources and sinks, e.g., characteristics of any pumping or injection wells, artificial recharge, ponds, etc.

- The presence of any confining units.

- For bedrock aquifers, the degree to which the aquifer system departs from assumptions regarding flow in porous media.

- Data from review of available information as well as drilling of wells, borings and piezometers, and water level measurements over regular intervals.

iii) Hydraulic Data

- Hydraulic conductivity and transmissivity data for consolidated and unconsolidated deposits.

- Porosity, effective porosity estimates, and storativity.

- The degree to which the aquifer(s) depart from assumptions of isotropy or homogeneity.

- The degree of interconnection between different aquifer units and leakage characteristics between different water-bearing units.

- Hydraulic data often is not available at the level of detail necessary and may require pumping tests on wells to determine aquifer anisotropy of bedrock systems and values for other hydraulic parameters such as transmissivity. Slug tests may suffice in bedrock wells where anisotropy is not a factor requiring consideration.

iv) Chemical and Contaminant Data

- Location, age and current status of source areas to the extent knowable.

- Types of contaminants and their chemical properties such as viscosity, solubility, biodegradability, density, toxicity, K_{oc} value, decay rate, etc.

- The magnitude and vertical and horizontal extent of contamination in soil and/or groundwater.

- Dissolved oxygen content and other electron acceptors in groundwater, if required by the model.

- Historical plume configuration based on existing monitoring data.

- Determination if the contaminant plume is at steady-state conditions or is continuing to migrate. This is a critical piece of information. Is the mass of contamination increasing, decreasing or relatively constant? This should be determined by monitoring the vertical and horizontal extent of groundwater contamination for a period of time sufficient to reveal the trend. These data will be useful in calibrating the model and making predictive simulations. In some cases, the monitoring data alone may be all that is needed to complete the fate and transport analysis, provided the monitoring record is sufficiently long.

- Review of chemicals used at the facility, which will help identify the chemicals of concern. Sampling soil, soil vapors, and groundwater from appropriately constructed monitoring wells, borings or excavations and checking for any free product will need to be performed. Geophysical methods may be useful to delineate areas needing further investigation or identifying sources.

e) Model Selection

When the site characterization is completed, and the conceptual model has been developed, selection of an appropriate model can be made. At sites where there is little variation in conditions over the model domain, with a simple plume geometry or conceptual model, relatively simple analytical models should be employed. At sites where the site characterization has determined significant variation in important parameters, or where more complex questions are being asked, a more sophisticated numerical solution may be needed.

The Department has prepared two spreadsheets that may be useful in completing a fate and transport analysis. All spreadsheets are based on the following equation:

$$C(x,y,z,t) = \left(\frac{C_o}{8}\right)\exp\left\{{}^{x}\!/_{2\alpha_x}\left[1-\left(1+{}^{4\lambda\alpha_x}\!/_{v}\right)^{\frac{1}{2}}\right]\right\} erfc\left\{\left[x - vt\left(\sqrt{1+4\lambda\alpha_{x}/v}\right)\right]/\,2\sqrt{\alpha_x vt}\right\}$$

$$\left\{erf\left[\left(y+Y/2\right)/\,2\sqrt{\alpha_y x}\right] - erf\left[\left(y-Y/2\right)/\,2\sqrt{\alpha_y x}\right]\right\}\left\{erf\left[\left(z+Z/2\right)2\sqrt{\alpha_z x}\right] - erf\left[\left(z-Z/2\right)/\,2\sqrt{\alpha_z x}\right]\right\}$$

Reference: An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species, P.A. Domenico, 1987, Journal of Hydrology, 91, 49-58.

The two spreadsheets are:

QUICK_DOMENICO.XLS

The Quick Domenico (QD) application spreadsheet calculates the concentration anywhere in a plume of contamination at any time after a continuous, finite source becomes active. A “User’s Manual for the Quick Domenico Groundwater Fate-and-Transport Model” accompanies the spreadsheet model on the PA DEP website.

SWLOAD.XLS

This spreadsheet uses a rearrangement of the Domenico equation to calculate concentrations at different points in the cross section of a plume at any distance from a continuous finite source at any time. The concentrations are then added and multiplied by the groundwater flux and can be used to estimate the mass loading of a particular contaminant from diffuse groundwater flow to a stream or surface water body.

As mentioned above, these spreadsheets and documentation can be downloaded from the PA DEP web site under “Standards, Guidance and Procedures,” “Guidance and Technical Tools,” “Fate and Transport Analysis Tools.” These spreadsheets will not be applicable to every situation involving modeling. The remediator should thoroughly review the help documents for the spreadsheet programs to determine if the modeling spreadsheets are suitable for the situation.

f) Calibration and Sensitivity

As stated in ASTM D 5447, calibration is the process of adjusting hydraulic parameters, boundary conditions and initial conditions within reasonable ranges to obtain a match between observed and simulated potentials, flow rates or other calibration targets. In working with sites under Act 2, an obvious calibration target is matching the model output to existing, and, if known, historical geometry and concentration of plume contaminants. The Act 2 final report should include a discussion of calibration targets, and an analysis and significance of residuals (differences between modeled and actual contaminant concentrations).

Sensitivity analysis is an evaluation of which model parameters have the most influence on model results. The parameters to which the model is most sensitive should be identified. Those parameters which have the most influence on model results are those which should be given the most attention in the data collection phase.

g) Predictive Simulations

Fate and transport models may be used in the Land Recycling Program (LRP) to make predictions of future contaminant concentrations. Uses may include:

- Predicting the maximum concentrations that will occur at downgradient compliance points (usually property boundaries) for the SHS in the case of both used and nonuse aquifers.

- Predicting whether groundwater contamination above an MSC will extend beyond 1,000 feet in the case of nonuse aquifers, and if it will be at or below the MSC for groundwater in these areas within the next 30 years.

- In cases where the fate and transport analysis indicates that a standard may not be maintained at some time in the future, a postremediation care plan will be needed.

- If postremediation care is required, a "post-audit" of the fate and transport model should be performed. In a post-audit, the fate and transport model's predictions are compared to continued monitoring data collected during the postremediation care period to check the validity and accuracy of previous model predictions. Monitoring wells for the post-audit must be located at points where they would be sensitive to auditing the model. This may not coincide with the property line compliance point if the plume would not be expected to migrate to the compliance point by the time of the post-audit.

- Post-audits should be performed on the model during the attainment monitoring phase (usually a minimum of two years) as a check on model predictions.

h) Fate and Transport Model Report

With the exception of those projects which do not require submission of a fate and transport model, the following general report format should be used to the extent applicable to adequately document the modeling effort:

1.0 Introduction

  1.1 General Setting

  1.2 Study Objectives - which Act 2 standard is being demonstrated and what is the purpose of the modeling

2.0 Conceptual Model

  2.1 Aquifer System Framework

  2.2 Groundwater Flow Model

- 2.3 Hydrologic Boundaries
- 2.4 Hydraulic Boundaries
- 2.5 Sources and Sinks

3.0 Analytical Model

- 3.1 Model Selection - justification for use of analytical, numerical or other analysis
- 3.2 Model Description - name and version of analysis, model assumptions and limitations, name of organization or person which has developed the analysis

4.0 Groundwater Flow Model Construction

- 4.1 Model Grid - state if fixed by model
- 4.2 Hydraulic Parameters - state source such as field determined or literature. Cite relevant section of Site Characterization report or literature reference.
- 4.3 Boundary Conditions - state if fixed by model
- 4.4 Selection of Calibration Targets

5.0 Calibration

- 5.1 Residual Analysis
- 5.2 Sensitivity Analysis
- 5.3 Model Verification, if applicable

6.0 Predictive Simulations - Indicate relation to applicable Act 2 standard

7.0 Summary and Conclusions

- 7.1 Model Assumptions/Limitations
- 7.2 Model Predictions
- 7.3 Recommendations - including planned post-audit activities during postremediation care plan if required

8.0 Figures and Tables

8.1 Model grid or axes oriented on the site map

8.2 Input and output files

3. Impacts to Surface Water from Diffuse Flow of Contaminated Groundwater

Sections 250.309 and 250.406 of the regulations provide for determining compliance with surface water quality standards from a diffuse surface or groundwater discharge. The following types of sites that are impacted by diffuse flow of a dissolved groundwater plume into a stream need to be analyzed incorporating the methods and models of DEP's Bureau of Clean Water:

- Some sites selecting the SHS for used aquifers with a total dissolved solids (TDS) concentration of 2,500 mg/L or less;
- All sites selecting the Statewide health nonuse aquifer groundwater standard;
- All sites selecting the SHS for used aquifers with a TDS greater than 2,500 mg/L; and
- All sites selecting the site-specific standard for groundwater.

All discharges involved with a remediation should be in compliance with the provisions of Chapter 93 to demonstrate attainment of the Statewide health and site-specific standards. This includes all applicable antidegradation requirements as outlined by Chapter 93.4(a) including the protection of exceptional value and high-quality waters. Any discharges to surface water should likewise be in compliance with the provisions summarized in Chapter 93.6 (no presence of floating materials and sheens) in addition to dissolved plumes.

a) Conceptual Framework

In order to understand how to evaluate the impact of diffuse groundwater plumes on surface water quality, several important concepts must be understood. These concepts apply to evaluating impacts of groundwater plumes on surface water regardless of the standard selected.

The first is the concept of "maximum average concentration." Surface water impacts must be evaluated for the time that the "maximum average concentration" in the groundwater plume is discharging into the stream. As a plume in groundwater begins to encroach onto a stream, the average concentration entering the stream will rise, and remain steady, or then fall depending on the nature of the source (continuous or pulse). For a constant source with a decaying contaminant, the maximum average concentration to the stream occurs when the plume has reached a steady-state condition. For a constant source and non-decaying contaminant, the maximum average concentration to the stream occurs when the mass discharging into the stream equals the mass emanating from the source. For a pulse or slug source, the maximum average concentration will occur at the time the peak concentrations in the pulse (or slug) pass into the stream. The Department has prepared a spreadsheet, SWLOAD5B (SWL5B), which will calculate the “maximum average concentration” for decaying and non-decaying plumes emanating from a constant source.

A second concept to understand concerns what is termed the plume “edge criterion.” The “edge criterion” is the concentration equal or above which the maximum average concentration and associated flow will be determined for the plume in question. This is needed to assure that concentrations below the criterion will not be used and serve to dilute the average concentration and/or increase the flow in the plume to a point where any and all discharges to surface water become acceptable. The “edge criterion” is contaminant specific. The following rules should be used in establishing the “edge criterion.” These rules apply to selection of the “edge criterion” regardless of the standard selected:

- For those compounds on Table III-1 of the technical guidance manual (TGM) which have established surface water criteria, further surface water compliance evaluation is not necessary. Demonstrating that the MSC is met at the POC or groundwater/surface water interface is sufficient to address surface water concerns.

- For all other compounds, further surface water compliance evaluation is necessary.

Maximum average concentrations and flow for input into Pennsylvania’s PENTOXSD surface water mixing model should only be calculated for portions of a groundwater plume that exceed the “edge criterion” for the compound being evaluated. The Department has prepared a spreadsheet, SWL5B, which incorporates the “edge criterion” for calculating inputs to PENTOXSD for decaying and non-decaying plumes emanating from a constant source. If no portion of a plume entering a stream at the time of maximum average concentration exceeds the “edge criterion,” no further demonstration of surface water attainment is needed.

A third concept to understand is that of “maximum modeled or measured concentration.” It is important to understand that the maximum concentration being referred to by this phrase is the maximum concentration in the plume at the time and place that the maximum average concentration is discharging into the stream. Therefore, a measured concentration is inappropriate, and a modeled concentration should be used in cases where:

- The plume has not yet reached the stream;

- The plume is entering the stream, but has not yet reached its maximum average concentration; or

- The number and/or location of wells is insufficient to assure the Department that the maximum concentration has been found.

A fourth concept to understand is where the concentrations should be measured with respect to the Act 2 property line POC. If a plume discharges off the property being remediated before discharging into a stream, then the criteria for waiving a PENTOXSD analysis can be measured at the POC. If the plume discharges into a stream before leaving the property, criteria must be demonstrated along the groundwater/surface water interface where the plume is discharging.

The spreadsheet SWL5B is constructed so that the "maximum modeled concentration" is compared to the "edge criterion" for each compound and a determination is automatically made if a PENTOXSD analysis is needed. By convention, the "edge criterion" in SWL5B is defined as the threshold for waiving a PENTOXSD analysis.

Two final comments need to be made regarding the demonstration of surface water quality attainment. First, worst-case source concentration and flow associated with the source can be input directly into PENTOXSD. Doing this will avoid groundwater modeling or measuring concentrations at the POC or groundwater/surface water interface in many situations.

Secondly, anytime it can be demonstrated conclusively that the maximum concentration in a plume is less than the lowest surface water quality criteria, attainment of surface water quality can be assumed. Surface water quality criteria for specific compounds may be found in Tables 3 and 5 in 25 Pa. Code Chapter 93, Surface Water Quality Standards.

b) Mathematical Framework

The basic mass balance equation to determine the concentration of a contaminant in surface water downstream of a diffuse groundwater contaminant discharge at design flow conditions with background contaminant levels included is:

$$C_{sw} = \frac{(Q_{gw} * C_{gw}) + (Q_{sw} * Y_c * C_{bsw})}{(Q_{sw} * Y_c) + Q_{gw}}$$

where:

C_{sw} = the concentration in surface water of a contaminant of concern downstream of the nonpoint source discharge into the surface water.

Q_{sw} = the quantity of stream flow above the nonpoint source discharge into surface water.

Q_{gw} = the quantity of flow in the groundwater plume discharging into the surface water.

C_{gw} = the maximum average concentration of a contaminant in the groundwater discharging into surface water.

Y_c = the partial mix factor (decimal per cent), derived from using the PENTOXSD model.

C_{bsw} = the background concentration in surface water of a contaminant of concern above the nonpoint source discharge.

The equation for determining the allowable groundwater concentration in a plume discharging to surface water is:

$$C_{gw} = C_x + \frac{Y_c * Q_{sw} * (C_x - C_{bsw})}{Q_{gw}}$$

where:

C_x = the water quality objective (criteria value most of the time, can be site–specific).

Other variables are as listed above at design flow conditions (e.g. $Q_{7\text{-}10}$ or Q_{hm}).

For surface water bodies exhibiting tidal effects (e.g. Delaware River estuary) 1% of the $Q_{7\text{-}10}$ and Q_h flows are acceptably conservative for calculations of Q_{sw} in estuaries.

c) Application

The general procedure for applying the mathematical framework above to applicable compounds requires estimating the flow and maximum average concentration of the contaminated groundwater plume for each parameter of concern at the groundwater/surface water boundary. These values, in turn, are the discharge flow and discharge concentration values to be evaluated using the Bureau of Clean Water’s PENTOXSD model to determine if the groundwater discharge to the stream meets the applicable surface water quality criteria. Users are referred to Technical Guide 391-2000-011 and PENTOXSD for Windows (Version 2.0D) Supplemental Information for information on using the PENTOXSD model.

The analysis will involve incorporating background concentrations in surface water for certain contaminants. Users are referred to TGM 391-2000-022 (Implementation Guidance for the Determination and Use of Background/Ambient Water Quality in the Determination of Wasteload Allocations and NPDES Effluent Limitations for Toxic Substances) for information on how and when to apply background water quality data.

For steady-state plumes which have compliance points at or very near a stream, the groundwater flow and concentrations (mass load) within the plume can and should be determined from direct measurements. The mass loading of groundwater plumes which have not yet reached the stream boundary, which are not at steady state at the stream boundary, or for which data at the stream boundary are not available, must be estimated in some way (e.g. using groundwater solute transport models, or by assuming, conservatively, that the highest concentrations measured in the plume are representative of those at the stream boundary).

The general guidelines and example problems presented below in this guidance apply to single source discharge analysis. If there is more than one source of a pollutant in a stream reach, it may be necessary to evaluate the cumulative impact of these sources. The stream reach is determined by the site-specific travel times, stream flow, discharge flow dilution and potency of the pollutant as it moves downstream. The term that describes this process is “multiple source discharge.” The Bureau of Clean Water recommends that the Equal Marginal Percent Reduction (EMPR) method of allocation be used for these situations.

EMPR is a two-step process:

- Baseline Analysis: this step evaluates each contributor individually to determine if it would exceed the water quality objective by itself. This step evaluates the contributor’s currently modeled load and compares it to the water quality objective. If the modeled load is greater than the water quality objective, the modeled load is reduced to the water quality objective. A baseline value is determined for every contributor. This baseline value is either the currently modeled load or the water quality objective. This step assures that no contributor would cause an exceedance of the water quality objective by itself.

- Multiple Analysis: this step evaluates the cumulative impact of multiple sources on the stream. The analysis is carried out by systematically moving downstream, adding the baseline pollutant loads, and determining if the water quality objective is met at all locations. Through this process the critical reach of the stream can be found and any further necessary reductions from the baseline values can be made to meet the water quality objective at all points in the stream. Any further reductions from the baseline are made on an equal percentage basis.

Further information regarding the EMPR process can be found in the Technical Reference Guide for the Wasteload Allocation Program for Dissolved Oxygen and Ammonia-Nitrogen on the Bureau of Clean Water web page.

d) Statewide Health Standard in Aquifers with 2,500 mg/L TDS or Less

For certain compounds that have SHSs established in Chapter 250, simply demonstrating attainment of the residential or nonresidential SHS MSC for groundwater in used aquifers with TDS less than or equal to 2,500 mg/L at the point of compliance, or at the groundwater/surface water interface when the plume discharges to surface water prior to or instead of passing through the property line POC, will satisfy the surface water criteria attainment demonstration. This is because either the MSC is equal to or below the lowest surface water quality criterion (LSWC) or the compound in question does not have any corresponding surface water criteria at this time. These compounds are listed in Table III-1.

For all other compounds, surface water compliance analysis is required to the compound's edge criterion. These are compounds where the MSC exceeds the LSWC. In some cases, the LSWC may be much lower than the laboratory PQL. In this case, please contact the Act 2 site project officer for further guidance.

Regardless of the standard selected, whenever the maximum concentration of a regulated substance in groundwater discharging to a stream at the time of maximum mass loading to the stream is quantified at a level lower than the LSWC, further demonstration of compliance with surface water criteria is not required.

It is also important to note that if the fate and transport modeling or actual in-stream sampling show that surface water quality criteria are exceeded, the remediator may be able to demonstrate that the site-specific standard can be attained by addressing the applicable exposure pathways. This would result in a waiver of the provisions of Chapter 93 Water Quality Standards as described in Section 250.406(c)(2) of the regulations.

e) Examples

i) Example 1: Groundwater Source Very Near or Adjacent to Surface Water Discharge

A site with an accumulation of gasoline as a separate phase liquid lies immediately adjacent to a small stream. Separate phase liquid is being collected by an interceptor/skimmer system that prevents its discharge to the stream. However, a dissolved phase hydrocarbon plume with maximum concentrations of certain compounds near their solubility limit is entering the stream. The remediator has selected the site-specific standard for these contaminants and must determine if surface water criteria are met without any treatment or removal of the dissolved phase plume. Because the groundwater concentrations exceeding the lowest surface water quality criteria are entering the stream, a PENTOXSD analysis is required.

Because the site is located very near the surface water discharge point, no opportunity for dispersion or decay of the groundwater plume prior to its discharge is expected. Data from the site characterization and attainment monitoring wells is assumed here to allow an accurate estimate of the quantity and concentration of the groundwater plume entering the stream, without any need for fate and transport modeling of groundwater. The following characteristics of the groundwater plume have been determined:

Plume (source) width: 100 feet

Plume depth: 10 feet

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
ACENAPHTHYLENE	208-96-8
ACEPHATE	30560-19-1
ACETALDEHYDE	75-07-0
ACETONITRILE	75-05-8
ACETOPHENONE	98-86-2
ACETYLAMINOFLUORENE, 2-(2AAF)	53-96-3
ACROLEIN	107-02-8
ACRYLIC ACID	79-10-7
ALACHLOR	15972-60-8
ALDICARB	116-06-3
ALDICARB SULFONE	1646-88-4
ALDICARB SULFOXIDE	1646-87-3
ALLYL ALCOHOL	107-18-6
ALUMINUM	7429-90-5
AMETRYN	834-12-8
AMINOBIPHENYL, 4-	92-67-1
AMITROLE	61-82-5
AMMONIUM SULFAMATE	7773-06-0
ANILINE	62-53-3
ANTHRACENE	120-12-7
ARSENIC	7440-38-2
ASBESTOS	12001-29-5
ATRAZINE	1912-24-9
AZINPHOS-METHYL (GUTHION)	86-50-0
BARIUM AND COMPOUNDS	7440-39-3
BAYGON (PROPOXUR)	114-26-1
BENOMYL	17804-35-2
BENTAZON	25057-89-0
BENZO(G,H,I)PERYLENE	191-24-2
BENZOIC ACID	65-85-0
BENZOTRICHLORIDE	98-07-7
BENZYL ALCOHOL	100-51-6
BERYLLIUM	7440-41-7
BETA PROPIOLACTONE	57-57-8
BIPHENYL, 1,1-	92-52-4
BIS(2-CHLOROETHOXY)METHANE	111-91-1
BIS(2-CHLOROISOPROPYL)ETHER	108-60-1
BIS(CHLOROMETHYL)ETHER	542-88-1
BISPHENOL A	80-05-7
BROMACIL	314-40-9

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
BROMOCHLOROMETHANE	74-97-5
BROMOMETHANE	74-83-9
BROMOXYNIL	1689-84-5
BROMOXYNIL OCTANOATE	1689-99-2
BUTADIENE, 1,3-	106-99-0
BUTYL ALCOHOL, N-	71-36-3
BUTYLATE	2008-41-5
BUTYLBENZENE, N-	104-51-8
BUTYLBENZENE, SEC-	135-98-8
BUTYLBENZENE, TERT-	98-06-6
CAPTAN	133-06-2
CARBARYL	63-25-2
CARBAZOLE	86-74-8
CARBOFURAN	1563-66-2
CARBON DISULFIDE	75-15-0
CARBOXIN	5234-68-4
CHLORAMBEN	133-90-4
CHLORIDE	7647-14-5
CHLORO-1, 1-DIFLUOROETHANE, 1-	75-68-3
CHLORO-1-PROPENE, 3- (ALLYL CHLORIDE)	107-05-1
CHLOROACETALDEHYDE	107-20-0
CHLOROACETOPHENONE, 2-	532-27-4
CHLOROANILINE, P-	106-47-8
CHLOROBENZENE	108-90-7
CHLOROBENZILATE	510-15-6
CHLOROBUTANE, 1-	109-69-3
CHLORODIFLUOROMETHANE	75-45-6
CHLOROETHANE	75-00-3
CHLORONITROBENZENE, P-	100-00-5
CHLOROPHENOL, 2-	95-57-8
CHLOROPRENE	126-99-8
CHLOROPROPANE, 2-	75-29-6
CHLOROTHALONIL	1897-45-6
CHLOROTOLUENE, O-	95-49-8
CHLOROTOLUENE, P-	106-43-4
CHLORPYRIFOS	2921-88-2
CHLORSULFURON	64902-72-3
CHLOROTHAL-DIMETHYL (DACTHAL) (DCPA)	1861-32-1

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
CHROMIUM, TOTAL	7440-47-3
COPPER	7440-50-8
CRESOL, DINITRO-O-4,6-	534-52-1
CRESOL(S)	1319-77-3
CRESOL, O-(METHYLPHENOL, 2-)	95-48-7
CRESOL, M (METHYLPHENOL, 3-)	108-39-4
CROTONALDEHYDE	4170-30-3
CROTONALDEHYDE, TRANS-	123-73-9
CUMENE (ISOPROPYL BENZENE)	98-82-8
CYANAZINE	21725-46-2
CYCLOHEXANE	110-82-7
CYCLOHEXANONE	108-94-1
CYFLUTHRIN	68359-37-5
CYROMAZINE	66215-27-8
DI(2-ETHYLHEXYL)ADIPATE	103-23-1
DIALLATE	2303-16-4
DIAMINOTOLUENE, 2-4-	95-80-7
DIBENZOFURAN	132-64-9
DIBROMO-3-CHLOROPROPANE, 1,2-	96-12-8
DIBROMOBENZENE, 1,4-	106-37-6
DIBROMOETHANE, 1,2- (ETHYLENE DIBROMIDE)	106-93-4
DIBROMOMETHANE	74-95-3
DICAMBA	1918-00-9
DICHLORO-2-BUTENE, 1,4-	764-41-0
DICHLORO-2-BUTENE, TRANS-1, 4-	110-57-6
DICHLOROACETIC ACID	79-43-6
DICHLOROBENZENE, P	106-46-7
DICHLORODIFLUOROMETHANE (FREON 12)	75-71-8
DICHLOROETHANE, 1,1-	75-34-3
DICHLOROETHYLENE, 1,1-	75-35-4
DICHLOROETHYLENE, TRANS-1,2-	156-60-5
DICHLOROPHENOL, 2,4-	120-83-2
DICHLOROPHENOXYACETIC ACID, 2,4- (2,4-D)	94-75-7
DICHLOROPROPANE, 1,2-	78-87-5
DICHLOROPROPIONIC ACID, 2,2- (DALAPON)	75-99-0
DICHLORVOS	62-73-7

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
DICYCLOPENTADIENE	77-73-6
DIFLUBENZURON	35367-38-5
DIISOPROPYL METHYLPHOSPHONATE	1445-75-6
DIMETHOATE	60-51-5
DIMETHOXYBENZIDINE, 3,3-	119-90-4
DIMETHRIN	70-38-2
DIMETHYLAMINOAZOBENZENE, P-	60-11-7
DIMETHYLANILINE, N,N-	121-69-7
DIMETHYLBENZIDINE, 3,3-	119-93-7
DINITROBENZENE, 1,3-	99-65-0
DINOSEB	88-85-7
DIOXANE, 1,4-	123-91-1
DIPHENAMID	957-51-7
DIPHENYLAMINE	122-39-4
DIQUAT	85-00-7
DISULFOTON	298-04-4
DITHIANE, 1,4-	505-29-3
DIURON	330-54-1
ENDOSULFAN	115-29-7
ENDOSULFAN SULFATE	1031-07-8
ENDOTHALL	145-73-3
EPICHLOROHYDRIN	106-89-8
ETHEPHON	16672-87-0
ETHION	563-12-2
ETHOXYETHANOL, 2- (EGEE)	110-80-5
ETHYL ACETATE	141-78-6
ETHYL ACRYLATE	140-88-5
ETHYL DIPROPYLTHIOCARBAMATE, S- (EPTC)	759-94-4
ETHYL ETHER	60-29-7
ETHYL METHACRYLATE	97-63-2
ETHYLENE CHLORHYDRIN	107-07-3
ETHYLENE GLYCOL	107-21-1
ETHYLENE THIOUREA (ETU)	96-45-7
ETHYLP-NITROPHENYL PHENYLPHOSPHOROTHIOATE	2104-64-5
FENAMIPHOS	22224-92-6
FENVALERATE (PYDRIN)	51630-58-1
FLUOMETURON	2164-17-2
FLUORIDE	16984-48-8

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
FLUOROTRICHLOROMETHANE (FREON 11)	75-69-4
FONOFOS	944-22-9
FORMIC ACID	64-18-6
FOSETYL-AL	39148-24-8
FURAN	110-00-9
FURFURAL	98-01-1
GLYPHOSATE	1071-83-6
HEXACHLOROETHANE	67-72-1
HEXANE	110-54-3
HEXAZINONE	51235-04-2
HEXYTHIAZOX (SAVEY)	78587-05-0
HMX	2691-41-0
HYDRAZINE/HYDRAZINE SULFATE	302-01-2
HYDROQUINONE	123-31-9
IPRODIONE	36734-19-7
IRON	7439-89-6
ISOBUTYL ALCOHOL	78-83-1
ISOPROPYL METHYLPHOSPHONATE	1832-54-8
KEPONE	143-50-0
LITHIUM	7439-93-2
MALATHION	121-75-5
MALEIC HYDRAZIDE	123-33-1
MANEB	12427-38-2
MANGANESE	7439-96-5
MERPHOS OXIDE	78-48-8
METHACRYLONITRILE	126-98-7
METHAMIDOPHOS	10265-92-6
METHANOL	67-56-1
METHOMYL	16752-77-5
METHOXYCHLOR	72-43-5
METHOXYETHANOL, 2-	109-86-4
METHYL ACETATE	79-20-9
METHYL ACRYLATE	96-33-3
METHYL CHLORIDE	74-87-3
METHYL ETHYL KETONE	78-93-3
METHYL HYDRAZINE	60-34-4
METHYL ISOCYANATE	624-83-9
METHYL METHACRYLATE	80-62-6
METHYL METHANESULFONATE	66-27-3

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
METHYL PARATHION	298-00-0
METHYL STYRENE (MIXED ISOMERS)	25013-15-4
METHYL TERT-BUTYL ETHER (MTBE)	1634-04-4
METHYLCHLOROPHENOXYACETIC ACID (MCPA)	94-74-6
METHYLENE BIS(2-CHLOROANILINE), 4,4’-	101-14-4
METHYLNAPHTHALENE, 2-	91-57-6
METHYLSTYRENE, ALPHA	98-83-9
METRIBUZIN	21087-64-9
MOLYBDENUM	7439-98-7
MONOCHLOROACETIC ACID	79-11-8
NAPHTHYLAMINE, 1-	134-32-7
NAPHTHYLAMINE, 2-	91-59-8
NAPROPAMIDE	15299-99-7
NITRATE-NITROGEN (TOTAL)	14797-55-8
NITRITE-NITROGEN (TOTAL)	14797-65-0
NITROANILINE, O-	88-74-4
NITROANILINE, P-	100-01-6
NITROGUANIDINE	556-88-7
NITROPHENOL, 2-	88-75-5
NITROPHENOL, 4-	100-02-7
NITROPROPANE, 2-	79-46-9
NITROSODIETHYLAMINE, N-	55-18-5
NITROSO-DI-N-BUTYLAMINE, N-	924-16-3
NITROSO-N-ETHYLUREA, N-	759-73-9
OCTYL PHTHALATE, DI-N-	117-84-0
OXAMYL (VYDATE)	23135-22-0
PARAQUAT	1910-42-5
PARATHION	56-38-2
PEBULATE	1114-71-2
PENTACHLOROBENZENE	608-93-5
PENTACHLOROETHANE	76-01-7
PENTACHLORONITROBENZENE	82-68-8
PERCHLORATE	7790-98-9
PHENACETIN	62-44-2
PHENOL	108-95-2
PHENYL MERCAPTAN	108-98-5
PHENYLENEDIAMINE, M-	108-45-2
PHENYLPHENOL, 2-	90-43-7

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
PHORATE	298-02-2
PHTHALIC ANHYDRIDE	85-44-9
PICLORAM	1918-02-1
PROMETON	1610-18-0
PRONAMIDE	23950-58-5
PROPANIL	709-98-8
PROPANOL, 2- (ISOPROPYL ALCOHOL)	67-63-0
PROPAZINE	139-40-2
PROPHAM	122-42-9
PROPYLBENZENE, N-	103-65-1
PROPYLENE OXIDE	75-56-9
PYRENE	129-00-0
PYRIDINE	110-86-1
QUINOLINE	91-22-5
QUIZALOFOP (ASSURE)	76578-14-8
RDX	121-82-4
RONNEL	299-84-3
SIMAZINE	122-34-9
STRONTIUM	7440-24-6
STRYCHNINE	57-24-9
STYRENE	100-42-5
SULFATE	7757-82-6
TEBUTHIURON	34014-18-1
TERBACIL	5902-51-2
TERBUFOS	13071-79-9
TETRACHLOROBENZENE, 1,2,4,5-	95-94-3
TETRACHLOROETHANE, 1,1,1,2	630-20-6
TETRACHLOROPHENOL, 2,3,4,6-	58-90-2
TETRAETHYL LEAD	78-00-2
TETRAETHYLDITHIOPYROPHOSPHATE	3689-24-5
TETRAHYDROFURAN	109-99-9
THIOFANOX	39196-18-4
THIRAM	137-26-8
TIN	7440-31-5
TOLUDINE, M-	108-44-1
TOLUDINE, O-	95-53-4
TOLUDINE, P-	106-49-0
TRIALLATE	2303-17-5
TRICHLORO-1,2,2-TRIFLUOROETHANE, 1,1,2-	76-13-1

Table III-1: Compounds Excluded from Further Surface Water Evaluation on Attainment of NR SHS for GW ≤ 2,500 TDS

SUBSTANCE	CAS Number
TRICHLOROACETIC ACID	76-03-9
TRICHLOROBENZENE, 1,3,5-	180-70-3
TRICHLOROETHANE, 1,1,1-	71-55-6
TRICHLOROPHENOL, 2,4,5-	95-95-4
TRICHLOROPHENOXYACETIC ACID, 2,4,5- (2,4,5-T)	93-76-5
TRICHLOROPHENOXYPROPIONIC ACID, 2,4,5- (2,4,5-TP)	93-72-1
TRICHLOROPROPANE, 1,1,2-	598-77-6
TRICHLOROPROPANE, 1,2,3-	96-18-4
TRICHLOROPROPENE, 1,2,3-	96-19-5
TRIETHYLAMINE	121-44-8
TRIETHYLENE GLYCOL	112-27-6
TRIFLURALIN	1582-09-8
TRIMETHYLBENZENE, 1,3,4- (TRIMETHYLBENZENE, 1,2,4-)	95-63-6
TRINITROGLYCEROL (NITROGLYCERIN)	55-63-0
TRINITROTOLUENE, 2,4,6-	118-96-7
VANADIUM	7440-62-2
VINYL ACETATE	108-05-4
VINYL BROMIDE (BROMOETHENE)	593-60-2
WARFARIN	81-81-2
ZINEB	12122-67-7

Conductivity: 1.90 ft/day

Gradient: .01 ft/ft

Groundwater flow represented by plume: 1,900 ft^3/day = 14,000 gallons/day

Average concentrations in groundwater at surface water interface (μg/L):

- Benzene: 12,000
- Toluene: 52,000
- Ethylbenzene: 1,500
- Total xylenes: 9,000

Using benzene for this example, the maximum average groundwater concentration is 12,000 µg/L and the plume flow is 14,000 gallons/day or 0.014 million gallons/day (MGD).

Assuming all groundwater discharges to the stream, an evaluation of the plume discharge to the stream can now be made with the above data using PENTOXSD for each of the contaminants. The approach is described and shown below for benzene:

Figures III-1 and III-2 are printouts from the PENTOXSD model for Example 1. PENTOXSD shows that the recommended effluent limit for benzene in this case is 181 µg/L, which is less than the 329 µg/L maximum effluent groundwater concentration daily limit expected for benzene calculated for this example. Therefore, a release of liability cannot be granted in this case until the maximum effluent groundwater concentration daily limit is reduced to at least 181 µg/L and other parameters in the example are shown to be at acceptable levels.

ii) Example 2: Groundwater Source at Distance from Surface Water Discharge – Steady-State Conditions

In this example, all conditions are the same as for Example 1 except the source is 100 feet from the stream. Additionally, one well is located 40 feet from the source in a downgradient direction toward the stream containing benzene at a concentration of 6,500 µg/L. Assume that wells cannot be drilled at the groundwater/surface water interface because of existing buildings and other obstacles. However, enough onsite and offsite data have been collected to reasonably calibrate a model and establish that the plume is at or near steady-state conditions. A groundwater solute transport model is chosen by the remediator to estimate the flow and concentration of the contaminants into the river. For purposes of this example, the QD and SWL5B spreadsheet applications will be used. A plan view model such as QD is being used because it is difficult or impossible to calibrate a cross-sectional model such as SWL5B using isoconcentration map data. Isoconcentration contours are usually developed and drawn in the plan-view or horizontal dimension. Once the model input parameters are finalized using the plan view model, they are easily transferred for use into the cross-sectional model. The Department does not require the use of these particular models; however, if another surface water loading model is used, the rules incorporated into selection of SWL5B's "edge criterion" for establishing the portion of the plume flow and average concentration must be used.

In order to complete the analysis, input values for the following additional parameters required by the model were developed during the site characterization phase. Those parameters and how they were determined for this example are as follows (See Figure III-3 for the actual values):

Longitudinal and Transverse Dispersion – fitted to plume data (isoconcentration map) using QD

Vertical Dispersion – set to 0.0001 because the entire plume is assumed to discharge into the stream and any vertically dispersed contamination would enter the stream.

Lambda – starting values may be found from Appendix A, Table 5A, Chapter 250 (and converted to the correct units).

Time – 11 years-established from historical records. Note that this is fixed at 1 x 1099 days in SWL5B to assure that output is at steady-state conditions. This assures that SWL5B will yield the maximum average concentration for plumes emanating from a constant source.

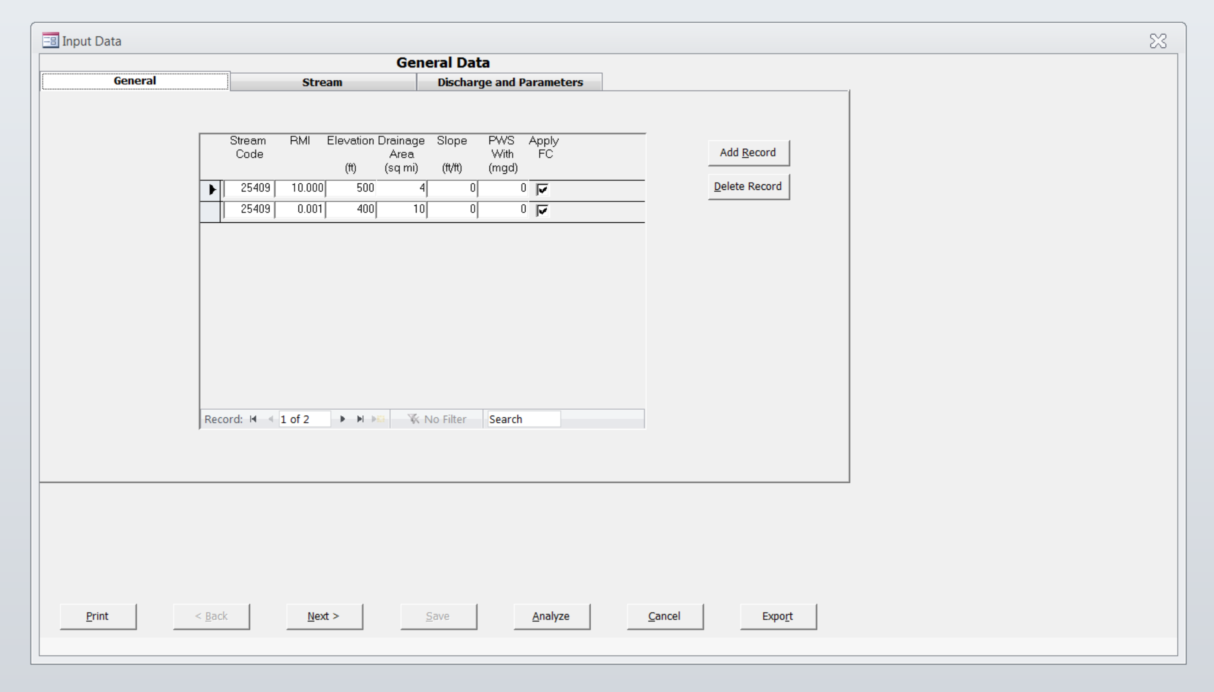
Porosity – determined by laboratory analysis of undisturbed samples.

Dry Bulk Density – estimated at 2.65 * (1-porosity).

K_{oc} – from Appendix A, Table 5, Chapter 250.

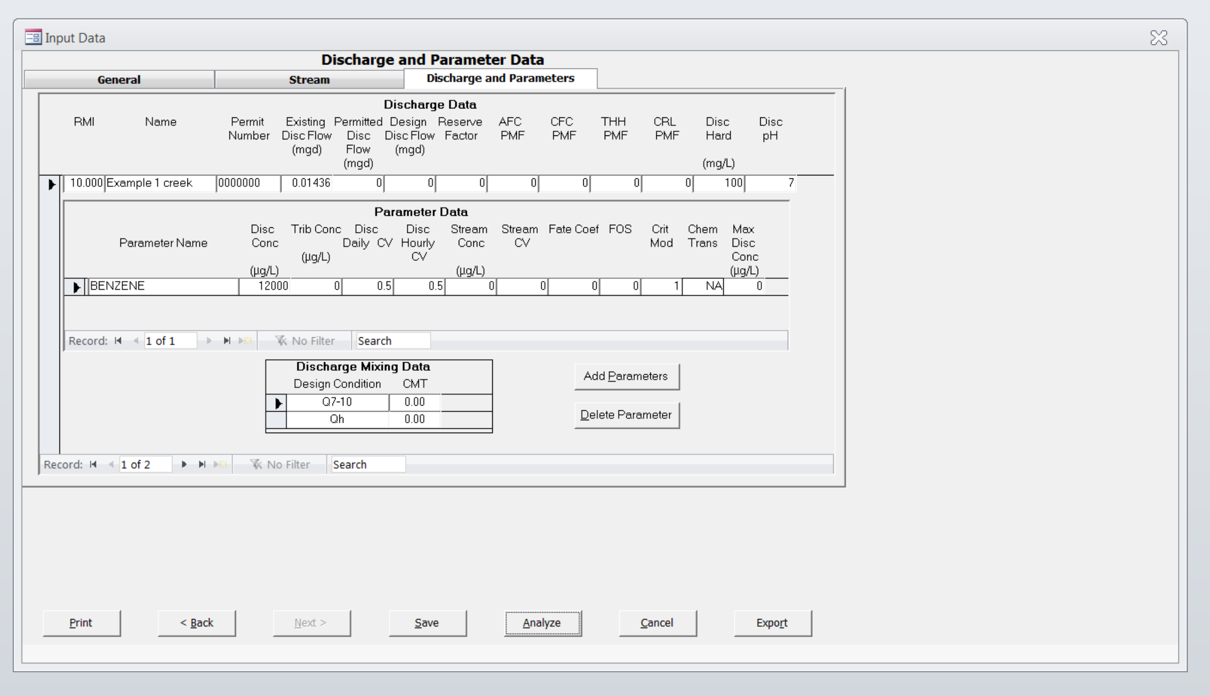
Fraction Organic Carbon – Can be estimated (Section III.A.1.b.ii).

Figure III-1: Example 1 – PENTOXSD Model Inputs



General Data

Stream Code	RMI	Elevation (ft)	Drainage Area (sq mi)	Slope (ft/ft)	PWS With (mgd)	Apply FC
25409	10.000	500	4	0	0	☑
25409	0.001	400	10	0	0	☑



Discharge and Parameter Data

Discharge Data

RMI	Name	Permit Number	Existing Disc Flow (mgd)	Permitted Disc Flow (mgd)	Design Disc Flow (mgd)	Reserve Factor	AFC PMF	CFC PMF	THH PMF	CRL PMF	Disc Hard (mg/L)	Disc pH
10.000	Example 1 creek	0000000	0.01436	0	0	0	0	0	0	0	100	7

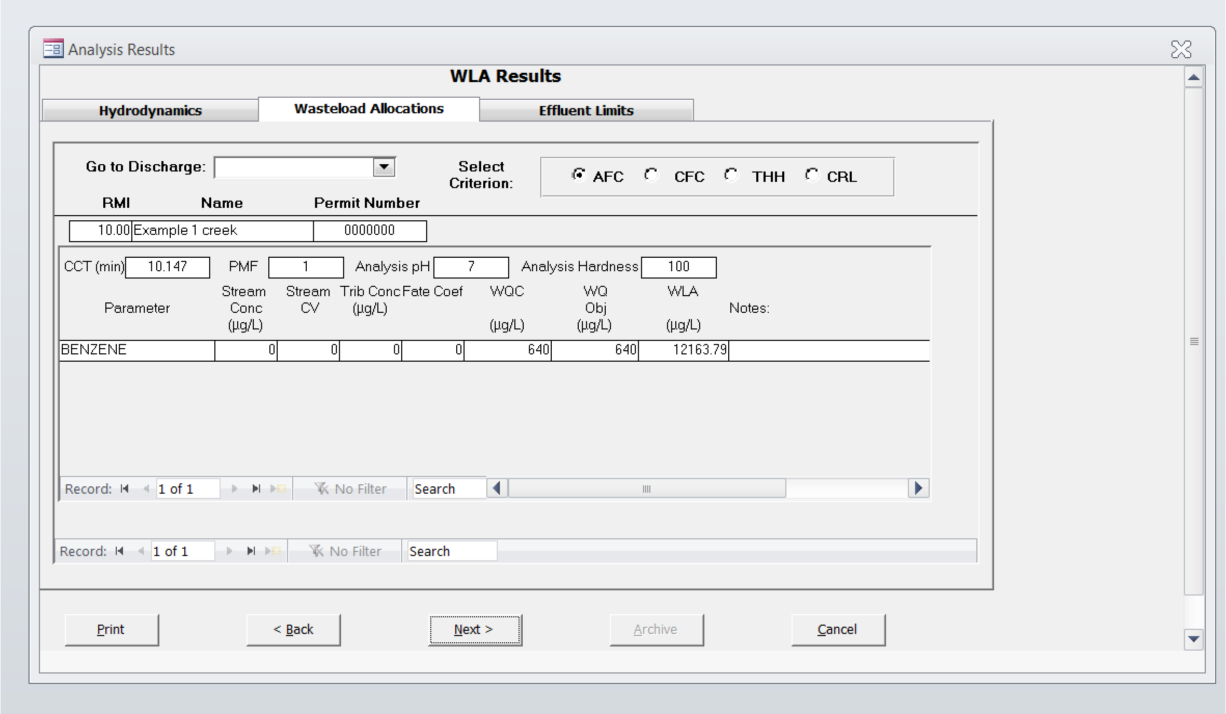
Parameter Data

Parameter Name	Disc Conc (µg/L)	Trib Conc (µg/L)	Disc Daily CV	Disc Hourly CV	Stream Conc (µg/L)	Stream CV	Fate Coef	FOS	Crit Mod	Chem Trans	Max Disc Conc (µg/L)
BENZENE	12000	0	0.5	0.5	0	0	0	0	1	NA	0

Discharge Mixing Data

Design Condition	CMT
Q7-10	0.00
Qh	0.00

Figure III-2: Example 1 –PENTOXSD Model Output



WLA Results

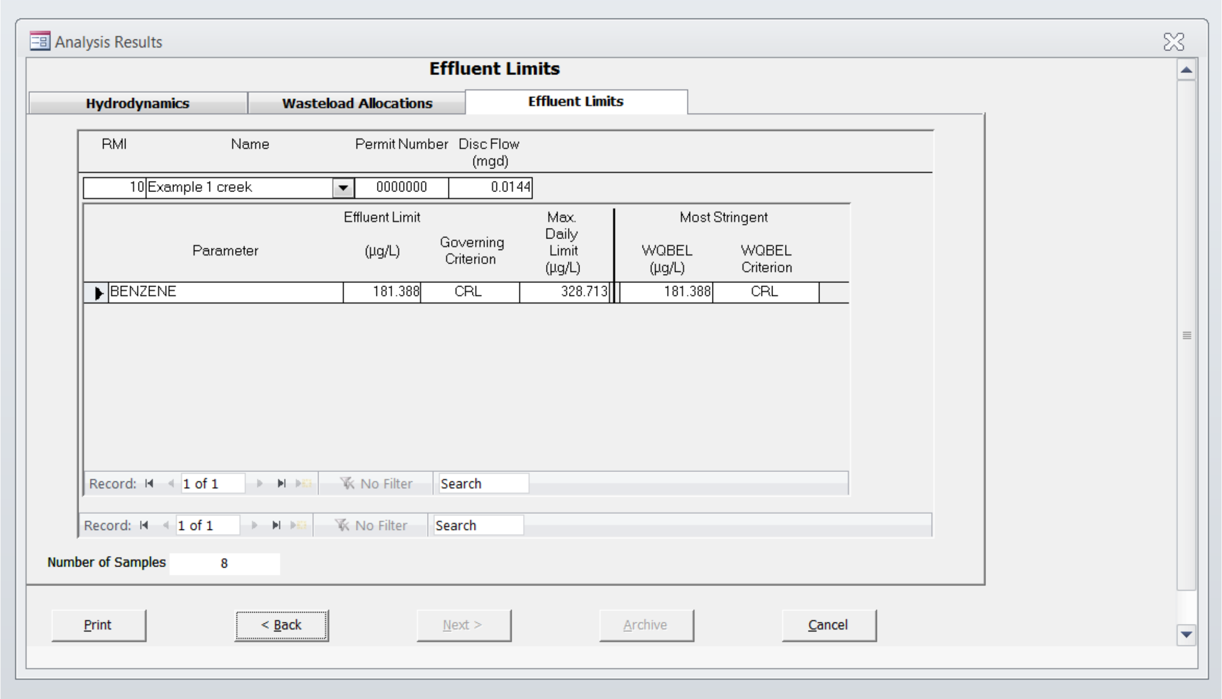
Go to Discharge:

Select Criterion: ● AFC ○ CFC ○ THH ○ CRL

RMI	Name	Permit Number
10.00	Example 1 creek	0000000

CCT (min) 10.147 PMF 1 Analysis pH 7 Analysis Hardness 100

Parameter	Stream Conc (µg/L)	Stream CV	Trib Conc (µg/L)	Fate Coef	WQC (µg/L)	WQ Obj (µg/L)	WLA (µg/L)	Notes:
BENZENE	0	0	0	0	640	640	12163.79	



Effluent Limits

RMI	Name	Permit Number	Disc Flow (mgd)
10	Example 1 creek	0000000	0.0144

Parameter	Effluent Limit (µg/L)	Governing Criterion	Max. Daily Limit (µg/L)	Most Stringent WQBEL (µg/L)	Most Stringent WQBEL Criterion
BENZENE	181.388	CRL	328.713	181.388	CRL

Number of Samples 8

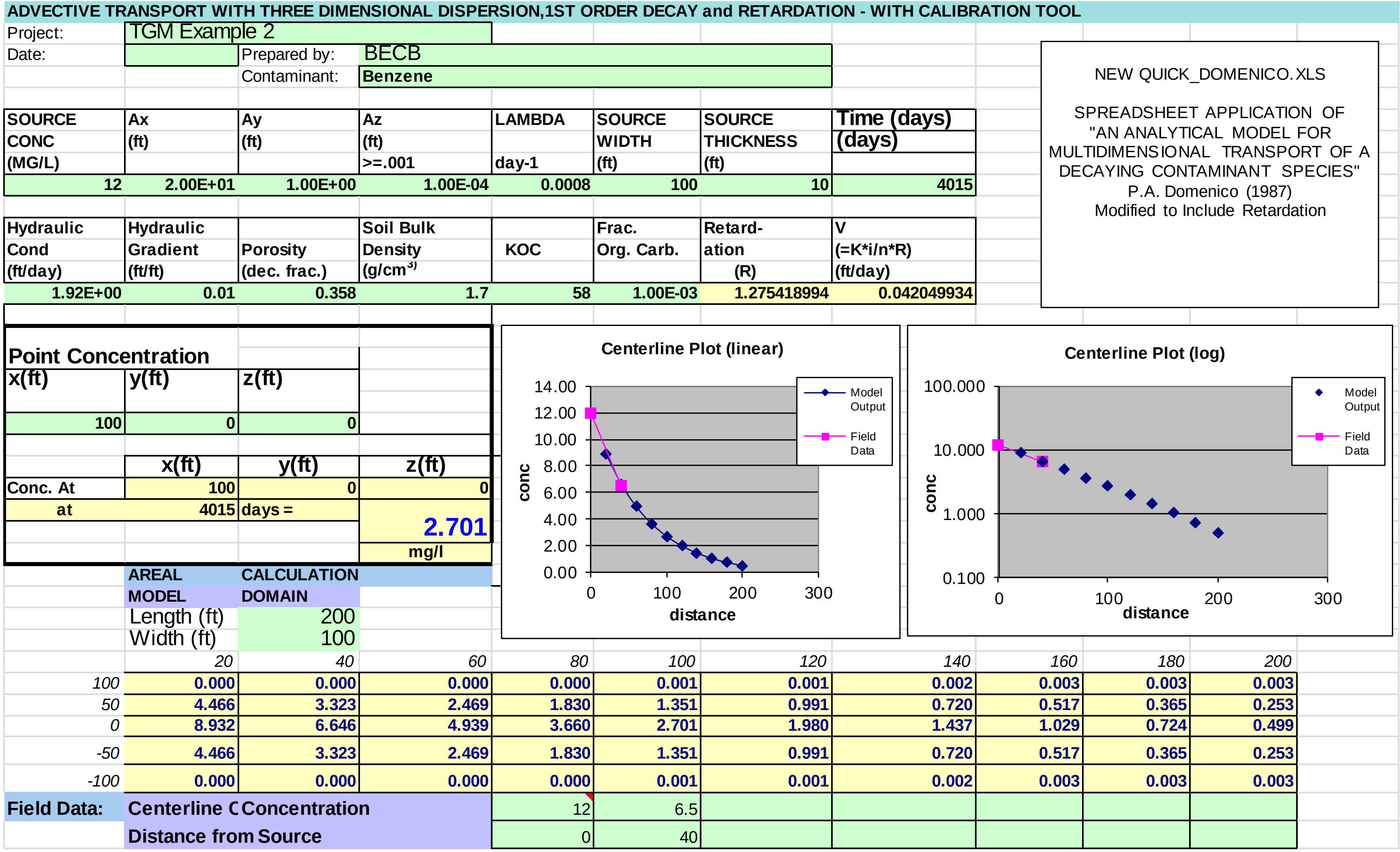
Once a satisfactory output matching the overall plume geometry at 11 years was achieved using QD, the flow and transport terms of QD, except for time, were input into SWL5B. The output from QD and SWL5B is shown in Figures III-3 and III-4.

The model indicates that the maximum average concentration in groundwater is 1.28 mg/L for benzene and the total flow through the plume is 0.00026 MGD. The model output indicates that PENTOX is required as the next step. These values (after any necessary conversion) then become the input values for existing discharge flow and discharge concentration of benzene in PENTOXSD. Note that the average concentration in the benzene plume is lower than in the first example because of first-order decay and dispersion. However, note also that, because the plume has dispersed, the cross-sectional flow is somewhat greater.

Documentation for using SWL5B to estimate plume flow, concentrations and mass loading is provided on the LRP web page under “Guidance and Technical Tools.”

Figures III-5 and III-6 are printouts from the PENTOXSD model run for Example 2. In this case, the recommended effluent limit for benzene is 9,953 µg/L, which is greater than the effluent groundwater concentration daily limit expected of 1,994 µg/L. Therefore, attainment of surface water criteria for benzene has been demonstrated. If attainment of the other parameters in the example with surface water criteria were also demonstrated, a release of liability would be conveyed.

Figure III-3: Example 2 – Quick Domenico Model Output



ADVECTIVE TRANSPORT WITH THREE DIMENSIONAL DISPERSION,1ST ORDER DECAY and RETARDATION - WITH CALIBRATION TOOL

Project: TGM Example 2
Date:
Prepared by: BECB
Contaminant: **Benzene**

SOURCE CONC (MG/L)	**Ax (ft)**	**Ay (ft)**	**Az (ft) >=.001**	**LAMBDA day-1**	**SOURCE WIDTH (ft)**	**SOURCE THICKNESS (ft)**	**Time (days) (days)**
12	**2.00E+01**	**1.00E+00**	**1.00E-04**	**0.0008**	**100**	**10**	**4015**

Hydraulic Cond (ft/day)	**Hydraulic Gradient (ft/ft)**	**Porosity (dec. frac.)**	**Soil Bulk Density (g/cm^3)**	**KOC**	**Frac. Org. Carb.**	**Retard-ation (R)**	**V (=K*i/n*R) (ft/day)**
1.92E+00	**0.01**	**0.358**	**1.7**	**58**	**1.00E-03**	**1.275418994**	**0.042049934**

NEW QUICK_DOMENICO.XLS

SPREADSHEET APPLICATION OF
"AN ANALYTICAL MODEL FOR
MULTIDIMENSIONAL TRANSPORT OF A
DECAYING CONTAMINANT SPECIES"
P.A. Domenico (1987)
Modified to Include Retardation

Point Concentration

x(ft)	**y(ft)**	**z(ft)**
100	**0**	**0**

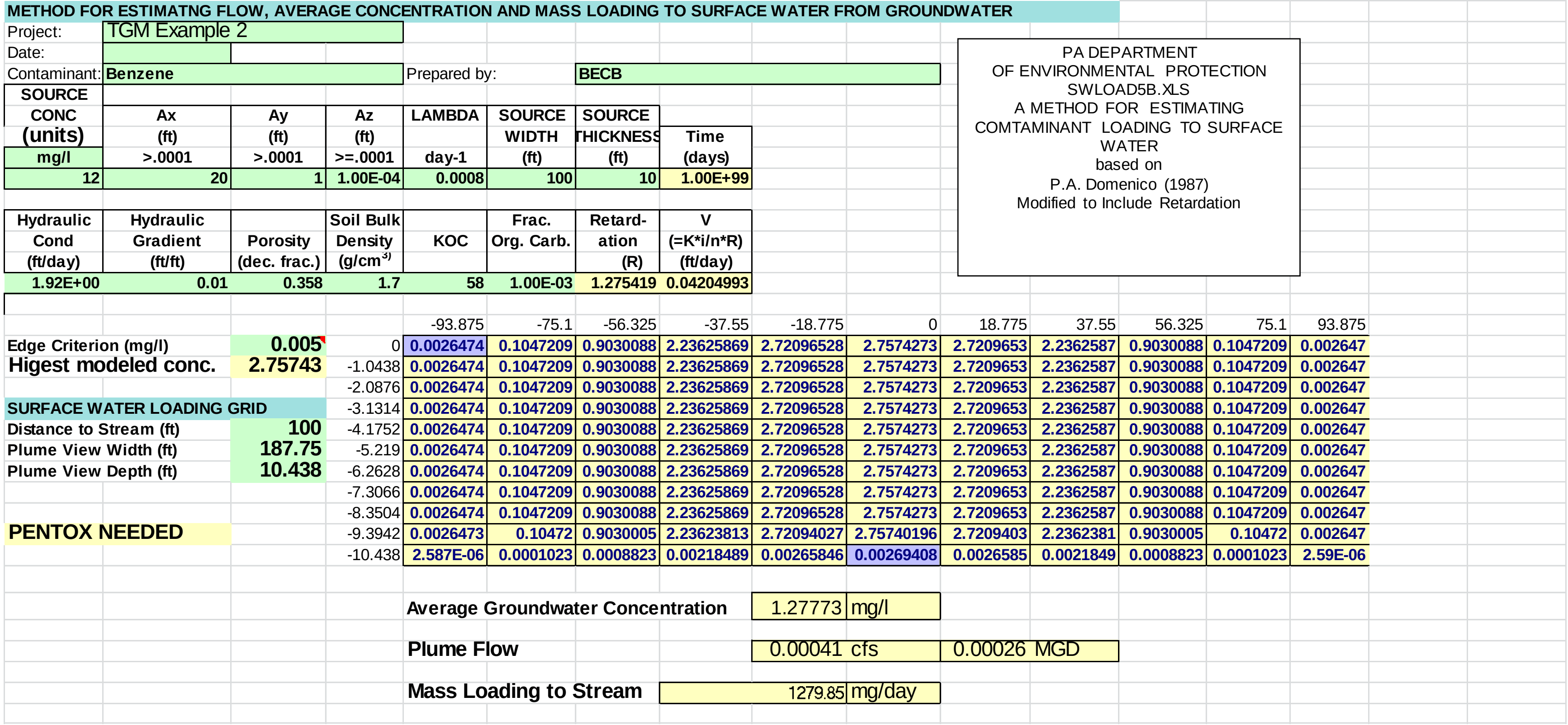
	x(ft)	**y(ft)**	**z(ft)**
Conc. At	**100**	**0**	**0**
at	**4015**	**days =**	**2.701**
			mg/l

AREAL CALCULATION
MODEL DOMAIN
Length (ft) 200
Width (ft) 100

	20	*40*	*60*	*80*	*100*	*120*	*140*	*160*	*180*	*200*
100	**0.000**	**0.000**	**0.000**	**0.000**	**0.001**	**0.001**	**0.002**	**0.003**	**0.003**	**0.003**
50	**4.466**	**3.323**	**2.469**	**1.830**	**1.351**	**0.991**	**0.720**	**0.517**	**0.365**	**0.253**
0	**8.932**	**6.646**	**4.939**	**3.660**	**2.701**	**1.980**	**1.437**	**1.029**	**0.724**	**0.499**
-50	**4.466**	**3.323**	**2.469**	**1.830**	**1.351**	**0.991**	**0.720**	**0.517**	**0.365**	**0.253**
-100	**0.000**	**0.000**	**0.000**	**0.000**	**0.001**	**0.001**	**0.002**	**0.003**	**0.003**	**0.003**

Field Data:	**Centerline C Concentration**	12	6.5
	Distance from Source	0	40

Figure III-4: Example 2 – SWLOAD Model Output



METHOD FOR ESTIMATNG FLOW, AVERAGE CONCENTRATION AND MASS LOADING TO SURFACE WATER FROM GROUNDWATER

Project: TGM Example 2
Date:
Contaminant: **Benzene**
Prepared by: **BECB**

PA DEPARTMENT
OF ENVIRONMENTAL PROTECTION
SWLOAD5B.XLS
A METHOD FOR ESTIMATING
COMTAMINANT LOADING TO SURFACE
WATER
based on
P.A. Domenico (1987)
Modified to Include Retardation

SOURCE CONC (units) mg/l	Ax (ft) >.0001	Ay (ft) >.0001	Az (ft) >=.0001	LAMBDA day-1	SOURCE WIDTH (ft)	SOURCE THICKNESS (ft)	Time (days)
12	20	1	1.00E-04	0.0008	100	10	1.00E+99

Hydraulic Cond (ft/day)	Hydraulic Gradient (ft/ft)	Porosity (dec. frac.)	Soil Bulk Density (g/cm³⁾	KOC	Frac. Org. Carb.	Retard-ation (R)	V (=K*i/n*R) (ft/day)
1.92E+00	0.01	0.358	1.7	58	1.00E-03	1.275419	0.04204993

Edge Criterion (mg/l) 0.005
Higest modeled conc. 2.75743

SURFACE WATER LOADING GRID
Distance to Stream (ft) 100
Plume View Width (ft) 187.75
Plume View Depth (ft) 10.438

PENTOX NEEDED

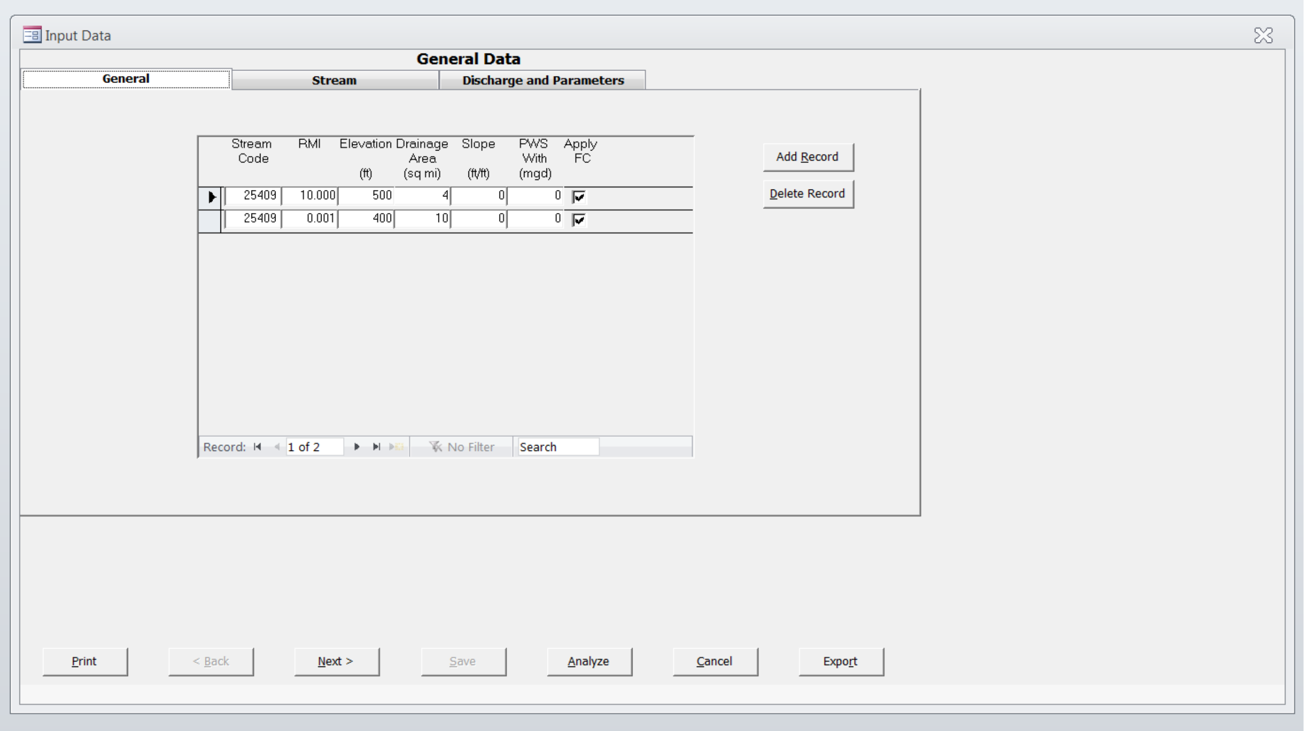
	-93.875	-75.1	-56.325	-37.55	-18.775	0	18.775	37.55	56.325	75.1	93.875
0	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-1.0438	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-2.0876	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-3.1314	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-4.1752	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-5.219	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-6.2628	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-7.3066	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-8.3504	0.0026474	0.1047209	0.9030088	2.23625869	2.72096528	2.7574273	2.7209653	2.2362587	0.9030088	0.1047209	0.002647
-9.3942	0.0026473	0.10472	0.9030005	2.23623813	2.72094027	2.75740196	2.7209403	2.2362381	0.9030005	0.10472	0.002647
-10.438	2.587E-06	0.0001023	0.0008823	0.00218489	0.00265846	0.00269408	0.0026585	0.0021849	0.0008823	0.0001023	2.59E-06

Average Groundwater Concentration 1.27773 mg/l

Plume Flow 0.00041 cfs 0.00026 MGD

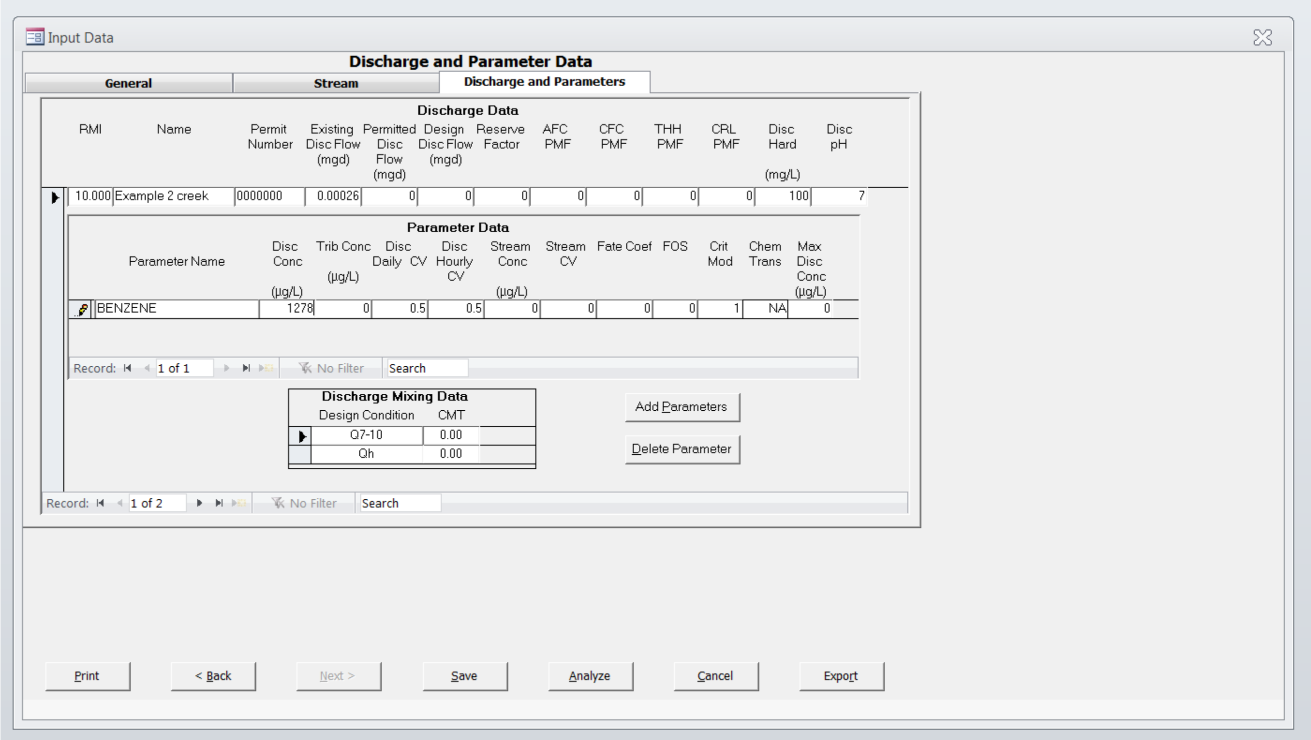
Mass Loading to Stream 1279.85 mg/day

Figure III-5: Example 2 – PENTOXSD Model Inputs



Stream Code	RMI	Elevation (ft)	Drainage Area (sq mi)	Slope (ft/ft)	PWS With (mgd)	Apply FC
25409	10.000	500	4	0	0	☑
25409	0.001	400	10	0	0	☑

Record: 1 of 2 No Filter Search



Discharge Data

RMI	Name	Permit Number	Existing Disc Flow (mgd)	Permitted Disc Flow (mgd)	Design Disc Flow (mgd)	Reserve Factor	AFC PMF	CFC PMF	THH PMF	CRL PMF	Disc Hard (mg/L)	Disc pH
10.000	Example 2 creek	0000000	0.00026	0	0	0	0	0	0	0	100	7

Parameter Data

Parameter Name	Disc Conc (µg/L)	Trib Conc (µg/L)	Disc Daily CV	Disc Hourly CV	Stream Conc (µg/L)	Stream CV	Fate Coef	FOS	Crit Mod	Chem Trans	Max Disc Conc (µg/L)
BENZENE	1278	0	0.5	0.5	0	0	0	0	1	NA	0

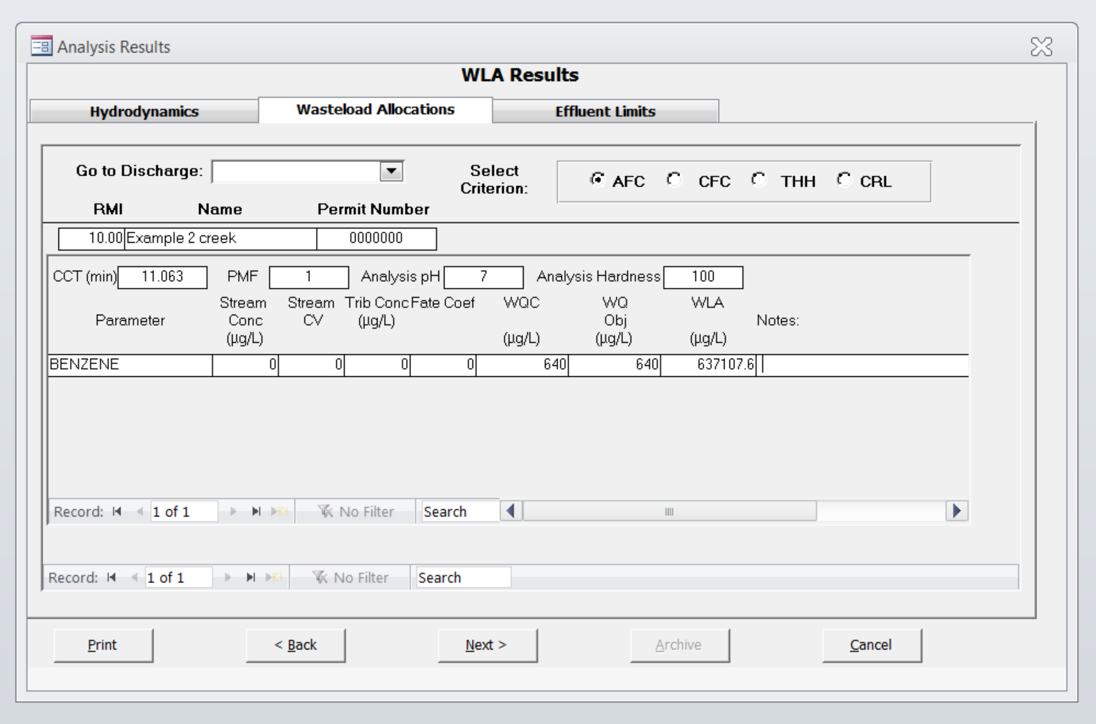
Record: 1 of 1 No Filter Search

Discharge Mixing Data

Design Condition	CMT
Q7-10	0.00
Qh	0.00

Record: 1 of 2 No Filter Search

Figure III-6: Example 2 – PENTOXSD Model Output



WLA Results

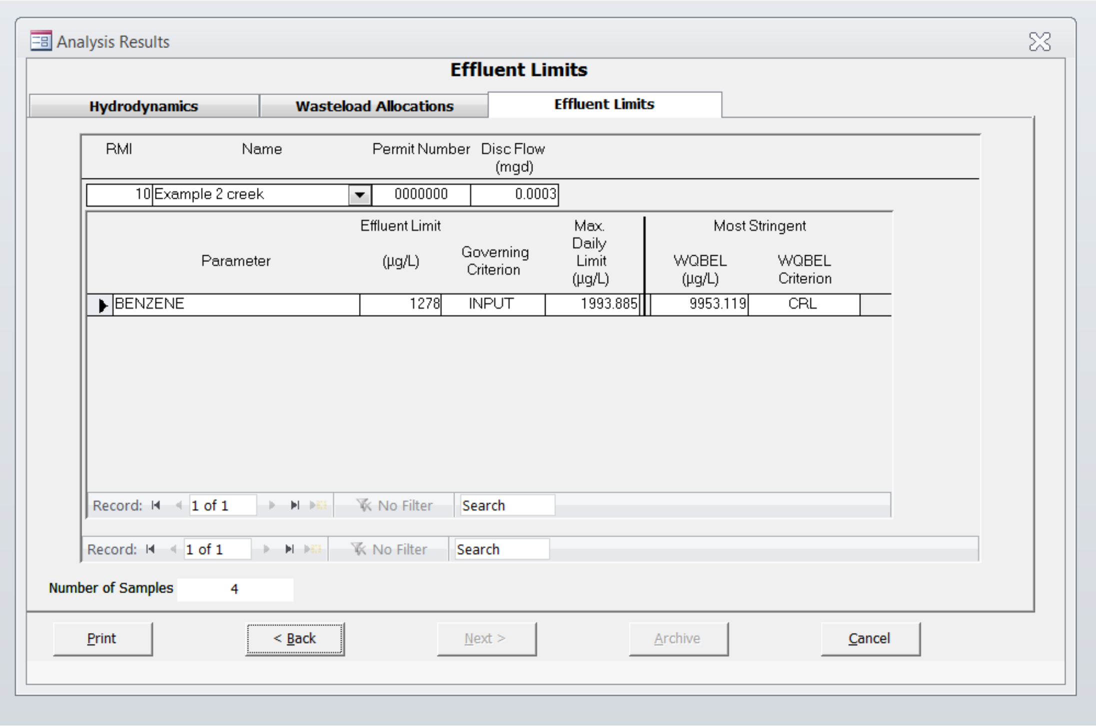
Go to Discharge:

Select Criterion: ● AFC ○ CFC ○ THH ○ CRL

RMI	Name	Permit Number
10.00	Example 2 creek	0000000

CCT (min) 11.063 PMF 1 Analysis pH 7 Analysis Hardness 100

Parameter	Stream Conc (µg/L)	Stream CV	Trib Conc (µg/L)	Fate Coef	WQC (µg/L)	WQ Obj (µg/L)	WLA (µg/L)	Notes:
BENZENE	0	0	0	0	640	640	637107.6	



Effluent Limits

RMI	Name	Permit Number	Disc Flow (mgd)
10	Example 2 creek	0000000	0.0003

Parameter	Effluent Limit (µg/L)	Governing Criterion	Max. Daily Limit (µg/L)	Most Stringent WQBEL (µg/L)	Most Stringent WQBEL Criterion
BENZENE	1278	INPUT	1993.885	9953.119	CRL

Number of Samples 4

B. Guidance for Attainment Demonstration with Statistical Methods

1. Introduction

The requirement to apply statistical methods to verify the cleanup of a site is emphasized in Act 2. Sections 302, 303 and 304 of Act 2 (35 P.S. §§ 6026.302-304) require that attainment of a standard be demonstrated by the collection and analysis of samples from affected media (such as surface water, soil, groundwater in aquifers at the point of compliance) through the application of statistical tests set forth in regulation. The Act also requires the Department to recognize those methods of attainment demonstration generally recognized as appropriate for that particular remediation.

Statistical methods are emphasized because there is a practical need to make decisions regarding whether a site meets a cleanup standard in spite of uncertainty. The uncertainty arises because we are able to sample and analyze only a small portion of the soil and groundwater at a site, yet we have to make a decision regarding the entire site.

The purpose of this section is to provide guidance for the use of statistics to demonstrate that a site has attained a cleanup standard under Act 2. It is intended to address certain key issues pertinent to the sampling and statistical analysis under Act 2, to provide references for proper statistical analysis and, if necessary, to provide examples of applying statistical procedures in detail. It is not intended to address every statistical issue.

For statistical attainment issues not addressed directly in this manual or in 25 Pa. Code Chapter 250, a person may consult the latest ITRC and EPA documents for additional guidance. The 2013 ITRC document *Groundwater Statistics and Monitoring Compliance* and EPA guidance documents (EPA 1992b, 1992c, 1996, 2002b, 2009) are particularly helpful. They provide detailed statistical procedures for demonstration of attainment and data analysis.

For groundwater characterization, remediators should consult Appendix A of this manual "Groundwater Monitoring Guidance" which provides general information on groundwater monitoring and sampling issues, such as monitoring well construction, locations and depths of monitoring wells, and well abandonment procedures. The Groundwater Monitoring Guidance provides a good summary of various statistical methods used for groundwater characterization.

For conducting statistical analyses, remediators may wish to utilize EPA's ProUCL Statistical Software for Environmental Applications. This free program is available on EPA's website and accompanied with a Technical Guide. ProUCL is able to run most of the statistical applications summarized in this section of the TGM.

Other standard statistics-related tests may be used to perform the procedures to demonstrate attainment as appropriate. If necessary, professional services should be obtained.

When we consider applying statistical methods to demonstrate the attainment of a risk-based cleanup standard, it is important to realize that three components may influence the overall stringency of this cleanup standard:

- The first component is the magnitude, level, or concentration that is deemed protective of human health and the environment. The development of risk-based cleanup standards is addressed in the regulations and Department's risk assessment guidances.
- The second component of the standard is the sampling that is done to evaluate whether a site is above or below the standard.
- The final component is how the resulting data are compared with the standard to decide whether the remedial action was successful (a statistical analysis).

Persons overseeing cleanup must look beyond the cleanup level and explore the sampling and statistical analysis that will allow evaluation of the site relative to the cleanup level. This guidance is intended to address statistical analysis and sampling components that may affect the stringency of cleanup standards.

2. Data Review for Statistical Methods

Preliminary data review for statistical analysis (also known as exploratory data analysis in the DEP Groundwater Monitoring Guidance Manual; PA DEP, 2001) includes the use of graphical techniques and calculation of summary statistics. By reviewing the data both numerically and graphically, one can learn the "structure" of the data and identify limitations for using the data. Graphical methods include histograms, probability plots, box charts, and time-series plots to visually review the data for trends or patterns. EPA and most statistical texts recommend that time-series data should be graphed. This visual approach allows for a quick assessment of the statistical features of the data. Calculations of summary statistics are typically done to characterize the data and make judgments on the central tendencies, symmetry, presence of outliers, etc. Preliminary data review is critical in selecting additional appropriate mathematical procedures.

Graphical and parametric statistical procedures discussed here are included in many introductory statistics textbooks (e.g., Iman and Conover, 1983 and Ott, 1988) and are available in many computer statistics packages.

a) Summary Statistics

Basic summary statistics can be used to characterize groundwater monitoring data. Summary statistics include median, interquartile range (IQR), mean, standard deviation, and range. Median and IQR are determined from percentiles. Median is the 50th percentile and IQR is the 25th to 75th percentile. Median indicates the "center" of data values. The mean is another measure of center but only if data are normally or symmetrically distributed. Mean and standard deviation are required values with parametric procedures. Range is the minimum to maximum values. Procedures for such summary statistics are found in introductory statistics texts.

b) Graphical Procedures

Refer to ITRC (2013) for a general reference on graphical procedures.

Histogram - A histogram is a graphic display of frequency distribution. The area within the bar represents the relative density of the data.

Boxplots - A boxplot summarizes a data set by presenting the percentile distribution of the data. The "box" portion indicates the median and interquartile range (IQR). IQR is the middle 50 percent of data. Difference in the size of box halves represents data skewness.

Normal and symmetrical distributions will have equal size box halves. Extreme outliers are displayed as individual points that are recognized easily. Boxplots can be constructed by hand; however, many computer statistical packages will prepare them.

The boxplot of a lognormal distribution will have noticeably different-sized box halves. Lack of IQR overlap for different data sets will indicate a probable significant difference. Boxplots of seasonally grouped data can be used to detect data seasonality.

Time Series Plots - A time series plot displays individual data points on a time scale. A monthly scale can help to identify seasonal variation. A yearly scale also can identify possible trends. Superimposing data from multiple sampling locations may provide additional information. Improved trend information is often available with data smoothing.

Control Charts - Control charts are used to define limits for an analyte that has been monitored at an uncontaminated well over time. This procedure is a graphical alternative to prediction limits.

A common technique is the Shewhart-CUSUM control chart that plots the data on a time scale. Obvious features such as trends or sudden changes in concentration levels could then be observed. With this method, if any compliance well has a value or a sequence of values that lie outside the control limits for that analyte, it may indicate statistically significant evidence of contamination.

The control chart approach is recommended only for uncontaminated wells, a normal or lognormal data distribution with few nondetects, and for a dataset that has at least eight independent samples over a one-year period. This baseline is then used to judge the future samples. See the EPA Guidance (EPA, 2009, Chapter 20).

3. Statistical Inference and Hypothesis Statements

A statistical procedure that is designed to allow the extrapolation from the results of a few samples to a statement regarding the entire site is known as statistical inference.

Statistical inference allows decision making under uncertainty and valid extrapolation of information that can be defended and used with confidence to determine whether the site meets the cleanup standard.

The goal of statistical inference, the process of extrapolating results from a sample to a larger population, is to decide which of two complementary hypotheses, null hypothesis and alternative hypothesis, is likely to be true.

In general, statistical inference procedures include the following steps:

(1) A null hypothesis and its alternative hypothesis are drawn up. The null hypothesis is developed in such a way that the probability of Type I error can be determined. The Type I error is an error that we falsely reject the null hypothesis, when the null hypothesis is true. Type I error is also known as false positive error.

(2) Decide the level of significance, α. This controls the risk of committing a Type I error.

(3) Establish a decision rule for each scale of decision making that is derived from step 4 of the Data Quality Objectives (DQO) process. (See Section III.G for more information on the DQO process).

(4) Determine the sample size, n. This is the number of environmental samples needed to make decision. Obtain data through the implementation of sampling and analysis plan.

(5) Apply the decision rule to the data. The null hypothesis is rejected or not rejected. Rejection of the null hypothesis implies acceptance of the alternative hypothesis.

Section 250.707(d)(1) of the regulations has specified the ground rules of hypothesis statements under Act 2. For demonstration of attainment of Statewide health or site-specific standards, the null hypothesis (H_o) is that the true site arithmetic average concentration is at or above the cleanup standard, and the alternative hypothesis (H_a) is that the true site arithmetic average concentration is below the cleanup standard. When statistical methods are to be used to determine that the background standard is exceeded, the null hypothesis (H_o) is that the background standard is achieved and the alternative hypothesis (H_a) is that the background standard is not achieved.

To understand the rationale of hypothesis testing, let us consider a nonstatistical hypothesis testing example - the process in which an accused individual is judged to be innocent or guilty in a criminal court. Under our legal system, we feel that it is a more grievous mistake to convict an innocent man than to let a guilty man go free. Therefore, the accused person is presumed to be innocent under our legal system. The burden of proof of his guilt rests upon the prosecution. The prosecutor must present sufficient evidence to the jury in order to convict the defendant, while the defendant’s lawyer would want to throw any reasonable doubt into the evidence presented by the prosecutor in order to get an acquittal verdict for the defendant. Using the language of hypothesis testing, we want to test a null hypothesis (H_o) that the accused man is innocent. That means that an alternative hypothesis (H_a) exists, that the defendant is guilty. The jury will examine the evidence and decide whether the prosecution has demonstrated sufficiently that the evidence is inconsistent with the null hypothesis (H_o) of innocent. If the jurors decide that the evidence is inconsistent with H_o, they reject that hypothesis and therefore accept the alternative hypothesis (H_a) that the defendant is guilty.

Similar to the above legal process example, because we feel that it is a more serious mistake to declare a contaminated site to be uncontaminated than to declare an uncontaminated site to be contaminated under the Statewide health and site-specific standards, we choose the following null hypothesis statement: the true site arithmetic average concentration is at or above the cleanup standard. The null hypothesis is assumed to be true unless substantial evidence shows that it is false. The demonstration of attainment must be presented with sufficient evidence in order to show that the postremediation condition at the site is not consistent with the null hypothesis. We use "true site arithmetic average concentration" here because arithmetic average concentration is representative of the concentration that would be contacted at a site over time and toxicity criteria that are used to develop cleanup standards are based on long-term average exposure. The arithmetic average is appropriate regardless of the type of statistical distribution that might best describe the sampling data. We do not use geometric average concentration because the geometric mean of a set of sampling data bears no logical connection to the cumulative intake that would result from long-term contact with site contaminants.

It should be noted that the above hypothesis statements referring to the arithmetic average concentration does not force everyone to use 95% upper confidence limit (UCL) to infer the true site arithmetic average concentration. Methods other than the 95% UCL, such as tests for percentiles or proportions, also may be used provided that a person can document that high coverage of the true population mean occurs, (i.e., the value used in a method equals or exceeds the true site arithmetic average concentration with high probability).

For the background standard, the null hypothesis (H_o) is that the background standard is achieved and the alternative hypothesis (H_a) is that the background standard is not achieved. The background standard is not risk-based. These hypothesis statements will allow some site concentrations to be higher than some background reference-area measurements without rejecting the null hypothesis. These hypothesis statements are consistent with EPA guidance documents (EPA, 2009). If we reverse the hypothesis statements and presume that the background standard is not achieved, we would require most site concentrations to be less than the reference measurements in order to declare a site to be clean. In considering the cost of remediation, both the Department and EPA believe that this requirement is unreasonable.

4. Selection of Statistical Methods

a) Factors Affecting the Selection of Statistical Methods

The selection of statistical methods for use in assessing the attainment of cleanup standards depends on the characteristics of the environmental media. In soils, concentrations of contaminants change relatively slowly, with little variation from season to season. In groundwater, the number of measurements available for spatial characterization is limited and seasonal patterns may exist in the data. As a result of these differences, separate procedures are recommended for the differing problems associated with soils and groundwater.

The selection of statistical methods also depends on remediation standards. There are three types of remediation standards under Act 2: background standards, Statewide health standards, and site-specific standards. Background standards are developed using background data. Many SHS and site-specific standards are risk-based standards that are concentration limits based on risk assessment methodologies. At some sites, a site-specific standard might use an engineering control, such as capping a site to eliminate pathways. The cap must be designed to meet certain engineering specifications prescribed in numerical levels. A background standard is not a single number, but rather a range of numbers. A statistical method used to demonstrate the attainment of the background standard is used to compare the distribution of data for a background reference area to the distribution of data for the impacted area. Different statistical methods are used to demonstrate the attainment of a risk-based concentration limit.

As a result of the above factors, recommended statistical approaches are addressed separately based on environment media and remediation standards. The flowchart in Figure III-7 provides a summary of recommended statistical methods described in the Chapter 250 regulations. Since Act 2 also requires the Department to recognize those methods of attainment demonstration generally recognized as appropriate for a particular remediation, the Department will also accept other appropriate statistical methods that meet the performance standards described in Section 250.707(d)(2) of the regulations.

Statistical methods generally can be classified into two categories: parametric procedures and nonparametric procedures. The selection of a parametric or a nonparametric procedure depends on the distribution of the data, the percentage of nondetects, and the database size. However, both procedures have assumptions that must be met to be considered valid analyses.

Parametric Procedure - Assumptions of parametric procedures include a specific data distribution such as normal (also known as Gaussian or the bell-shaped curve) or lognormal (normality achieved by log-transforming the data), and data variances that are similar. In addition, the data are assumed to be independent.

Nonparametric Procedure - Assumptions for nonparametric tests also are important. Nonparametric procedures assume equal variances and that the type (shape) of distribution of the population is the same. In other words, nonparametric methods do not require a specific type of data distribution, which is different from assuming a normal distribution when using parametric statistics.

Nonparametric procedures may be preferred because they:

- are free from normal distribution assumptions, thereby eliminating the need for normality tests and data transformations;
- are resistant to effects of outliers; and
- are usable when censored (i.e., less than detection values) data are present.

b) Recommended Statistical Procedures

In consideration of the factors described above, Section 250.707 of the regulations provides recommended statistical procedures that can be used to demonstrate attainment of cleanup standards. The following discussions provide background information of these recommended methods.

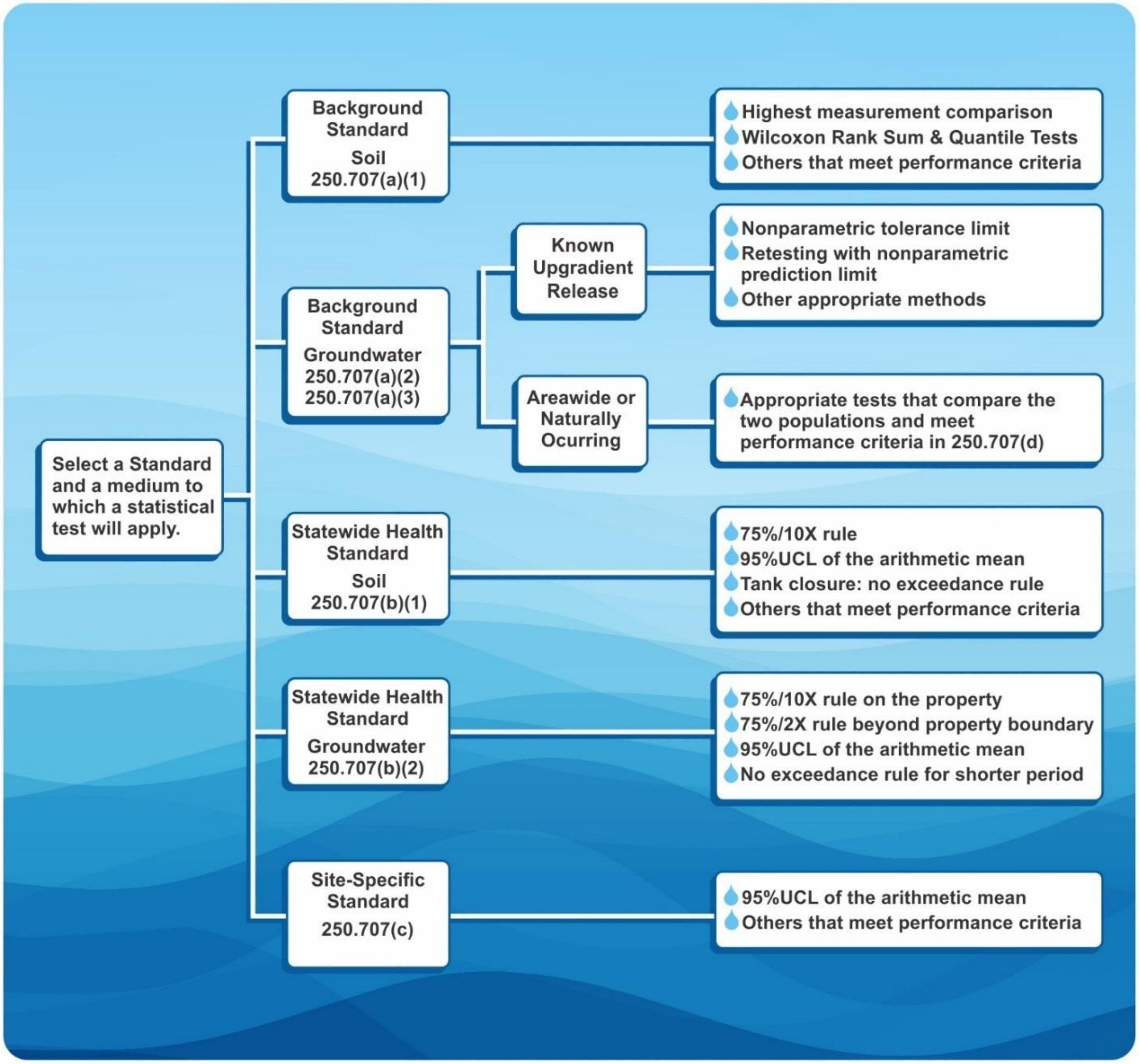
Unless otherwise specified or approved by the Department, systematic sampling (grid sampling) designs should be used in developing the sampling and analysis plan for demonstrating attainment of soil cleanup standards. (See 25 Pa. Code § 250.703(c)). Systematic random sampling is a grid sampling design with a random starting point. Systematic random sampling provides better coverage of the soil study area than simple random sampling. Limitations and procedures to implement systematic sampling can be found in Sections 5.3 and 6.5 of EPA guidance (EPA, 1989b). A square grid and a triangular grid are two common patterns used in systematic sampling. To avoid grid pattern corresponding to patterns of contamination, EPA (EPA 1992c) recommended the use of unaligned grid sampling design (Gilbert, 1987, p. 94). Unaligned grid sampling design maintains the advantage of uniform coverage while incorporating an element of randomness in the choice of sampling locations. To obtain an unbiased estimate of the variance of the mean, the multiple systematic sampling approach (Gilbert, 1987, p. 97) may be needed.

To generate a grid sampling design, a computer random number generator or a random number table may be used. To assist remediators with systematic random sampling, a spreadsheet program which creates a grid covering a soil study area is provided on the LRP web page.

i) Soil Risk-Based Standards

For risk-based standards, the selection of statistical parameters, such as mean, median or an upper percentile, to use in the statistical assessment decision depends on the toxicity criteria. Mean and median are useful for cleanup standards based on carcinogenic or chronic health effects and long-term average exposure. Upper proportion or percentile should be used if the health effects of the contaminant are acute or worst-case effects. Because the SHS values are based on the evaluation of carcinogenic or chronic health effects and long-term average exposure, the Cleanup Standards Scientific Advisory Board (CSSAB) has recommended that mean or median should be the statistical parameter of choice. The regulations allow the remediator to use the 75%/10X rule or the 95% UCL of arithmetic mean to demonstrate attainment of the SHS in soils. The 75%/10X rule is valid ONLY for the SHS. For UST release sites that have only localized (soil) contamination as defined in the storage tank program's Underground Storage Tank Closure Guidance, and where the confirmatory samples taken in accordance with this TGM result in fewer samples being taken than otherwise required [including the sampling procedure for petroleum contaminated soils outlined in Section 250.707(b)(1)(iii)(B) of the regulations], all sample results must meet the SHS. For the site-specific standard, the regulations recommend the use of the 95% UCL of the arithmetic mean to demonstrate attainment in soils. Sections 250.707(b) and (c) of the regulations discuss statistical tests appropriate to demonstrating compliance of surface soils with the Statewide health and site-specific standards.

Figure III-7: Flow Chart of Recommended Statistical Methods



(a) 75%/10X Rule

The 75%/10X rule is a statistical ad hoc rule that tests whether the true site median concentration is below the cleanup standard. This rule requires that 75% of the samples collected for demonstration attainment be equal to or below the risk-based cleanup standard and that no single sample result exceeds the risk-based standard by more than ten times. (See 25 Pa. Code § 250.707(b)(1)(i)).

For the 75%/10X rule, the number of sample points required for each distinct area of contamination is specified in Section 250.703(d) of the regulations and is as follows:

- For soil volumes equal to or less than 125 cubic yards, at least eight (8) samples.
- For soil volumes up to 3,000 cubic yards, at least twelve (12) sample points.
- For each additional volume of up to 3,000 cubic yards, an additional twelve (12) sample points.
- Additional sampling points may be required based on site-specific conditions.

This recommendation of 8 to 12 samples at minimum is based on a simulation study using lognormal distributions (CSSAB 1996). Because the heterogeneity of a volume of soil increases as the volume increases, the number of samples required to accurately demonstrate attainment would also increase.

In a situation where compliance with two different SHS MSCs are required, such as an MSC for surface soil and another MSC for subsurface soil, two separate attainment tests, each applying the 75%/10x rule, would be required (0-2 feet and 2-15 feet).

It should be noted that the 75%/10X rule should not be used to demonstrate attainment of the site-specific standard. The site-specific standard is based on site-specific risk assessment methodology, including the assumption that a receptor’s long-term exposure is related to the true site arithmetic average concentration of a contaminant. Therefore, the 75%/10X rule is not appropriate for the site-specific standard.

(b) The 95% Upper Confidence Limit (UCL) of Arithmetic Mean

Using 95% UCL of the arithmetic mean as described in Sections 250.707(b)(1)(ii) and 250.707(c) of the regulations is well documented in various EPA risk assessment or statistical guidances (EPA, 1989, 1992c, 1996, 2002a). It should be noted that this statistical test may be applied to each distinct area of contamination for demonstration of attainment at a site. Site characterization data may not be suitable for inclusion in determining a 95% UCL for attainment demonstration.

The following formula can be used for calculating sample size (number of discrete soil samples) needed to estimate the mean:

$$n_d = \sigma^2\{(Z_{1-\beta} + Z_{1-\alpha})/(C_s - \mu_1)\}^2$$

where α is the false positive rate; β is the false negative rate; $Z_{1-\alpha}$ and $Z_{1-\beta}$ are the critical values for the normal distribution with probabilities of $1-\alpha$ and $1-\beta$; C_s is the cleanup standard; μ_1 is the value of population mean under the alternative hypothesis for which the specific false negative rate (β) is to be controlled; σ is an estimate of true standard deviation of the population.

Please note that the above equation may generate exceedingly large sample size numbers (e.g., >>50). When some adjustments of the sample size are necessary based on practical and cost considerations, a person may use the equation to generate a smaller sample size by increasing the false negative rate or the detection difference $C_s-\mu_1$. Professional judgment should be used in calculating sample size versus the reliability of the statistical test. The false positive rate must not be greater than 0.20 for a nonresidential site or 0.05 for a residential site (25 Pa. Code § 250.707(d)(2)(vii)).

Procedures to calculate 95% UCL of arithmetic mean are provided in Sections III.B.6 and III.B.7 of this TGM.

The following decision rule is used to determine if a site meets the cleanup standard:

- If 95% UCL of arithmetic mean is greater than or equal to C_s, conclude that the sample results do not meet the cleanup standard.

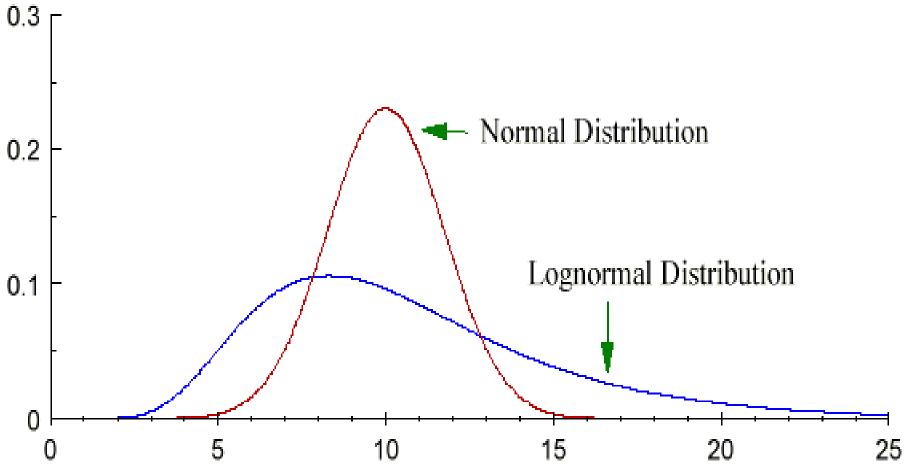
- If 95% UCL of arithmetic mean is less than C_s, conclude that the sample results meet the cleanup standard.

Note that this rule uses the 95% UCL of the arithmetic mean to estimate the limit of the population mean. The decision rule is consistent with the hypothesis statements.

The primary assumptions of this method are independence of the data, and sample mean is approximately normally distributed or data are lognormally distributed. Examples of normal and lognormal distributions are shown in Figure III-8. When the population is normally distributed, the sample mean is normally distributed, no matter the sample size. However, if the population distribution is unknown, Central Limit Theorem states that the distribution of sample means of random samples with fixed sample size (n) from a population with an unknown distribution will be approximately normally distributed provided the sample size (n) is large. This means that moderate violation of the assumption of normality for the population is acceptable when sample size is large.

For sample sizes up to 50, EPA recommends using Shapiro Wilk test for testing normality (EPA, 2009). Other tests for normality, such as Shapiro-Francia test and other goodness-of-fit tests are discussed in EPA's Unified Guidance (EPA, 2009). To test the independence of data, ordinary-runs test (Gibbons, 1990) can be used.

Figure III-8: Examples of Normal Distribution and Lognormal Distribution



An important consideration regarding the 95% UCL of arithmetic mean is the use of composite sampling approach. Unless composite sampling is considered inappropriate (such as for volatile organic compounds (VOCs)), data from composite sampling can be more cost-efficient to estimate population mean and population variance than discrete sampling (Edland et al., 1994; Patil et al., 1994). Composite sampling can reduce the laboratory analysis cost. Composite sampling may be considered, if appropriate, to obtain the 95% UCL of arithmetic mean. Equations to calculate the 95% UCL of arithmetic mean for composite sampling are available (Edland et al., 1994; Patil et al., 1994).

(c) No Exceedance Rule

For cleanup of releases of petroleum products where full site characterization has not been conducted and remediation is guided by visual observation and/or field screening, the no exceedance rule must be used as described in Section 250.707(b)(1)(iii) of the regulations as follows:

For sites where there is localized contamination as defined in the document "Closure Requirements for Underground Storage Tank Systems" (DEP technical document No. 263-4500-601), samples shall be taken in accordance with that document.

For sites with contamination that does not qualify as localized under that document, samples shall be taken from the bottom and sidewalls of the excavation in a biased fashion that concentrates on areas where any remaining contamination above the SHS would most likely be found. The samples shall be taken from these suspect areas based on visual observation and the use of field instruments. If a sufficient number of samples has been collected from all suspect locations and the minimum number of samples has not been collected, or if there are no suspect areas, then the locations to meet the minimum number of samples shall be based on a random procedure. The number of sample points required shall be determined in the following way:

- For 250 cubic yards or less of excavated contaminated soil, five samples shall be collected.

- For each additional 100 cubic years of excavated contaminated soil, one sample shall be collected.

- For excavation involving more than 1,000 cubic yards of contaminated soil, the Department will approve the confirmatory sampling plan.

- Where water is encountered in the excavation and no obvious contamination is observed or indicated, a minimum of two of the soil samples identified above shall be collected just above the soil/water interface. These samples shall meet the MSC determined by using the saturated soil component of the soil-to-groundwater numeric value.

- Where water is encountered in the excavation and no obvious contamination is observed or indicated, a minimum of two water samples shall also be collected from the water surface in the excavation.

All sample results shall meet the SHS.

For sites where there is a release to surface soils resulting in excavation of 50 cubic yards or less of contaminated soil, samples shall be collected as described above, except that two samples shall be collected.

ii) Groundwater Risk-Based Standards

Statistical tests appropriate to demonstrating compliance with groundwater standards are presented in Section 250.707(b)(2) of the regulations. Groundwater cleanup activities generally include site investigation, groundwater remediation, a post-treatment period allowing the groundwater to stabilize, sampling and analysis to assess attainment, and possible post-cleanup monitoring. Different statistical procedures are applicable at different stages in this cleanup process. The statistical procedures used must account for the changes in the groundwater system over time due to natural or man-induced causes. The specific statistical procedures used depend on the goals and quality of the monitoring data. The methods selected should be consistent with the goals of the monitoring. For example, a remediator may want to use regression analysis to decide when to stop treatment of groundwater. Regression analysis can be used to detect trends in contaminant concentration levels over time, to determine variables that influence concentration levels, and to predict chemical concentrations at future points in time. After terminating groundwater treatment, a remediator may want to use time trend analysis or plotted data to find if the groundwater has stabilized. After the groundwater has reached a steady state, the remediator may compare monitoring well concentrations to background reference well concentrations to determine whether the post-cleanup contamination concentrations are acceptable compared to the cleanup standards and may perform trend analysis or use plotted data to determine whether the post-cleanup contamination concentrations are likely to remain acceptable.

Once the groundwater has stabilized, it is recommended to use the 95% UCL of the mean (EPA, 2002a) or the following CSSAB ad hoc rule to compare with groundwater risk-based standards: In monitoring wells beyond the property boundary, the attainment criteria would be 75% of the sampling results from any given well below the standard with no individual value being more than 2 times the standard (75%/2X rule). This rule would have to be met in each individual monitoring well.

To use the CSSAB ad hoc rule, eight samples from each compliance well must be obtained during eight consecutive quarters. A shorter sampling period (25 Pa. Code § 250.704(d)) requires the use of the no exceedance rule (25 Pa. Code § 250.704(d)(3)) with written approval of the Department.

iii) Soil Background Standards

The determination of attainment of soil background standards is based on a comparison of the distributions of the background concentrations of a regulated substance with the concentrations in an impacted area. The regulations allow a remediator to use highest measurement comparison, combination of Wilcoxon Rank Sum (WRS) test and Quantile test, or other appropriate methods to demonstrate attainment of background standards (25 Pa. Code §250.707(a)(1)). No matter which method is used, the regulations require that the minimum number of samples to be collected is ten from the background reference area and ten from each cleanup unit. This requirement of ten samples is to ensure that any selected statistical test has sufficient power to detect contamination. The regulations do not specify the false negative rate because it is more appropriate to determine the false negative rate on a site-specific basis. For the background standard, the false negative rate is the probability of mistakenly concluding that the site is clean when it is contaminated. It is the probability of making a Type II error.

Background soil sampling locations must be representative of background conditions for the site, including soil type and depth below ground surface. Randomization of sampling at background reference and onsite locations must be comparable. EPA (EPA, 1992c) recommends that samples be collected from background reference areas and cleanup units based on a random-start equilateral triangular grid. When a triangular grid may miss the pattern of contamination, EPA recommends the use of an unaligned grid (Gilbert, 1987, p. 94) to determine the sampling locations.

(a) Wilcoxon Rank Sum Test

This procedure (also known as Mann-Whitney U test) is a nonparametric test for differences between two independent groups. See EPA, 2009, ITRC (2013) and Section 250.707(a)(1)(ii) of the regulations.

For the WRS test, the EPA states that Noether's formula may be used for computing the approximate total number of samples to collect from the background reference area and in the cleanup unit (EPA 1992c).

$$N = \frac{\left(Z_{1-\alpha} + Z_{1-\beta}\right)^2}{12c(1-c)(Pr-0.5)^2(1-R)}$$

(Noether's formula) = total number of required samples.

where

α = specified Type I error rate

β = specified Type II error rate

$Z_{1-\alpha}$ = the value that cuts off $(100\alpha)\%$ of the upper tail of the standard normal distribution

$Z_{1-\beta}$ = the value that cuts off $(100\beta)\%$ of the upper tail of the standard normal distribution

c = specified proportion of the total number of required samples, N, that will be collected in the reference area

m = number of samples required in the reference area = c x N

Pr = specified probability greater than 1/2 and less than 1.0 that a measurement of a sample collected at a random location in the cleanup unit is greater than a measurement of a sample collected at a random location in the reference area. This value is specified by the user. See Section 6.2.2 of EPA, 1992c for methods to determine Pr.

R = expected rate of missing or unusable data

n = number of samples required in the cleanup unit = N – m

The underlying assumptions for the WRS test are random sampling, independence assumption of selecting sampling points, and that the distributions of the two populations are identical in shape and dispersion. The distributions need not to be symmetric. When applied with the Quantile test, the combined tests are most powerful for detecting true differences between two population distributions. When using the combined test, caution should be exercised to ensure that the underlying assumption of equal variance is met. An appropriate test for dispersion, such as Levene’s test can be used. Unequal dispersion of data due to higher concentration of contaminant at the site should be properly addressed.

Procedures and an example of using the WRS test are in Section III.B.8.

(b) Quantile Test

The Quantile test (Johnson et al. 1987), described in Sections 250.707(a)(1) and 250.707(a)(1)(ii) of the regulations, is performed by first listing the combined reference-area and cleanup-unit measurements from smallest to largest, as was done for the WRS test. Then, among the largest r measurements (i.e., r is the number of measurements) of the combined data sets, a count is made of the number of measurements, k, that are from the cleanup unit. If k is sufficiently large, then we conclude that the cleanup unit has not attained the reference-area cleanup standard. The Quantile test is more powerful than the WRS test for detecting when only one or a few small portions of the cleanup unit have concentrations larger than those in the reference area. Also, the Quantile test can be used when a large proportion of the data is below the limit of detection. See Chapter 7 of the EPA attainment guidance (EPA, 1992c). See ProUCL Version 4.0 (2007) for further details.

For Quantile test, EPA recommends using look-up tables to determine the number of measurements that are needed from the background reference area and the cleanup unit (Section 7.2 of EPA, 1992c).

Procedures and an example of using the Quantile test are in Section III.B.9 of this TGM. The null hypothesis (H_o) and alternative hypothesis (H_a) statements for the Quantile test are:

H_o: $\varepsilon = 0, \Delta/\sigma = 0$

H_a: $\varepsilon > 0, \Delta/\sigma > 0$

where

ε = the proportion of the soil in the cleanup unit that has not been remediated to background reference levels

Δ/σ = amount (in units of standard deviation, σ) that the distribution of 100ε% of the measurements in the remediated cleanup unit is shifted to the right (to higher measurements) of the distribution in the background reference area

The underlying assumptions for Quantile test are random sampling, independence assumption of selecting sampling points, and that the distributions of the two populations have the same dispersion (variance).

iv) Groundwater Background Standards

Background conditions include two general categories. The first is naturally occurring background or area-wide contamination. The second is background associated with a release of regulated substances at a location upgradient from the site that may be subject to such patterns and trends.

For naturally occurring background or area wide contamination, it is recommended that a minimum of 12 samples be collected from any combination of upgradient monitoring wells, provided that all data collected are used in determination of background concentrations. This same number of samples must then be collected from monitoring wells impacted by a release on the site during the same sampling event. In both cases, this sampling may be accelerated such that all samples are collected as quickly as possible, so long as the frequency does not result in serial correlation in the data. The resulting values may be compared using nonparametric or parametric methods to compare the two populations, such as using the combination of WRS test and Quantile test described previously. When comparing with the background results, the sampling results in the onsite plume may not exceed the sum of the arithmetic average and three times standard deviation calculated for the background reference area (25 Pa. Code §250.707(a)(1) § 250.707(a)(3)(vii)).

For background associated with a release of regulated substances at a location upgradient from a property, the background groundwater concentrations will be determined at the hydrogeological upgradient property line of the property, or a point hydrogeologically upgradient from the upgradient property line that is unaffected by the release (25 Pa. Code §250.204(f)(8)).

Attainment of the background standard must be demonstrated wherever the contamination occurs. Some mass of a particular contaminant may be added to groundwater on the property. However, that additional mass cannot result in concentrations which exceed the concentration measured at the property line, nor can it be used to allow releases on the property. In some cases, contaminants may degrade in groundwater (e.g. chlorinated solvents). In situations such as these where biodegradation is occurring, the total contaminant mass must not increase at the POC for the site. Background concentrations are not related to a release at the site (Section 103 of Act 2).

In the event contamination migrates off the property, concentrations at the downgradient property boundary must be equal to or less than the background concentrations measured where groundwater enters the property. If a release on-property has occurred, the plume migrating beyond the property boundary must also meet the background standard (25 Pa. Code § 250.203(a)).

For background associated with an upgradient release of regulated substances, allows the use of the nonparametric tolerance limit procedure (25 Pa. Code § 250.707(a)(2). The nonparametric tolerance limit procedure requires at least 8 samples from each well over 8 quarters to have sufficient power to detect contamination. When the nonparametric upper tolerance limit is established for upgradient data, data from downgradient compliance wells can be compared to the limit. A resampling strategy must be used when an analyte exceeds the nonparametric upper tolerance limit. The well is retested for the analyte of concern, and the value is compared to the nonparametric upper prediction limit. These two-phase testing strategies can be very effective tools for controlling the facility-wide false positive rate while maintaining a high power of detecting contamination.

5. Additional Information on Statistical Procedures

This section provides an overview regarding various other statistical methods available to use to determine if a cleanup activity is successful. The EPA Addendum (EPA, 1992a), EPA Groundwater Attainment (EPA, 1992b), EPA Soil Reference-Based Standards Attainment (EPA, 1992c), EPA QA/G-9 (EPA, 1996), and EPA Unified Guidance (2009) describe and provide examples for both the parametric and nonparametric methods. See additional discussions in Helsel and Hirsch (1992), Conover (1980), Gilbert (1987), and Davis and McNichols (1994, Parts I and II), and ITRC's Groundwater Statistics and Monitoring Compliance (2013). It is important to note that EPA's ProUCL, free statistical software for environmental applications, can run all of the tests summarized in the following sections.

a) Interval Tests

Statistical Intervals - Statistical interval tests can be used independently for comparing with a numerical value or in combination with other tests for comparing populations. Statistical intervals include three main types: tolerance intervals, prediction intervals, and confidence intervals. Which ones are used depend on the goals of the data analysis.

Tolerance Intervals - Tolerance intervals will typically be the most useful interval test. They are used to determine the extent of data that is within a standard (like an MCL) or ambient level. Parametric tolerance intervals can be computed by assuming a lognormal distribution.

Prediction Intervals - Prediction intervals are used to determine if the next one or more samples are within the existing data distribution at a certain confidence level. The prediction interval contains 100 * (1- α value) percent of the distribution. A smaller α value will include a larger range of data. Prediction intervals are used for intrawell (single well) comparisons, and with comparison of a compliance well with a background well.

Confidence Intervals - Confidence intervals contain a specified parameter of the distribution (such as the mean of the data) at a specified confidence level. Confidence intervals do not address extreme values. The step-by-step procedures to calculate the upper confidence of mean are provided in Sections III.B.6 and III.B.7.

b) Tests for Comparing Populations

The following tests are some of the EPA's recommended tests for analysis of groundwater data between upgradient and downgradient well groups, downgradient wells and a health-based standard, or of intrawell (single well) comparisons. This does not include all potentially satisfactory statistical tests.

Analysis of Variance (ANOVA) - ANOVA includes a group of procedures used for comparing the means of multiple (3 or more) independent groups such as upgradient wells and downgradient wells. The ANOVA methods are used to determine if there is statistically significant evidence of contamination at downgradient wells compared to an upgradient well, or groups of wells.

The one-way ANOVA method is described with examples in Section 17 of the EPA Unified Guidance (EPA, 2009). This is the EPA recommended procedure for comparing data that do not violate the assumptions of normal distribution and approximately equal variances.

However, as the number of wells (or groups) increases at a site, the power of ANOVA to detect individual instances of contamination decreases. For this reason, tolerance and prediction intervals with retesting provisions are often much better procedures to use.

Kruskal-Wallis Test - If assumptions of the one-way ANOVA test are "grossly" violated, the nonparametric Kruskal-Wallis test is used for more than 2 independent groups of data. It can be used for comparison of upgradient water quality to water quality from many downgradient wells in one procedure. Alternatively, if the wells are grouped by some characteristic (e.g., depth, geology, location, season), comparisons among other groups can be made.

If the null hypothesis (no change) is rejected by Kruskal-Wallis (i.e., the test statistic exceeds the tabulated critical value), then pairwise comparisons should be made to determine what wells are contaminated (see Gilbert (1987), Section 18.2.2; the EPA Addendum (1992a), Section 3.1; and the EPA Unified Guidance (2009), Section 17.1.2). The underlying assumptions are the distributions of the independent populations are identical in shape (variance), but the distributions need not to be symmetric.

t-test - The t-test is a parametric, ANOVA type of test used to assess differences in means of two independent groups. This test assumes normal distributions and equal variances for both groups. The t-test is best limited to situations where the data sets are too small to use nonparametric procedures. For example, if background water quality is limited to two or three samples, the t-test can be used to test for differences between background and compliance data.

c) Trend Tests

Considerations - When monitoring data have been collected over several years or more, trend tests allow the determination of the change in distribution of data over time. In addition to water quality trends, a time series of monitoring data may contain characteristics of seasonality and serial correlation. Other complicating factors include changes in laboratories or procedures involving the sampling and analysis of the analyte.

Seasonality and serial correlation interfere with trend tests either by reducing the power to detect trends or giving erroneous probabilities. Correction for seasonality is available for tests presented here. Serial correlation exists if a data point value is at least partially dependent on nearby data point values. For a given data set, serial correlation decreases with increasing temporal distance between samples. Harris, *et al.* (1987) reported difficulty detecting serial correlation in 10 years or less of quarterly groundwater data. Therefore, correction is not recommended for quarterly data. Serial correlation correction is available for the Seasonal Kendall trend test (Hirsch and Slack, 1984), but has reduced power with small data sets and is not recommended for a monthly time series that is less than 5 years.

Parametric Trend Tests - Parametric trend tests are based on regression methods and allow compensation for exogenous effects (outside influences). Regression analysis between two variables can be used to calculate the correlation coefficient (r). The closer r is to one, the closer the relationship is between the two variables. A t-test of correlation can be done on r to see if it is significant (see Davis, 1987, Chapter 2; EPA, 1996, Section 4.3.2; EPA, 2009).

Mixed (i.e., parametric and nonparametric methods) methods also are available when removing the effects of exogenous variables. Helsel and Hirsch (1992) present a thorough review of trend analysis. Methods for detecting trends also are presented in Chapter 16 of Gilbert (1987).

Because regression techniques are based on the assumption of a normal distribution of the data, a nonparametric approach may have to be used.

Nonparametric Trend Tests - The Mann-Kendall trend test is a nonparametric test for monotonic (steadily upward or downward) trend. (Gilbert, 1987; Section 4.3.4 of EPA, 1996; Section 17.3.2 of EPA, 2009).

This test requires constant variance in data. Non-constant variance may be changed to constant variance with a power transformation. Logarithm transformation is usually most appropriate. This transformation does not affect the test statistic. Decision rules, exact test tables, normal approximation formulas, and correction for ties can be found in Helsel and Hirsch (1992); Gilbert (1987) and many introductory statistics texts. When a trend is present, the slope of fitted line can be estimated using Sen’s estimator (see Gilbert, 1987; Section 4.3.3 of EPA, 1996; Section 17.3.3 of EPA, 2009).

The Seasonal Kendall trend test is a seasonally corrected Mann-Kendall trend test. This should be applied when time series graphs or boxplots of data indicate the presence of seasonal variation. See Chapter 17 of Gilbert (1987).

The following sections present the methodology of several statistical tests which may be utilized in the course of demonstrating attainment of an Act 2 standard. Again, it is worthwhile to note that statistical computer software, such as EPA's ProUCL, has been developed to perform these tests.

6. Calculation of UCL of Mean When the Distribution of the Sampling Mean is Normal

The following is a step-by-step description of the approach used to calculate confidence limits of an arithmetic mean when the distribution of the sampling mean is normal. For data sets of lognormal distribution, the approach in Section III.B.7 should be used instead.

1. Calculate the sample mean by dividing the sum of the total readings by the total number of readings:

$$\overline{X} = (X_1 + X_2 + Xn)/n$$

2. Calculate the sample variance (Sb^2) by taking the sum of the squares of each reading minus the mean and dividing by the degrees of freedom (df, the total number of samples minus one):

$$Sb^2 = [(X_1 - \overline{X})^2 + (X_2 - \overline{X})^2 + +(Xn - \overline{X})^2]/(n-1)$$

3. Calculate the standard deviation (Sb) by taking the square root of the variance (Sb^2):

$$Sb = \sqrt{(Sb^2)}$$

4. Calculate the standard error of the mean (Sx). Standard error is inversely proportional to the square root of the number of samples (increasing n from 4 to 16 reduces Sx by 50%) where Sx equals Sb/$\sqrt{n}$. [Note: The above procedure is for simple random samples. For systematic sampling, the calculation of standard error should follow instructions in Section 6.5 of EPA soil attainment guidance (EPA, 1989b). For multiple systematic sampling, the equation to calculate unbiased estimate of variance is also available (Gilbert, 1987, p. 97).]

5. Since the concern is only whether the upper limit of a confidence interval is below or above the Act 2 regulatory threshold (RT), the lower confidence limit (LCL) need not be considered. The upper confidence limit (UCL) can be calculated using the one-tailed (one-sided) t values with n-1 degrees of freedom (df) derived from a table of the student's t distribution, $t_{1-a, n-1}$ (Table III-3).

6. The 95% UCL (α=0.05; one-sided) is calculated by using the following formula and substituting the values determined above plus the appropriate t value obtained from the student's t table where UCL equals $\overline{X} + t_{1-a, n-1} * Sx$.

The UCL number resulting from this formula will indicate with a 95% probability that it is either above or below the Act 2 regulatory threshold (RT) developed for the regulated substance subjected to the test.

7. Calculation of UCL of Mean of a Lognormal Distribution

Following is a step-by-step description of the approach used to calculate confidence limits of an arithmetic mean when the distribution of the data set is lognormal. This method is used in risk assessment by EPA (EPA, 1992d).

1. Transform all sample data Xi to Yi (i = 1,2,….n) using the natural logarithm function:

$$Yi = \ln Xi$$

2. Calculate the arithmetic mean of transformed data by dividing the sum of the transformed data by the total number of data:

$$\overline{Y} = (Y_1 + Y_2 + Yn)/n$$

3. Calculate the variance (Sy^2) of transformed data by taking the sum of the squares of each data minus the mean and dividing by the degrees of freedom (df, the total number of samples minus one):

$$Sy^2 = [(Y_1 - \overline{Y})^2 + (Y_2 - \overline{Y})^2 + +(Yn- \overline{Y})^2]/(n-1)$$

4. Calculate the standard deviation (Sy) by taking the square root of the variance (Sy^2):

$$Sy = \sqrt{\left(Sy^2\right)}$$

5. Since the concern is only whether the upper limit of a confidence interval is below or above the Act 2 regulatory threshold (RT), the lower confidence limit (LCL) need not be considered. The UCL can be calculated using the one-tailed (one-sided) H_{1-a} values associated with sample size n from the table of H_{1-a} for computing a one-sided upper 95% confidence limit on a lognormal mean.

6. The 95% UCL (α=0.05; one-sided) is calculated by using the following formula and substituting the values determined above plus the appropriate H_{1-a} value obtained from the table of H_{1-a} where UCL equals

$$\exp\left(\overline{Y} + 0.5 * Sy^2 + Sy * H_{1-\alpha} / \sqrt{n-1}\right).$$

The UCL number resulting from this formula will indicate with a 95% probability that it is either above or below the Act 2 regulatory threshold (RT) developed for the regulated substance subjected to the test.

Note: The H_{1-a} tables can be found in “Selected Tables in Mathematical Statistics, Volume III, American Mathematical Society,” pp. 385-419, C. E. Land, 1975. A subset of Land’s tables also can be found in “Statistical Methods for Environmental Pollution Monitoring,” Tables A10-A13, R. O. Gilbert, 1987. The value of H_{1-a} depends on Sy, n, and the confidence level α. If H_{1-a} is required for values of Sy and n not given in the tables, Land (1975) indicated that four-point Lagrangian interpolation appeared to be adequate with these tables.

The equation used in four-point Lagrangian interpolation is:

$$y = f(x) = \frac{y_1(x-x_2)(x-x_3)(x-x_4)}{(x_1-x_2)(x_1-x_3)(x_1-x_4)} + \frac{(x-x_1)y_2(x-x_3)(x-x_4)}{(x_2-x_1)(x_2-x_3)(x_2-x_4)}$$

$$+\frac{(x-x_1)(x-x_2)y_3(x-x_4)}{(x_3-x_1)(x_3-x_2)(x_3-x_4)} + \frac{(x-x_1)(x-x_2)(x-x_3)y_4}{(x_4-x_1)(x_4-x_2)(x_4-x_3)}$$

where $y_1 = f(x_1)$

$y_2 = f(x_2)$

$y_3 = f(x_3)$

$y_4 = f(x_4)$

The interpolation procedure may include four interpolation steps which are performed along the columns of the table and one interpolation step performed along the rows of the table. The following example illustrates the procedure to apply the four-point Lagrangian interpolation:

H_{1-A} Table		Sample Size, n 3	5	7	10
	0.1	2.750	2.035	1.886	1.802
	0.2	3.295	2.198	1.992	1.881
Sy	0.3	4.109	2.402	2.125	1.977
	0.4	5.220	2.651	2.282	2.089

The above table only provides values for sample sizes of 3, 5, 7, and 10, and Sy values of 0.1, 0.2, 0.3 and 0.4. To interpolate a value for a sample size of 6 and an Sy value of 0.25, the first step is to interpolate a value corresponding to an Sy of 0.25 and a sample size of 3 using the four-point Lagrangian interpolation equation, where

$x = 0.25$

x_1 = 0.10 y_1 = 2.750

x_2 = 0.20 y_2 = 3.295

x_3 = 0.30 y_3 = 4.109

x_4 = 0.40 y_4 = 5.220

The result of this interpolation step is $y = f(0.25) =$ 3.667.

The second step is to interpolate a value corresponding to Sy of 0.25 and a sample size of 5 using the four-point Lagrangian interpolation equation, where

x = 0.25

x_1 = 0.10 y_1 = 2.035

x_2 = 0.20 y_2 = 2.198

x_3 = 0.30 y_3 = 2.402

x_4 = 0.40 y_4 = 2.651

The result of this interpolation step is $y = f(0.25) =$ 2.295.

The third step is to interpolate a value corresponding to an Sy of 0.25 and a sample size of 7 using the four-point Lagrangian interpolation equation, where

x = 0.25

x_1 = 0.10 y_1 = 1.886

x_2 = 0.20 y_2 = 1.992

x_3 = 0.30 y_3 = 2.125

x_4 = 0.40 y_4 = 2.282

The result of this interpolation step is $y = f(0.25) =$ 2.055.

The fourth step is to interpolate a value corresponding to an Sy of 0.25 and a sample size of 10 using the four-point Lagrangian interpolation equation, where

x = 0.25

x_1 = 0.10 y_1 = 1.802

x_2 = 0.20 y_2 = 1.881

x_3 = 0.30 y_3 = 1.977

x_4 = 0.40 y_4 = 2.089

The result of this interpolation step is $y = f(0.25) =$ 1.927.

The last step is using the results obtained from steps 1 - 4 to perform another four-point Lagrangian interpolation to generate a value corresponding to an Sy of 0.25 and a sample size of 6, where

x = 6

x_1 = 3 y_1 = 3.667

x_2 = 5 y_2 = 2.295

x_3 = 7 y_3 = 2.055

x_4 = 10 y_4 = 1.927

The resulted interpolation value is 2.087.

8. Procedure and Example for Conducting the Wilcoxon Rank Sum Test

Procedure

For each cleanup unit and pollution parameter, use the following procedure to compute the WRS test statistic and to determine on the basis of that statistic if the cleanup unit being compared with the background reference area has attained the background standard.

1. Collect the m samples in the reference area and the n samples in the cleanup unit (m + n = N).

2. Measure each of the N samples for the pollution parameter of interest.

3. Consider all N data as one data set. Rank the N data from 1 to N; that is, assign the rank 1 to the smallest datum, the rank 2 to the next smallest datum, and the rank N to the largest datum.

4. If several data are tied, i.e., have the same value, assign them the midrank, that is, the average of the ranks that would otherwise be assigned to those data.

5. If some of the reference-area and/or cleanup-unit data are less-than data (i.e., data less than the limit of detection) consider these less-than data to be tied at a value less than the smallest measured (detected) value in the combined data set. Assign the midrank for the group of less-than data to each less-than datum. For example, if there were 10 less-than data among the background reference and cleanup-unit measurements, they would each receive the rank 5.5, which is the average of the ranks from 1 to 10. The assumption that all less-than measurements are less than the smallest detected measurement should not be made lightly because it may not be true for some pollution parameters, as pointed out by Lambert et al. (1991). However, the development of statistical testing procedures to handle this situation are beyond the scope of this document.

   i. The above procedure is applicable when all measurements have the same limit of detection. When there are multiple limits of detection, the adjustments given in Millard and Deveral (1988) may be used.

   ii. Do not compute the WRS test if more than 40% of either the reference-area or cleanup unit measurements are less-than values. However, still conduct the Quantile test.

6. Sum the ranks of the n samples from the cleanup unit. Denote this sum by WRS.

7. If both m and n are less than or equal to 10 and no ties are present, conduct the test of H_o (cleanup standard attained, Pr = 1/2) versus H_a (cleanup standard not attained, Pr > 1/2) by comparing WRS to the appropriate critical value in Table A.5 in Hollander and Wolfe (1973). Then go to Step 12 below.

8. If both m and n are greater than 10, go to Step 9. If m is less than 10 and n is greater than 10, or if n is less than 10 and m is greater than 10, or if both m and n are less than or equal to 10 and ties are present, then consult a statistician to generate the required tables.

9. If both m and n are greater than 10 and ties are not present, compute Equation A3-1 and go to Step 11.

   i.
$$Zrs = \frac{WRS - n(N+1)/2}{\sqrt{mn(N+1)/12}} \qquad \text{(A3-1)}$$

10. If both m and n are greater than 10 and ties are present, compute

i.
$$Zrs = \frac{WRS - n(N+1)/2}{\sqrt{(nm/12)\left[N + 1 - \sum_{j=1}^{g} t_j\left(t_j^{\,2} - 1\right)\Big/\left(N(N-1)\right)\right]}} \qquad \text{(A3-2)}$$

ii. where g is the number of tied groups and t_j is the number of tied measurements in the jth group.

11. Reject H_o (cleanup standard attained) and accept H_a (cleanup standard not attained) if *Zrs* (from Equation A3-1 or A3-2, whichever was used) is greater than or equal to $Z_{1-\alpha}$, where $Z_{1-\alpha}$ is the value that cuts off 100α% of the upper tail of the standard normal distribution.

12. If H_o is not rejected, conduct the Quantile test.

EXAMPLE

TESTING PROCEDURE FOR THE WILCOXON RANK SUM TEST

1. Suppose that the number of samples was determined using the following specification:

β = specified Type II error rate = 0.30

α = specified Type I error rate = 0.05

c = specified proportion of the total number of required samples, N, that will be collected in the reference area = 0.50

Pr = specified probability greater than 1/2 and less than 1.0 that a measurement of a sample collected at a random location in the cleanup unit is greater than a measurement of a sample collected at a random location in the reference area = 0.75

R = expected rate of missing or unusable data = 0.10

For these specifications we found that m = n = 14 based on Noether's formula.

2. Rank the reference-area and cleanup-unit measurements from 1 to 28, arranging the data and their ranks as illustrated. Measurements below the limit of detection are denoted by ND and assumed to be less than the smallest value reported for the combined data sets. The data are lead measurements (mg/kg).

3. The sum of the ranks of the cleanup unit is

$$WRS = 3 + 7 + ... + 27 + 28 = 272.$$

4. Compute Zrs using Equation A3-2 because ties are present. There are t = 5 tied values for the g = 1 group of ties (ND values). We obtained:

$$Zrs = \frac{272 - 14(28+1)/2}{\sqrt{(14 * 14/12)\left[28+1-5(5*5-1)/(28(28-1))\right]}}$$

$$= \frac{69}{21.704} = 3.18$$

5. From the table of z (Table III-4) we find that $Z_{1-\alpha}$ = 1.645 for α = 0.05 (α = 0.05, the Type I error rate for the test, was specified in Step 1 above). Since 3.18 > 1.645, we reject the null hypothesis H_o: Pr = 1/2 and accept the alternative hypothesis H_a: Pr > 1/2.

6. Conclusion:

   The cleanup unit does not attain the cleanup standard of Pr = 1/2. This test result occurred because most of the small ranks were for the reference area and most of the large ranks were for the cleanup unit. Hence, WRS was large enough for H_o to be rejected.

Example - Wilcoxon Rank Sum Test

Reference Area		**Cleanup Unit**	
Data	**Rank**	**Data**	**Rank**
ND	3		
ND	3	ND	3
ND	3		
ND	3		
39	6		
		48	7
49	8		
		51	9
53	10		
59	11		
61	12		
65	13		
67	14		
70	15		
72	16		
75	17		
		80	18
		82	19
		89	20
		100	21
		150	22
		164	23
		193	24
		208	25
		257	26
		265	27
		705	28
		WRS = 272	

9. Procedure and Example for Conducting the Quantile Test

Table Look-Up Procedure

A simple table look-up procedure for conducting the Quantile test when m and n are specified *a priori* is given in this section. It is assumed that m and n representative measurements have been obtained from the reference area and the cleanup unit, respectively. The procedure in this section is approximate because the Type I error rate, α, of the test may not be exactly what is required. However, the difference between the actual and required levels will usually be small. Moreover, the exact α level may be computed.

The testing procedure is as follows:

1. Specify the required Type I error rate, α. The available options in this document are α equal to 0.01, 0.025, 0.05 and 0.10.

2. Turn to Table A.6, A.7, A.8, or A.9 in Appendix A of EPA 1992 guidance document (EPA, 1992c) if α is 0.01, 0.025, 0.05, or 0.10, respectively.

3. Enter the selected table with m and n (the number of reference-area and cleanup-unit measurements, respectively) to find

   - values of r and k needed for the Quantile test.

   - actual α level for the test for these values of r and k (the actual α may differ slightly from the required α level in Step 1)

4. If the table has no values of r and k for the values of m and n, enter the table at the closest tabled values of m and n. In that case, the α level in the table will apply to the tabled values of m and n, not the actual values of m and n. However, the α level for the actual m and n can be computed using the following equations:

$$\alpha = \frac{\sum_{i=k}^{r} \binom{m+n-r}{n-i} \binom{r}{i}}{\binom{m+n}{n}} \qquad \text{(A4-1)}$$

where $$\binom{a}{b} \equiv \frac{a!}{b!(a-b)!}$$

and $a! = a*(a-1)*(a-2)*.....*3*2*1$

5. Order from smallest to largest the combined m + n = N reference-area and cleanup-unit measurements for the pollution parameter. If measurements less than the limit of detection are present in either data set, assume that their values are less than the rth largest measured value in the combined data set of N measurements (counting down from the maximum measurement). If fewer than r measurements are greater than the limit of detection, then the Quantile test cannot be performed.

6. If the rth largest measurement (counting down from the maximum measurement) is among a group of tied (equal-in-value) measurements, then increase r to include that entire set of tied measurements. Also increase k by the same amount. For example, suppose from Step 3 we have r = 6 and k = 6. Suppose the 5th through 8th largest measurements (counting down from the maximum measurement) have the same value. Then we would increase both r and k from 6 to 8.

7. Count the number, k, of measurements from the cleanup unit that are among the r largest measurements of the ordered N measurements, where r and k were determined in Step 3 (or Step 6 if the rth largest measurement is among a group of tied measurements).

8. If the observed k (from Step 7) is greater than or equal to the tabled value of k, then reject H_o and conclude that the cleanup unit has not attained the reference area cleanup standard ($\varepsilon = 0$ and $\Delta/\sigma = 0$).

9. If H_o is not rejected, then do the WRS test. If the WRS test indicates the H_o should be rejected, then additional remedial action may be necessary.

EXAMPLE

TABLE LOOK-UP TESTING PROCEDURE FOR THE QUANTILE TEST

1. We illustrate the Quantile test using the measurements listed in the example of Section III.B.8. There are 14 measurements in both the reference area and the cleanup unit. Suppose we specify $\alpha = 0.05$ for this Quantile test.

2. Turn to Table A.8 in EPA 1992 guidance (EPA, 1992c; because the table is for $\alpha = 0.05$). We see that there are no entries in that table for m = n = 14. Hence, we enter the table with n = m = 15, the values closest to 14. For n = m = 15 we find r = 4 and k = 4. Hence, the test consists of rejecting the H_o if all 4 of the 4 largest measurements among the 28 measurements are from the cleanup unit.

3. The N = 28 largest measurements are ordered from smallest to largest in the Example of Section III.B.8.

4. From the Example of Section III.B.8, we see that all 4 of the r = 4 largest measurements are from the cleanup unit. That is, k = 4.

5. Conclusion:

   Because k = 4, we reject the H_o and conclude that the cleanup unit has not attained the cleanup standard of $\varepsilon = 0$ and $\Delta/\sigma = 0$. The Type I error level of this test is approximately 0.05.

Note: The exact Type I error level, α, for this test is not given in Table A.8 in EPA 1992 guidance (EPA, 1992c) because the table does not provide r, k, and α for m = n = 14. However, the exact α level can be computed using Equation (A4-1).

The remediator is reminded that the Quantile Test can be run using EPA’s ProUCL free statistical software, version 4.0.

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Table III-2: Random Number Table

67 35 39 82 14	21 81 21 96 81	65 41 49 04 80	38 34 13 03 15	96 42 55 62 54
43 25 59 81 92	29 54 98 87 58	77 38 02 09 27	06 83 23 00 90	63 39 04 52 72
93 16 47 22 58	33 01 43 61 70	10 55 75 64 68	40 17 24 98 10	53 93 00 31 43
76 77 01 14 64	62 38 18 48 04	77 42 32 38 34	34 34 91 42 14	98 51 98 29 05
69 46 32 94 85	32 27 87 78 37	73 39 25 48 92	91 57 68 52 55	11 08 99 13 55
79 92 47 00 30	13 95 52 30 16	41 45 60 80 42	90 05 38 89 84	04 33 13 21 72
84 35 41 19 11	63 65 09 06 44	43 71 87 58 78	95 27 91 41 54	10 42 38 55 83
18 57 74 64 75	42 79 88 46 32	90 31 29 09 90	07 59 89 22 74	50 05 90 43 37
14 18 29 77 76	54 35 67 41 92	09 28 91 97 68	05 60 09 22 47	04 96 99 06 24
49 02 18 20 81	94 15 81 23 52	28 84 83 75 19	13 55 96 13 70	49 79 66 85 27
49 44 95 16 39	39 13 83 99 97	38 48 63 01 40	03 95 68 71 39	36 99 24 29 55
62 07 74 32 26	41 64 83 37 57	55 37 51 98 24	99 16 02 88 85	13 65 61 81 59
75 35 06 72 07	45 22 98 59 25	90 22 41 03 96	33 89 33 58 78	01 32 36 92 82
12 50 08 09 64	33 54 62 98 24	41 72 97 33 34	11 73 67 33 79	95 62 31 23 87
16 95 18 38 50	33 78 48 00 83	01 43 77 97 26	74 84 53 05 49	29 75 77 02 32
76 23 56 61 20	15 68 82 18 28	35 82 40 18 40	31 78 53 98 45	21 87 21 31 95
74 26 53 14 97	14 09 11 22 65	74 81 52 44 80	03 86 84 78 02	55 45 90 71 49
93 69 54 96 15	66 92 23 22 51	38 42 26 71 37	01 70 87 82 47	97 83 49 24 10
85 99 75 39 81	83 56 56 87 09	32 47 40 14 72	95 74 21 08 69	47 94 65 84 88
86 43 28 23 92	54 05 55 03 89	12 57 75 16 83	36 93 99 23 59	67 24 69 74 30
22 91 19 64 96	84 66 44 09 48	80 12 65 25 43	76 36 68 27 47	52 35 61 03 33
65 82 01 56 34	08 22 38 56 21	68 55 13 18 97	45 90 91 27 25	92 06 69 84 31
51 41 63 38 07	27 96 11 21 06	24 45 33 45 37	44 40 67 80 81	39 80 77 98 43
97 80 96 04 25	30 36 44 40 25	84 23 42 79 14	41 11 64 23 14	38 29 48 18 65
89 63 32 14 59	33 78 24 52 88	02 79 97 35 74	67 96 31 61 18	00 44 59 88 88
54 14 28 53 79	48 05 74 00 98	15 74 72 91 47	45 90 66 55 38	99 60 85 09 01
77 14 06 84 47	46 88 91 03 36	75 64 77 72 11	96 46 87 33 07	29 48 37 86 66
67 33 09 75 00	76 85 28 80 71	36 29 40 32 52	52 72 89 43 05	89 50 25 84 26
75 48 93 50 88	27 76 21 90 66	48 55 88 37 76	57 00 14 83 60	67 20 35 37 18
75 86 22 20 23	27 17 67 16 38	16 33 28 72 13	47 84 57 36 12	75 86 75 23 51
40 41 19 44 32	22 13 31 25 77	28 93 89 37 04	52 71 49 87 72	32 30 69 94 36
70 94 88 25 57	99 94 82 56 91	38 22 09 52 01	84 00 60 04 91	53 10 10 51 94
42 06 41 49 47	44 71 23 61 25	64 16 16 04 48	20 65 84 89 71	43 89 73 79 80
90 55 23 36 61	93 34 69 43 83	38 03 93 00 03	13 04 77 54 90	61 26 88 01 26
22 71 21 14 59	41 29 51 06 96	62 92 63 96 16	62 48 56 86 21	16 58 33 07 41
65 63 59 60 55	36 77 10 63 48	11 60 55 27 52	73 11 95 03 79	46 12 07 26 52
74 20 65 77 78	83 37 34 09 07	47 57 86 13 47	91 17 32 50 29	72 25 87 96 71
12 16 90 59 89	14 66 72 99 45	88 86 45 48 35	26 30 34 73 46	78 29 91 46 44
52 14 41 65 84	73 55 53 00 76	43 83 09 28 13	82 07 62 72 74	60 34 43 69 26
19 87 80 56 89	83 28 45 99 87	37 02 53 39 74	08 91 23 30 13	59 59 10 57 10
29 13 62 89 16	81 78 54 60 92	31 01 04 83 60	16 42 66 81 37	42 39 74 64 40
37 30 72 00 39	53 83 30 75 48	44 30 38 98 76	94 55 60 35 12	22 82 36 18 48
66 17 13 28 82	64 10 76 67 69	53 39 05 71 22	35 13 39 97 27	48 26 94 74 53
86 41 73 49 70	03 41 05 77 28	37 71 01 30 86	36 42 65 97 78	09 34 36 56 01
56 52 43 82 45	20 20 45 49 83	52 73 63 70 47	89 93 77 32 26	73 70 50 75 10
17 89 69 72 84	80 48 78 32 51	66 12 29 79 90	25 11 33 37 44	25 47 18 40 74
11 29 91 99 26	43 90 15 09 64	20 54 89 91 59	01 93 40 33 04	46 91 86 33 90
96 68 63 61 19	29 71 05 42 14	05 84 10 36 27	60 49 40 84 92	29 23 10 45 05
29 12 44 07 75	41 74 25 36 05	49 36 50 27 64	37 51 92 47 32	05 02 21 20 71
79 00 54 24 24	32 03 96 86 98	90 65 41 87 39	29 39 75 07 20	14 94 28 87 23

EXAMPLE

USING THE RANDOM NUMBER TABLE (TABLE III-2)

Assume we need to select 10 random numbers with four digits between 0000 and 6000. We need to select a starting point on the table and a path to be followed. The common way to locate a starting point is to look away and arbitrarily point to a starting point. Suppose the number we located this way was 3848. (It is located in the upper left corner of the block that is in the third large block from the left and the third large block down.) From here we will proceed down the column, then go to the top of the next set of columns, if necessary. The first selected number is 3848. Proceeding down the column, we find 5537 next. This is the second selected number. The number 9022 is next. This number is discarded. Continue down this column, the selected 10 random numbers will be 3848, 5537, 4172, 0143, 3582, 3842, 3247, 1257, 2445, and 0279. (The numbers 9022, 7481, 8012, 6855 and 8423 were discarded because they are greater than 6000.)

Table III-3: Student’s t-Distribution for Selected Alpha and Degrees of Freedom

		α for determining t 1-a,n-1							
one-tailed		0.450	0.250	0.200	0.100	0.050	0.025	0.010	0.005
		α for determining t 1-a/2,n-1							
two-tailed		0.900	0.500	0.400	0.200	0.100	0.050	0.020	0.010
	1	0.158	1.000	1.376	3.078	6.314	12.706	31.821	63.657
	2	0.142	0.816	1.061	1.886	2.920	4.303	6.925	9.925
	3	0.137	0.765	0.978	1.638	2.353	3.182	4.541	5.841
	4	0.134	0.741	0.941	1.533	2.132	2.776	3.747	4.604
	5	0.132	0.727	0.920	1.476	2.015	2.571	3.365	4.032
	6	0.131	0.718	0.906	1.440	1.943	2.447	3.143	3.707
	7	0.130	0.711	0.896	1.415	1.895	2.365	2.998	3.499
	8	0.130	0.706	0.889	1.397	1.860	2.306	2.896	3.355
	9	0.129	0.703	0.883	1.383	1.833	2.262	2.821	3.250
	10	0.129	0.700	0.879	1.372	1.812	2.228	2.764	3.169
	11	0.129	0.697	0.876	1.363	1.796	2.201	2.718	3.106
	12	0.128	0.695	0.873	1.356	1.782	2.179	2.681	3.055
	13	0.128	0.694	0.870	1.350	1.771	2.160	2.650	3.012
	14	0.128	0.692	0.868	1.345	1.761	2.145	2.624	2.977
	15	0.128	0.691	0.866	1.341	1.753	2.131	2.602	2.947
	16	0.128	0.690	0.865	1.337	1.746	2.120	2.583	2.921
	17	0.128	0.689	0.863	1.333	1.740	2.110	2.567	2.898
	18	0.127	0.688	0.862	1.330	1.734	2.101	2.552	2.878
df	19	0.127	0.688	0.861	1.328	1.729	2.093	2.539	2.861
	20	0.127	0.687	0.860	1.325	1.725	2.0S6	2.528	2.845
	21	0.127	0.686	0.859	1.323	1.721	2.080	2.518	2.831
	22	0.127	0.686	0.858	1.321	1.717	2.074	2.508	2.819
	23	0.127	0.685	0.858	1.319	1.714	2.069	2.500	2.807
	24	0.127	0.685	0.857	1.318	1.711	2.064	2.492	2.797
	25	0.127	0.684	0.856	1.316	1.708	2.060	2.485	2.787
	26	0.127	0.684	0.856	1.315	1.706	2.056	2.479	2.779
	27	0.127	0.684	0.855	1.314	1.703	2.052	2.473	2.771
	28	0.127	0.683	0.855	1.313	1.701	2.048	2.467	2.763
	29	0.127	0.683	0.854	1.311	1.699	2.045	2.462	2.756
	30	0.127	0.683	0.854	1.310	1.697	2.042	2.457	2.750
	40	0.126	0.681	0.851	1.303	1.684	2.021	2.423	2.704
	60	0.126	0.679	0.848	1.296	1.671	2.000	2.390	2.660
	120	0.126	0.677	0.845	1.289	1.658	1.980	2.358	2.617
	∞	0.126	0.674	0.842	1.282	1.645	1.960	2.326	2.576

Table III-4: Table of z for Selected Alpha

α	$Z_{1-\alpha}$
0.450	0.124
0.400	0.253
0.350	0.385
0.300	0.524
0.250	0.674
0.200	0.842
0.100	1.282
0.050	1.645
0.025	1.960
0.010	2.326
0.0050	2.576
0.0025	2.807
0.0010	3.090

C. Storage Tank Program Guidance

1. Corrective Action Process

The corrective action process (CAP) for storage tanks regulated under The Storage Tank and Spill Prevention Act (35 P.S. §§ 6021.101-6021.2104) ("Storage Tanks Act") was established in 25 Pa. Code Chapter 245 Subchapter D on August 21, 1993 (23 Pa.B. 4033) and revised on December 1, 2001(31 Pa.B. 6615). These regulations provide a streamlined and flexible approach to corrective action. In cases where interim remedial actions (e.g., excavation of contaminated soil) can adequately address a release, the person performing the cleanup is only required to submit one report (site characterization) to the Department. Where localized contamination is associated with the closure of a regulated storage tank system, the Department has offered a standardized closure report form, which may be used to satisfy the site characterization report requirements. The regulation is flexible in that it authorizes the Department to modify or combine elements of the CAP based on the complexity of the release. For example, a responsible party may submit the site characterization report and remedial action plan as one report in some instances.

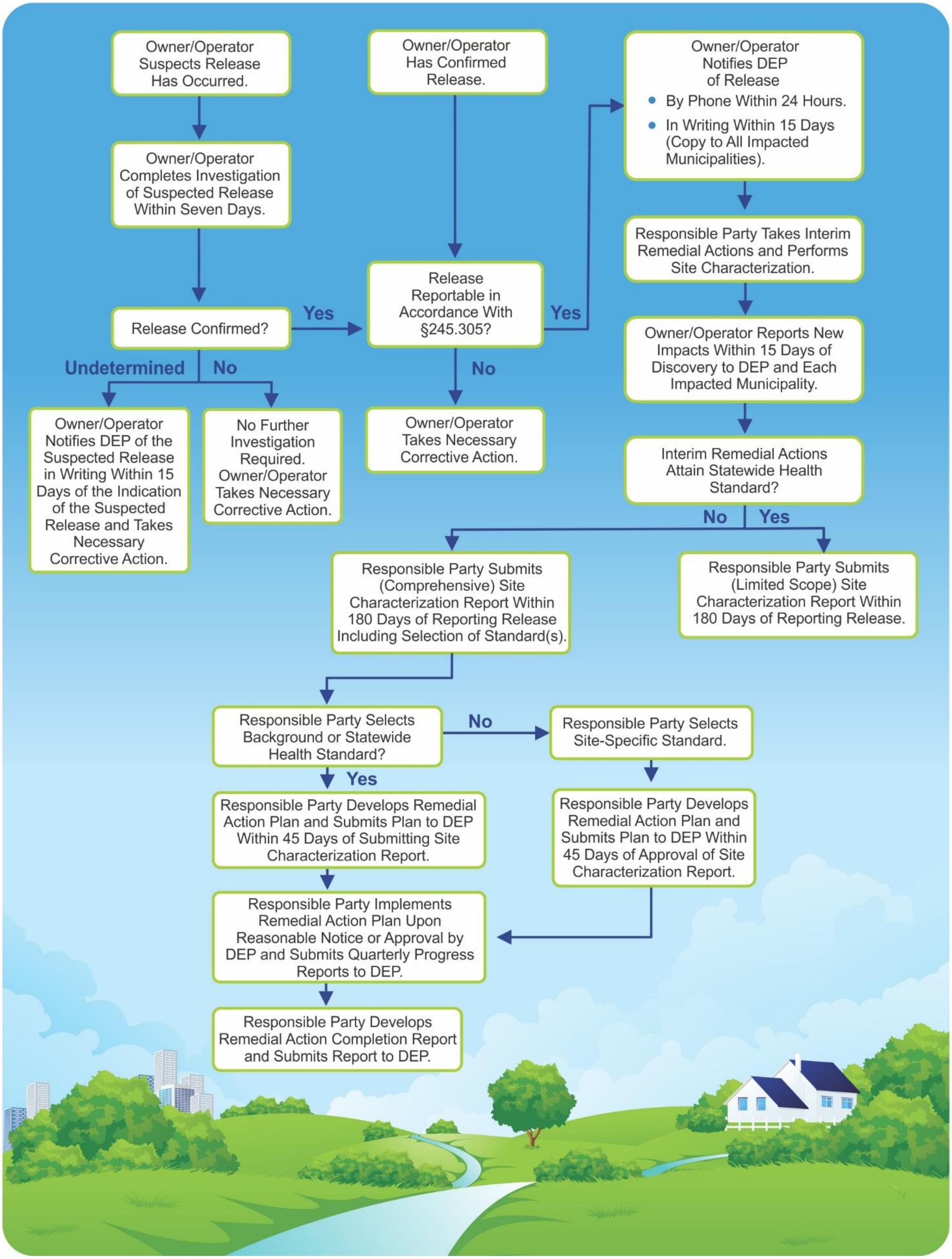
The CAP regulations allow Act 2 cleanup standards to be used to demonstrate remediation of releases from regulated storage tanks. In order to facilitate cleanups, the Department has identified those regulated substances, or "chemicals of concern," that should be quantified by the laboratory for commonly encountered petroleum products. These substances and the accompanying methodologies should be utilized to demonstrate attainment for storage tank remediations as well as other remediations involving petroleum products. Only these substances need to be analyzed and evaluated when petroleum products are released if they are not contaminated by other sources. These analytical requirements appear in the *Site Assessment Sampling Requirements at Regulated Storage Tank System Closures* booklet number 2630-BK-DEP4699 and as Table III-5 in this manual. The Department does not recommend analysis for indicator parameters such as total petroleum hydrocarbons, as they have no standards established by Act 2.

For remediations conducted under the CAP, the person performing the remediation must demonstrate attainment of an Act 2 standard (25 Pa. Code § 245.313(b)). Upon approval by the Department of the report demonstrating attainment, the person is eligible for Act 2 liability protection.

2. Corrective Action Process Checklist

The flow chart in Figure III-9 shows the major steps and the decision-making process that responsible parties must follow when a release from a regulated storage tank is confirmed. This process was designed to be as flexible as possible in order to accommodate the wide range of specific circumstances associated with releases. The following are the major steps of the process:

Figure III-9: The Regulated Storage Tank Corrective Action Process Flowchart



- If a release is confirmed, owners or operators must notify the DEP regional office responsible for the county in which the release occurred, by telephone in accordance with Section 245.305 of the regulations, within 24 hours of confirmation of a release. In addition to basic facility and owner information, the notice must provide, to the extent information is available:

  – the regulated substance involved;

  – the quantity of the regulated substance involved;

  – when and where the release occurred;

  – the affected environmental media;

  – impacts to water supplies, buildings, sewer or other utility lines;

  – interim remedial actions planned, initiated, or completed; and

  – a description of the release.

- Within 15 days of the telephone notice, the owner or operator must follow up with a written notification to the appropriate DEP regional office and any municipality impacted by the release. This written notice must include the same information as provided in the telephone notification and also should include any new information obtained within the 15 days.

- The owner or operator must provide follow-up written notification to the Department and any impacted municipality regarding new impacts to environmental media or water supplies, buildings or sewer or other utility lines, not previously reported, within 15 days of their discovery.

- The Department has prepared a form, number 2630-FM-BECB0082, which can be used to satisfy the written notification requirements. In situations where the release is small, contained and immediately cleaned up, this form may be all that is necessary to complete the CAP.

- Also, upon confirmation of a release, responsible parties must immediately initiate interim remedial actions. These are required response actions from the time a release is confirmed until the time a formal long-term remedial action plan is implemented. Interim remedial actions help maintain or restore public health and safety and prevent the additional release of a regulated substance to the environment and the spread of contamination.

  Interim remedial actions may be all that are necessary to adequately address certain releases. These releases may involve spills and overfills, and cases where a release is confined to the excavation zone of an underground tank.

While all appropriate interim remedial actions must be taken in order to bring a release under control, the first priority at any release site is to identify and eliminate any threat to the health and safety of onsite personnel or nearby residents. See Section 245.306 of the regulations for requirements for interim remedial actions. These interim actions can include:

- checking for and venting product vapors from sewer lines or buildings that have been impacted;
- calling emergency personnel such as local fire and public safety officials for assistance where fire, explosion or safety hazards exist;
- relocating residents until potentially explosive vapors have been reduced to safe levels;
- restricting access to the site by nonessential personnel and establishing a buffer area around the site;
- recovering free product leaking into subsurface structures such as basements and sewers.

Attention should be turned to preventing any further release of the regulated substance to the environment either concurrently with these emergency actions, or as soon as any immediate threats to human health and safety have been eliminated or reduced to acceptable levels. This may include:

- scheduling and conducting the necessary tests to identify and confirm all sources of the release;
- removing product from the storage tanks;
- removing the storage tanks;
- excavating product-saturated soils when practicable;
- recovering free product on the water table;
- recovering product from the excavation;
- placing booms in, or interceptor trenches along, streams, gullies or drainageways where surface water has been impacted or may be impacted; and
- identifying and sampling affected water supplies or water supplies with the potential to be affected, and reporting sampling results to the Department and water supply owner within five days of receipt from the laboratory.

Interim remedial actions planned, initiated or completed are to be indicated during the telephone notification and updated in the 15-day initial and any subsequent written notification as required in Section 245.305 of the regulations. A more detailed discussion of interim remedial actions conducted at the site of the release is to be included in the site characterization report. This report is required to be submitted to the Department within 180 days of reporting a release.

- Any responsible party that affects or diminishes a water supply as a result of a release must restore or replace the affected or diminished water supply at no cost to the owner of the supply (35 P.S. § 6021.1303(b)). A water supply is affected if a measurable increase in a concentration of one or more contaminants occurs (e.g., benzene or MTBE) in the water supply. A water supply is diminished if the quantity of water provided by a water supply is decreased. For example, a water supply well may lose flow as a result of groundwater pumping during a remediation effort. (See definition of "affect or diminish" in 25 Pa. Code § 245.1). The requirement to restore or replace an affected or diminished water supply remains with the responsible party regardless of attainment of an Act 2 standard.

  The responsible party must provide a temporary water supply (e.g., bottled water or water tank) to residents whose water supply is affected or diminished by the release no later than 48 hours after the responsible party receives information, or is notified by the Department, that a water supply has been affected or diminished (25 Pa. Code § 245.307(c)).

  The responsible party must provide a permanent water supply within 90 days after the responsible party receives information, or is notified by the Department, that a water supply has been affected or diminished (25 Pa. Code § 245.307(d)). A permanent water supply may include a well or hookup to a public water supply or treatment system. Where the responsible party provides the affected party with access to a public system, the responsible party is not required to pay for the quantity of water being supplied.

- Responsible parties must properly handle, store and manage excavated contaminated soil which commonly results from tank closures and interim remedial actions (25 Pa. Code § 245.308). In general, petroleum contaminated soil is a residual waste regulated under the Solid Waste Management Act (SWMA) (35 P.S. §§ 6018.101-6018.1003) and must:

  - be stored in accordance with the Department's residual waste management regulations (25 Pa. Code Chapter 299) relating to standards for storage of residual waste;

  - be completely and securely covered for the duration of the storage period, with an impermeable material of sufficient strength, anchoring or weighting to prevent tearing or lifting of the cover, infiltration of precipitation or surface water, and exposure of the soil to the atmosphere;

  - be stored in a manner to prevent public access to the storage area, including use of fencing, security patrols or warning signs; and

  - not present a threat to human health or the environment and must either be undergoing active treatment or disposed of within 90 days from the first day of storage. Active treatment includes methods such as enhanced bioremediation in piles, soil vapor extraction and low-temperature thermal desorption. Active treatment does not include letting the soil pile sit in place.

- At the same time as the interim remedial actions are taking place, responsible parties must conduct a site characterization to determine the extent and magnitude of contamination which has resulted from the release. The CAP regulations provide the objectives of any site characterization and a list of elements that may be necessary or required to be conducted (25 Pa. Code § 245.309). This manual also provides information which should be considered when conducting site characterization work at storage tank release sites. A site characterization report must be submitted to the appropriate DEP regional office within 180 days of confirming the release (25 Pa. Code § 245.310(a)). It is very important that the site characterization report identify the Act 2 cleanup standard selected for the remediation. Interpretations of geologic and hydrogeologic data should be prepared by a professional geologist licensed in Pennsylvania.

- Where interim remedial actions (e.g., removal of contaminated soil) have attained the SHS, and soil is the only medium of concern, the responsible party may submit a site characterization report to DEP limited to the elements in Section 245.310(b) of the regulations. In this case, the site characterization report should describe the entire CAP from site characterization to demonstration of attainment of the SHS.

- Where soil contamination no more than three feet from the tank system is the only contamination observed during the closure of a storage tank system, the responsible party may submit the appropriate Storage Tank System Closure Report Form to satisfy the requirements of the site characterization report identified in Section 245.310(b) of the regulations. A completed closure report form, including adherence to the confirmatory sampling protocol in the closure guidance document appropriate for either aboveground or underground storage tank systems, will be adequate to demonstrate that the requirements of the SHS have been met. Note that the confirmatory sample locations in the closure guidance do not apply if the contamination has extended more than three feet from any part of the tank system. Also, because only limited sampling is required in localized contamination situations, the most conservative medium-specific concentrations (MSCs) are used as action levels. The most current action levels are provided in Tables 3 and 4 in DEP Booklet number 2630-BK-DEP4699.

- Where a site-specific standard is being pursued and a risk assessment report is required under Section 250.405 of the regulations, the report should be submitted to the appropriate DEP regional office with the site characterization report and should contain those elements as described under the site-specific standard of this manual.

- If the comprehensive site characterization report indicates that the interim remedial actions did not adequately address the release, and the background or SHS is selected, responsible parties must develop and submit a remedial action plan to the appropriate DEP regional office within 45 days of submission of the site characterization report. In cases where the site-specific standard is chosen, the remedial action plan is due 45 days after the Department's approval of the site characterization report (25 Pa. Code § 245.311).

- The responsible party must implement the remedial action consistent with the schedule in the remedial action plan upon reasonable notice or approval of the remedial action plan by DEP. Remedial action progress reports must be submitted quarterly to the appropriate DEP regional office (25 Pa. Code § 245.312).

- When the standard(s) established in the remedial action plan has/have been achieved, the responsible party must submit a remedial action completion report. The remedial action completion report must demonstrate that the requirements of one or more of the Act 2 standards have been met and include, if applicable, a postremediation care plan (25 Pa. Code § 245.313).

- In order to receive Act 2 liability protection, the cleanup standards for all regulated substances stored in the tank system, as identified in the site characterization report, must be achieved.

- Petroleum-contaminated media and debris associated with certain underground storage tanks (e.g., soil and groundwater, but not free product) that fail the test for D018-D043 TCLP only and are subject to the federal corrective action regulations under 40 CFR Part 280 are specifically excluded as hazardous waste (40 CFR § 261.4(b)(10). This exclusion does not apply to contaminated media and debris from aboveground tanks, farm and residential motor fuel underground storage tanks of less than 1,100-gallon capacity, as well as heating oil underground storage tanks used for consumptive purposes at the property where located (i.e., tanks not regulated under 40 CFR Part 280). Petroleum-contaminated media and debris that are classified as hazardous waste are subject to the deed notice requirements of SWMA (35 P.S. § 6018.405).

- While the CAP regulations specify when the Department is to receive the site characterization report, remedial action plan and remedial action progress reports, the regulations also provide the Department with the flexibility to shorten or extend the timeframes based on the circumstances of a particular release.

- In addition, the CAP regulations establish Department review timeframes for site characterization reports, remedial action plans and remedial action completion reports. These reports are deemed approved if the Department does not take an action within those timeframes unless the Department and the responsible party agree in writing to an alternative timeframe. The review timeframes are as follows:

- The Department will review a site characterization report submitted under Subsection 245.310(b) within 60 days of receipt, or a site characterization report submitted under Subsection 245.310(a) selecting the site-specific standard within 90 days of receipt.

- Site characterization reports submitted under Subsection 245.310(a) for the background or Statewide health standard will be reviewed within 60 days of receipt of a remedial action plan designed to attain those standards. The review will include the remedial action plan.

- Site characterization reports and remedial action plans for the background or Statewide health standard which are submitted together will be reviewed within 60 days of receipt.

- A remedial action plan designed to attain the site-specific standard will be reviewed within 90 days of receipt by the Department.

- Remedial action completion reports for the background and Statewide health standard will be reviewed within 60 days of receipt. A remedial action completion report demonstrating attainment of the site-specific standard will be reviewed within 90 days of receipt.

Responsible parties are strongly encouraged to properly identify the report or plan being submitted in order to facilitate review of reports and plans by the Department. Figure III-10 is a cover sheet which can be used with CAP submissions.

3. Use of the Short List of Regulated Substances for Releases of Petroleum Products

Petroleum products contain many regulated substances. However, it is not always practical to examine all the regulated substances in a petroleum product. The Department has developed a “short list” of regulated substances for various petroleum products (Table III-5) to be analyzed to demonstrate attainment under any of the Act 2 cleanup standards when a release of these petroleum products occurs and is uncontaminated by other sources.

The Department will accept use of the short list to demonstrate attainment of the SHS if the following conditions are also met:

1. For soil media, no free liquids are left in the soil based on visual observation, and the soil does not create an odor nuisance. The location and level of odor remaining in soil must not result in an odor complaint to the Department, since odor is an indicator which may be attributed to residual free product.

2. For groundwater media, no free-floating product exists at the point of compliance (property line). Free-floating product must be recovered to the maximum extent

practicable and any remaining product cannot pose an unacceptable risk to human health or the environment.

The rationale for the application of these conditions is that the SHS numeric values cannot exceed their saturation and solubility limits in soil and groundwater, respectively. Since the Department is accepting an attainment demonstration for the short list of regulated substances rather than all regulated substances contained in a particular petroleum product, these conditions are necessary to assure that all SHSs applicable to the petroleum product are met.

If the remediator chooses to use the short list, and meets these conditions, then the Remedial Action Completion Report approval will stipulate that Act 2 liability coverage is for the short list substances only.

The short list of petroleum products may be periodically revised as determined necessary by the Department. For sites in the CAP for which a site characterization report has been received, attainment demonstration will be made using the previous list of substances. Sites which commence investigations to characterize or verify releases after the date the new list becomes effective should use the new list for characterization and attainment demonstration purposes to avoid a disapproval.

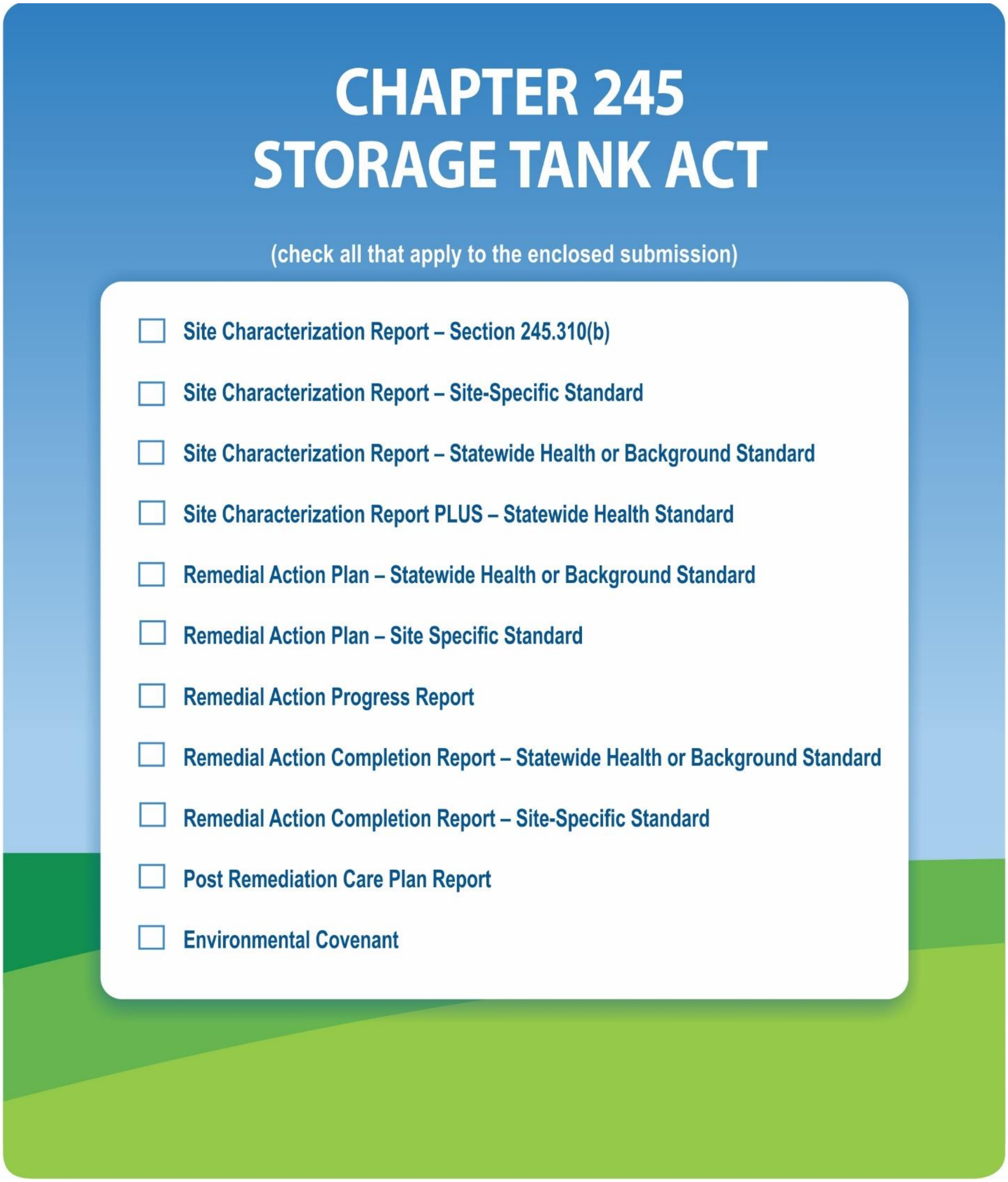
4. Maximum Extent Practicable

EPA has approved Pennsylvania’s UST program in 25 Pa. Code Chapter 245 as consistent with federal law (68 FR 53520 (September 11, 2003)). EPA regulations under 40 CFR § 280.64 require owners and operators to remove “free product” to the maximum extent practicable (MEP) as determined by the implementing agency. Section 280.64(b) requires owners and operators to use abatement of “free product” migration as a minimum objective for the design of the free product removal system. The Department equates “free product,” as the EPA uses the term, to be equivalent to “separate phase liquid” (SPL) as the Department has used that term in the past. Thus, to meet the corrective action requirement for underground storage tanks in Pennsylvania, a remediator must demonstrate the following two requirements, based upon technical data:

- SPL has been removed to the MEP, and

- the release has been demonstrated to attain an Act 2 cleanup standard.

Figure III-10: Corrective Action Process Report/Plan Cover Sheet



CHAPTER 245
STORAGE TANK ACT

(check all that apply to the enclosed submission)

☐ Site Characterization Report – Section 245.310(b)
☐ Site Characterization Report – Site-Specific Standard
☐ Site Characterization Report – Statewide Health or Background Standard
☐ Site Characterization Report PLUS – Statewide Health Standard
☐ Remedial Action Plan – Statewide Health or Background Standard
☐ Remedial Action Plan – Site Specific Standard
☐ Remedial Action Progress Report
☐ Remedial Action Completion Report – Statewide Health or Background Standard
☐ Remedial Action Completion Report – Site-Specific Standard
☐ Post Remediation Care Plan Report
☐ Environmental Covenant

Table III-5: Short List of Petroleum Products

PRODUCT STORED	PARAMETERS TO BE TESTED IN SOIL	ANALYTICAL METHOD (reported on a dry weight basis)	PARAMETERS TO BE TESTED IN WATER	ANALYTICAL METHOD[1]
Leaded Gasoline, Aviation Gasoline, and Jet Fuel	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5- Dichloroethane, 1,2-	EPA Method 5035/8021B or 5035/8260B	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5- Dichloroethane, 1,2-	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Dibromoethane, 1,2- Dibromide)		Dibromoethane, 1,2-(Ethylene	EPA Method 8011 or 504.1
	Lead (total)	EPA Method 6010B or 7420	Lead (dissolved)	EPA Method 6020, 7421, 200.7, 200.8, or 200.9
Unleaded Gasoline	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether (MTBE) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether (MTBE) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2
Kerosene, Fuel Oil No. 1	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2
Diesel Fuel, Fuel Oil No. 2	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2

Table III-5: Short List of Petroleum Products (cont.)

PRODUCT STORED	PARAMETERS TO BE TESTED IN SOIL	ANALYTICAL METHOD (reported on a dry weight basis)	PARAMETERS TO BE TESTED IN WATER	ANALYTICAL METHOD[1]
Fuel Oil Nos. 4, 5 and 6, and Lubricating Oils and Fluids	Benzene Naphthalene	EPA Method 5035/8021B or 5035/8260B	Benzene Naphthalene	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Fluorene Anthracene Phenanthrene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Benzo(g,h,i)perylene	EPA Method 8270C or 8310	Phenanthrene Pyrene Chrysene	EPA Method 8270C, 8310 or 525.2
Used Motor Oil	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) Naphthalene	EPA Method 5035/8021B or 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) Naphthalene	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene	EPA Method 8270C or 8310	Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene	EPA Method 525.2
	Lead (total)	EPA Method 6010B or 7420	Lead (dissolved)	EPA Method 6020, 7421, 200.7, 200.8, or 200.9
Mineral Insulating Oil	PCB-1016 (Aroclor) PCB-1221 (Aroclor) PCB-1232 (Aroclor) PCB-1242 (Aroclor) PCB-1248 (Aroclor) PCB-1254 (Aroclor) PCB-1260 (Aroclor)	EPA Method 8082	PCB-1016 (Aroclor) PCB-1221 (Aroclor) PCB-1232 (Aroclor) PCB-1242 (Aroclor) PCB-1248 (Aroclor) PCB-1254 (Aroclor) PCB-1260 (Aroclor)	EPA Method 8082 or 508A
	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8021B or 5035/8260B	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8021B, 5030B/8260B or 524.2
Other Petroleum Products Blended Petroleum Products Unknown Petroleum Products Other Regulated Substances	Contact the DEP Regional Office responsible for the county in which the tank is located			

[1] Samples from potable water supplies must be analyzed using a method applicable to drinking water.

Notes:
When reporting nondetects (ND), the data must be accompanied by a numerical quantitation limit that takes into account dilution, sample preparation, and matrix effects.
The responsible party has the obligation to ensure that the analytical methodologies and techniques employed are suitable to provide data that meets the minimal data quality objectives outlined and referenced in this document.
Laboratories must document that samples meet all applicable preservation requirements.

As the implementing agency, the Department considers MEP under 40 CFR § 280.64 as the extent of removal necessary to prevent migration of SPL to uncontaminated areas and prevent or abate immediate threats to human health or the environment.

It is important to note that removing SPL to the MEP is not required under Chapter 250. Although removal is not required, if groundwater and/or soil is impacted above a standard, then removing SPL may greatly assist the remediator in attaining a standard. A dissolved phase plume may not be stable if there is a migrating SPL body. Migrating SPL is an SPL body and its associated phases that are documented to be spreading or expanding laterally or vertically into previously uncontaminated areas. Residual and mobile SPL and related terms are discussed further in Section V.D. of this guidance.

In the majority of cases, releases at regulated storage tank sites are liquids with a density less than water, or light non-aqueous phase liquids (LNAPLs). Recent advances in the understanding of LNAPL behavior have illustrated that in some cases, continued attempts to reduce LNAPL to a measured thickness in a monitoring well (e.g., 0.01 ft. or less) may not be practicable. Even in cases where the presence of LNAPL is the only reason for remediation, continued recovery of LNAPL may provide little positive impact on the environment.

5. Management of Light Nonaqueous Phase Liquids (LNAPL) under Act 32

LNAPL typically has been viewed as SPL that is less dense than water and can be measured in a well or on a water surface. Even when measurable LNAPL is not detected within a well, LNAPL can remain trapped in nearby soils or bedrock. Depending on site conditions and how conditions can change, this residual LNAPL may remain trapped or become mobile. Therefore, it is important to keep the following in mind:

- The absence of measurable LNAPL in a well does not definitively establish the absence of mobile LNAPL at a site.

- The presence of measurable LNAPL in a well does not definitively establish the size, volume, thickness, or recoverability of LNAPL at the site or in the vicinity of the well.

- The measured LNAPL thickness in a well may not be indicative of the actual LNAPL thickness or volume within the formation.

- The presence of recoverable LNAPL in a well may only indicate that mobile LNAPL exists in the immediate vicinity of that well.

- The observation that LNAPL is no longer accumulating at a significant or appreciable rate in a well may only indicate that the LNAPL in the vicinity of the well is no longer mobile under the present conditions.

- The mass of residual LNAPL remaining in the soil and/or rock matrix after recovery to the MEP may be orders of magnitude larger than the amount of mobile LNAPL that was recovered at the site.

- LNAPL may spread in many directions not necessarily coincident with groundwater gradients (including but not limited to structural influences, preferential pathways, permeability contrasts, and pumping well influences). See “Sources and Pathways” in Section III.C.5(i).

- LNAPL migration rates may not be the same as the groundwater flow rates.

- Some mobile LNAPL is persistent and can be bailed, but quantities removed may be relatively small. Product bailing alone rarely achieves significant LNAPL recovery.

LNAPL exists in residual and non-residual (mobile) phase, so some LNAPL may remain at the site after reaching removal to the MEP. Although the remaining LNAPL may take years to degrade, the low recoverability along with a demonstration of low risk posed by the LNAPL source may make recovery of remaining LNAPL infeasible or unnecessary. In such instances, evaluating the site for terminating LNAPL recovery is warranted. Information necessary to determine when LNAPL removal meets the MEP is identified below.

a) Site Characterization and LNAPL Conceptual Site Model

Section 245.309 of the regulations requires completion of a site characterization. A complete and concise site characterization is an important step in identifying the presence, properties, distribution and migration of LNAPL. Simple visual observations during site work and interpretation of analytical results can help identify the presence of LNAPL. The characterization of a site with LNAPL includes the development of an appropriate LNAPL Conceptual Site Model (LCSM). The level of detail required for a given LCSM is site-specific and based on the complexity of environmental conditions at each site. As the corrective action progresses, the LCSM should be regularly re-evaluated in light of additional site/LNAPL data, pilot test data, remedial technology performance metrics, and monitoring data. A complete and up-to-date LCSM allows the best possible decisions about application and operation of remedial technologies to be made and when removal actions are no longer necessary. Documents that should be used to guide the development of an LCSM are included in the list of references in Sections III.C.6 and V.F. The LCSM may require revisions as site conditions change due to remediation and other site factors. Table III-6 is a worksheet that can be used when preparing an LCSM.

Older LNAPL cases which pre-date this guidance may require additional assessment to update the LCSM for the purposes of making MEP decisions. Results from an updated LCSM may provide additional information about LNAPL recovery potential for the site. While technologies may appear costly or overly complex, the use of these technologies may assist responsible parties, consultants, and staff to develop the most cost-effective decision regarding LNAPL recovery or case closure. Information needed to characterize LNAPL at a site and develop a thorough LCSM typically includes, but is not limited to:

- **Delineation:** LNAPL does not necessarily form a “pancake” on the groundwater surface, but shares the pore space in the vadose zone, the capillary fringe, and/or beneath the water table within the smear zone. Different industry standard practices can be used to identify LNAPL trapped in soils or bedrock (ranging from shake test to Laser-Induced Fluorescence (LIF) in conjunction with core photography).

- **Sources and Pathway:** Geologic or manmade features such as fractures in bedrock or clay and fill material adjacent to underground utilities may also contain LNAPL and may serve as pathways for enhanced migration of SPL vapor and dissolved phases. These features include fractures in bedrock or clay and fill material adjacent to underground utilities, old foundations, and old tank system cavities. Their presence may significantly increase risk by accelerating potential migration to receptors. Monitoring well placement should consider the movement and storage of LNAPL in these features as part of the site characterization.

- **Volume:** Where possible, the volume (or plausible volume range) of LNAPL within the subsurface should be established to allow the development and selection of an appropriate recovery strategy as well as a basis for the risk evaluation. Historic records for the site should be reviewed to identify past releases that may have contributed to the volume of LNAPL.

- **Age and Chemical/Physical Character:** LNAPL and groundwater can be analyzed to identify or verify the type of product as well as assess if the product poses a risk to receptors. As LNAPL weathers, the physical and chemical properties of the LNAPL can change. Weathered LNAPL can be more viscous and therefore less mobile and less recoverable than unweathered LNAPL. LNAPL properties can also assist in determining a probable date or timeframe for the product release. Knowing the amount of time the product has been present compared to the known impacts (or lack thereof) can provide valuable insight on whether case closure is advisable.

- **LNAPL Migration:** LNAPL moving into previously uncontaminated areas indicates that LNAPL is migrating. It is a condition requiring immediate recovery as per Section 245.306(a)(3)(ii) of the regulations. The potential for mobile LNAPL to migrate may depend on geologic conditions, changing hydraulic or LNAPL gradients as well as precipitation and groundwater recharge. The presence of other contaminants may impact migration of LNAPL.

Table III-6: LNAPL Conceptual Site Model (LCSM) Worksheet

LCSM - describes the physical properties, chemical composition, occurrence and geologic setting of the LNAPL body from which estimates of flux, risk and potential remedial action can be generated (definition taken from ASTM E2531-06).

Site Characterization	**Yes**	**No**	**N/A**	**Comments**
1. Do you know the past and present site use?				
2. Do you know the geology of the site (i.e., soil and bedrock characteristics)?				
3. Do you know the hydrogeology of the site?				
3.a. Unconfined aquifer?				
3.b. Confined/Semi-confined aquifer?				
3.c. Perched aquifer?				
4. Is the source known?				
4.a. If yes, what is the source and quantity released?				
5. Has the vertical and horizontal extent of the LNAPL body been delineated?				
5.a. If yes, have direct and/or indirect indicators been used to detect presence of LNAPL trapped in soils and/or bedrock?				

Site Characterization	Yes	No	N/A	Comments
6. Has dissolved phase or vapor phase plume data been evaluated?				
6.a. Do any dissolved concentrations in groundwater approach their effective solubility?				
7. Have the physical (density, viscosity, interfacial tension, vapor pressure) and chemical properties (constituent solubilities and mole fractions) of the LNAPL been determined?				
8. Have potential migration pathways been identified (i.e. fractures in bedrock and clay, karst features, utilities)?				
9. Are there complete or potentially complete exposure pathways present (potable wells, surface water, vapor intrusion, etc.)?				
10. Are there ecological receptors impacted by the LNAPL body?				
11. Has sufficient gauging data been gathered to determine if LNAPL is mobile?				
11.a. Has gauging taken place during drought or after heavy precipitation events?				
12. Has LNAPL transmissivity been determined?				

Site Characterization		Yes	No	N/A	Comments
13.	Has a qualitative assessment of Natural Source Zone Depletion (NSZD) been completed?				
14.	Does characterization indicate that the LNAPL is no longer migrating?				

- **LNAPL Mobility:** LNAPL needs to exist at saturations greater than its residual saturation in order to be mobile. It is the mobile portion of the LNAPL body that is typically recovered by LNAPL extraction and recovery technologies. However, the presence of mobile LNAPL in a well does not necessarily indicate that the LNAPL body is migrating. Gauging or recovery data from drought and heavy precipitation events may provide mobility data.

- **LNAPL Recoverability/Transmissivity:** LNAPL Transmissivity (LNAPL Tn) is a useful metric for determining the recoverability of mobile LNAPL. Since LNAPL Tn accounts for multiple LNAPL properties such as density, viscosity, and LNAPL saturation, LNAPL Tn can be more useful than just the measured thickness for determining LNAPL recoverability (ASTM E2856). However, LNAPL Tn can vary over time due to subsurface conditions such as groundwater fluctuations, corrective action implementation (reduced LNAPL saturation), or weathering of LNAPL.

  LNAPL Tn tests should be performed at sites where LNAPL is present to aid in determining the recoverability of the LNAPL. LNAPL Tn tests can also be completed over time to document the progress of LNAPL recovery efforts. The ASTM Standard E2856 discusses several LNAPL Tn test methods and how to select the most appropriate method for site conditions. More information about LNAPL Tn may be found in the references to this section, particularly ASTM Standard E2856.

  Characterization of LNAPL is found through direct and indirect indicators. Both types of indicators determine where and how much LNAPL is on the property and are especially important if the release history is unknown. The level of detail needed when using these methods is commensurate with the complexity of the site.

  Some direct methods of detecting the presence of LNAPL include:

  - Direct push technologies that can measure for the presence of LNAPL such as LIF, Rapid Optical Screening Tool LIF, Membrane Interface Probes and cone penetrometers.

  - Observation of LNAPL presence in wells, borings, or test pits.

  - Field screening tests such as staining, odors, Organic Vapor Analyzers, Photo Ionization Detectors, Flame Ionization Detectors, shake test using oleophyllic dyes, paint filter test (EPA method 9095B), and paper towel tests.

  - Ultraviolet light boxes and soil cores.

  - Soil and rock core lab analysis.

- Core photography under UV light, pore fluid saturations, soil properties, fluid properties, and LNAPL fingerprinting.

LIF is used to collect real-time, in-situ field screening of residual and nonaqueous phase hydrocarbons in undisturbed vadose, capillary fringe and saturated subsurface soils and groundwater. Detailed information regarding this technology can be found at EPA's Contaminated Site Clean-Up Information website.

LNAPL presence in wells, borings or test pits indicates that LNAPL is in the surrounding formation. In unconfined conditions, the LNAPL could rise and fall with the fluctuation of the water table. However, it is not a reliable indicator of vertical and lateral extent in the formation or for determining the volume of the release. The absence of LNAPL in a well does not necessarily mean the source is eliminated; it may be trapped deeper in the formation by a high-water table.

Some indirect indicators of LNAPL presence in the formation include:

- A persistent dissolved phase plume.

- Dissolved phase groundwater concentrations that are close to the effective solubility of the LNAPL that was released.

- Total Petroleum Hydrocarbons (TPH) concentrations (EPA Method 418.1) that are greater than the Carbon Saturation (Csat) in a given soil type.

Other potential indirect indicators of LNAPL presence are found in EPA's petroleum vapor intrusion guidance document (510-R-15-001, Table 3, p. 52, 2015).

b) Is the LNAPL Body Migrating?

Removal of LNAPL must be conducted to prevent the spread of contamination into previously uncontaminated zones. Following a release, LNAPL can move at higher rates than groundwater due to a large LNAPL hydraulic head. The LNAPL can be upgradient of the release point due to the mounding effect. Removal of the source will shorten the time until the LNAPL body stops migrating.

In order to demonstrate that an LNAPL body is not migrating, the Department requires an evaluation of migration potential. The following can be used to make this determination. A more detailed description of each follows the list. This list is not all inclusive. Some methods that may be used to demonstrate that LNAPL is not migrating include:

- Monitoring results

- LNAPL velocity
- Recovery rate
- Age of the release
- Tracer test

Monitoring results are most important in evaluating migration potential. Assuming that there is an adequate monitoring network and sufficient temporal data, there are several factors that are evidence for a stable footprint, which include a stable or decreasing thickness of LNAPL in monitoring wells, sentinel wells outside of the LNAPL zone that remain free of SPL, and a shrinking or stable dissolved phase plume.

Calculating the potential LNAPL velocity using Darcy's Law is also important in the evaluation. The key parameter is LNAPL conductivity, which may be estimated from bail-down tests, or from the measured LNAPL thickness, soil capillary parameters and a model that assumes static equilibrium. The American Petroleum Institute (API) Interactive LNAPL Guide is one tool that may be used to estimate the LNAPL velocity using this model. It is important to recognize that use of Darcy's Law would be precluded for some site conditions, such as a fractured bedrock site.

The recovery rate that is observed as LNAPL is removed from a well is important to the evaluation. Although not directly correlated to LNAPL migration, declining recovery rates would generally indicate reduced potential for LNAPL to migrate.

The age of the release, when known, aids in determining migration potential. If a relatively long time has transpired since the release, there is reduced potential for migration due to smearing of LNAPL within soil and weathering of LNAPL through dissolution, volatilization, and biodegradation.

Tracer tests using hydrophobic dye can also be used for this evaluation. The dilution rate of the dye gives an indication of the rate of movement of the LNAPL. Monitoring wells need to have at least 0.2 feet of LNAPL for this method to work.

c) Remedial Action Plan (RAP)

After a complete Site Characterization as outlined in Section 245.309 of the regulations has been completed and when LNAPL recovery continues, a RAP addressing the technologies and methods to remediate both the LNAPL and the dissolved phase portion of the contamination is required under Section 245.311 of the regulations. The RAP should specify remediation goals and endpoints that can be obtained with the most cost-effective solutions/technologies currently proven to remediate the identified contaminants.

If the RAP recommends the ceasing of or no LNAPL recovery, the RAP should clearly list the lines of evidence that demonstrate the LNAPL is not recoverable, is stable, is not migrating and poses no risk to human health and the environment. Once the soil and dissolved phase in groundwater have met attainment under the selected remediation standard, a Remedial Action Completion Report (RACR) can be submitted.

d) Demonstrating LNAPL Meets MEP Criteria

To determine when LNAPL recovery is no longer necessary or if a case with LNAPL can be recommended for closure, several lines of evidence should show that LNAPL has been recovered to the MEP and that the remaining LNAPL is not migrating and poses no risk. These lines of evidence should also show that natural attenuation processes are continuing, further demonstrating that the LNAPL body is stable and not migrating. Lines of evidence should be documented in the RAP and RACR for the Storage Tanks Act and in the Cleanup Plan and/or FR for Act 2. Lines of evidence may include the following:

- An estimate, or supportable estimated range, of the total volume of LNAPL released and present in the subsurface. Volume estimates help determine dissolved plume longevity and the potential to migrate to new areas.

- A discussion, including supporting data, regarding the importance of site-specific soil structure, geology/hydrostratigraphy with an emphasis on the possible existence of macropores, fractures, or conduits in karst. All potential pathways for migration should be analyzed to ensure LNAPL migration to new areas is not occurring.

- A discussion with supporting data that establishes whether LNAPL at the site is a function of groundwater level or confined conditions. Since LNAPL thicknesses are often exaggerated under confined conditions, the LCSM must provide adequate characterization of hydrostratigraphy to determine if confining layers are present.

- A demonstration that constituents in the vapor phase do not present a risk to potential receptors. All potential pathways for vapor migration should be analyzed to ensure migration to new areas is not occurring.

- Documentation that demonstrates the areal extent of the LNAPL plume at the site is stable or decreasing. Monitoring of LNAPL thickness in wells over time is needed to determine stability.

- Documentation that demonstrates the areal extent of the dissolved phase plume at the site is stable or decreasing.

- Documentation that shows concentrations of chemicals of concern are below the standards attained and dissolved plume is undergoing attenuation.

- An evaluation that shows the effective solubility of remaining LNAPL and dissolved-phase concentrations are below the standards attained.

- LNAPL Tn data that documents LNAPL recoverability over a range of aquifer conditions. If LNAPL Tn as measured by ASTM E2856 is below 0.1 ft^2/day, then hydraulic recovery is not feasible. If values exceed 0.1 ft^2/day, demonstrate that LNAPL body is not migrating or that Tn values have been decreasing with recovery efforts and have reached asymptotic conditions.

- A qualitative assessment of natural attenuation.

- A description of the removal methods and technologies which have been used and/or evaluated. Evaluation of the results of product removal including whether data shows asymptotic recovery trends through seasonal water table variations. Data that demonstrates the technologies and additional recovery are not effective.

- Supporting data which contains current site and area maps that show all current receptors, preferential pathways (such as utilities), basements, drinking water wells, and surface water bodies including High Quality and Exceptional Value streams, wetlands, and sensitive ecological areas.

- Documentation that the NSZD (ITRC, LNAPL-1, 2009) of the LNAPL body and natural attenuation of the dissolved-phase plume are continuing at the site and are expected to further mitigate risk from the release.

e) Closure of Sites with LNAPL

For purposes of this guidance, recovery to MEP is considered complete if the following have been demonstrated:

- LNAPL remains onsite, but the following have been achieved:

  Receptor evaluation demonstrates that remaining LNAPL, dissolved phase constituents, and associated vapors are not a risk to human health or the environment, and the following:

  i. Natural Source Zone Depletion of the LNAPL body and natural attenuation of the dissolved-phase plume are documented as occurring at the site and are expected to further mitigate risk from the release;

  ii. Multiple lines of evidence demonstrate that LNAPL had been recovered to MEP;

iii. For sites with active LNAPL recovery, evaluation of corrective actions performed at the site shows asymptotic recovery trends through seasonal water table variations; and

iv. Remaining LNAPL is not recoverable or has low mobility/recoverability (as evidenced by LNAPL Tn tests).

Situations do exist in which LNAPL can justifiably remain at a site after case closure. However, the Department should have a full understanding of the site-specific geological, hydrogeological, and receptor risk factors before closing a case with measurable LNAPL.

If an institutional or engineering control is needed to attain a standard, then an environmental covenant would be needed.

Note: A closed case may be re-opened if significant previously unidentified environmental problems related to the original release (for example, additional LNAPL, extensive saturated soils, or an impacted receptor) are discovered.

6. References

ASTM E2856, Standard Guide for Estimation of LNAPL Transmissivity.

EPA. 2015. Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites. EPA 510-R-15-001.

ITRC (Interstate Technology & Regulatory Council) 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. LNAPL-1. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org

EPA. Contaminated Site Clean-Up Information. http://clu-in.org/characterization/technologies/lif.cfm

D. Mass Calculations

The following sections demonstrate methods to calculate groundwater and soil mass utilizing site specific measurements of contaminants and volume of the specific soil or liquid plumes.

1. Groundwater Mass Calculation

Calculate Water Volume (WV)

Water Volume(WV-ft^3) = Length of plume(L) x Average Thickness of plume(H) x Average Width of plume(W) x porosity(n)

Calculate Water Mass (WM)

Water Mass(WM-lb.) = Water Volume(WV-ft^3) x 62.5 lb./ft^3

Calculate Mass of Contaminant

Water Mass(WM-lb.) x Contaminant Concentration(C-ppm)/ 10^6 = Contaminant Mass(lb.)

2. Soil Mass Calculation

These soil mass calculations provide a way of quantifying contaminants in soil that under an Act 2 remediation would track the estimations of the mass of contaminants removed from public exposure as a measure of program success. Contaminants removed from public exposure can be any one or a combination of excavation and disposal, treatment or pathway elimination measures. The mass calculations would not include areas of the site where site characterization found concentrations to be at or below the applicable standard. This area remains unchanged and thus there is no reduction in exposure as part of the remediation.

$M(x) = D_{(soil)} \times V_{(total)} \times C_{ave.}(x)$

Where:

M(x) = The mass of a specific contaminant in soil (lb)

$D_{(soil)}$ = Density of soil, assume to be a default value of 110 lb/ft^3

$V_{(total)}$ = Volume based on the soil site characterization data with respect to the horizontal and vertical depth of the soil samples collected in areas above the applicable standard. The volume sum of each plot would equate to the total volume.

$C_{ave.}(x)$ = The soil contaminant concentration would be the arithmetic mean concentration of the contaminant throughout the soil column. This is the free and absorbed phase of the soil contaminant in areas above the applicable standard and expressed in $lb_{contaminant}/lb_{soil}$ (ppmw = ppm/10^6).

E. Long-Term Stewardship

1. Introduction

Long-term stewardship is generally accepted as the establishment and maintenance of physical and non-physical controls that are necessary to maintain the effectiveness of an approved remedy at cleanup sites where remaining regulated substances do not allow for the unrestricted use of the property. It also includes any long-term obligations (e.g., sampling, operation and maintenance, etc.) that ensure the effectiveness of the remedy after completion of the response action.

This section provides general guidelines on the methodology of long-term stewardship, which includes the use of a postremediation care plan. The plan shall be submitted as part of the final report and approved by the Department. The approved postremediation care plan will become a condition of attainment of the chosen standard(s) under Act 2. The plan shall identify the activities that will be conducted after closure and the frequency of those activities.

Answer the questions from the matrix in Table III-7, relative to your chosen standard(s), to determine when a postremediation care plan is required. The proposed postremediation care requirements shall be included in the cleanup plan for Department approval, as specified in Section 250.410(b)(5) of the regulations.

If any of the answers in the following matrix are yes, relative to the selected standard(s), a postremediation care plan shall be included as part of the final report.

2. Uniform Environmental Covenants Act

On Dec. 18, 2007, the Uniform Environmental Covenants Act (UECA) (27 Pa. C.S. § 6501-6517) was signed into law, and was subsequently implemented via Chapter 253, adopted November 19, 2010 (40 Pa.B. 6654). UECA provides a standardized process for creating, documenting and assuring the enforceability of activity and use limitations (AULs) on contaminated sites. Under UECA, an environmental covenant will be required whenever an engineering or institutional control is used to demonstrate the attainment of an Act 2 remediation standard. Environmental covenants are legal documents affecting property rights so remediators are encouraged to seek legal counsel with respect to the contents of the environmental covenant. For the purposes of Act 2, environmental covenants will take the place of deed notices in relation to any restrictions required to attain or maintain the standard.

A model environmental covenant is provided on the LRP website. The model is provided as an example of what type of information should be provided in an environmental covenant. However, it is important to note that each site is unique, so the content of each covenant will vary from site to site.

At some sites additional AULs may be put in place but not included in the environmental covenant, because they are not needed for attainment/maintenance of an Act 2 cleanup standard. Environmental covenants are difficult to modify, so land use restrictions not associated with the attainment/maintenance of an Act 2 standard may unnecessarily impede the ability to redevelop a property. Thus, a mechanism other than an environmental covenant is recommended for any additional AULs on a site. Regardless, the submitted postremediation care plan should only review the mechanisms required to attain/maintain an Act 2 cleanup standard. Only those AULs that are necessary to attain and/or maintain the selected standard are required for inclusion within the environmental covenant. In addition, the property owner’s consent and signature are required to implement an environmental covenant (27 Pa. C.S. § 6504).

Table III-7: Postremediation Care Decision Matrix

Background

		Yes	No
1.)	Is an ENGINEERING CONTROL(s) needed to attain and/or maintain the background standard? § 250.204(g)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to maintain the background standard? § 250.204(g)		
3.)	Does the FATE & TRANSPORT analysis indicate that the background standard may be exceeded at the point of compliance in the future? § 250.204(g)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.204(g)		

Statewide Health

1.)	Is an ENGINEERING CONTROL(s) needed to attain and/or maintain the Statewide health standard? § 250.312(e)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to maintain the Statewide health standard? § 250.312(e)		
3.)	Does the FATE & TRANSPORT analysis indicate that the Statewide health standard, including the solubility limitation in § 250.304(b), may be exceeded at the point of compliance in the future? § 250.312(e)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.312(e)		
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a postremedy use be relied on to eliminate complete exposure pathways, as set forth in § 250.311(e)(2) or § 250.312(b)?		
6.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will mitigation measures be implemented, as set forth in § 250.311(f)(1-4)? [If yes, follow guidelines in § 250.312(b)(1-3) for reporting requirements.]		

Site-Specific

1.)	Is an ENGINEERING CONTROL(s) needed to attain and/or maintain the Site-specific standard? § 250.411(d)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to maintain the Site-specific standard? § 250.411(d)		
3.)	Does the FATE & TRANSPORT analysis indicate that the Site-specific standard may be exceeded at the point of compliance in the future? § 250.411(d)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.411(d)		
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a postremedy use be relied on to eliminate complete exposure pathways, as set forth in § 250.311(e)(2)?		
6.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will mitigation measures be implemented, as set forth in § 250.311(f)? [If yes, follow guidelines in § 250.411(f)(1-3) for reporting requirements.]		

3. Institutional versus Engineering Controls

An institutional control, by definition of Act 2, is a measure taken to limit or prohibit certain activities that may interfere with the integrity of a remedial action or result in exposure to regulated substances at a site. These include, but are not limited to, fencing or restrictions on the future use of the site (35 P.S. § 6026.103).

An engineering control, by definition of Act 2, is a remedial action directed exclusively toward containing or controlling the migration of regulated substances through the environment. These include, but are not limited to, permanent capping of contaminated soils with parking lots or building slab construction, leachate collection systems, groundwater recovery trenches, and vapor mitigation systems.

Example: A groundwater use restriction, as documented in an environmental covenant, is an institutional control. An impermeable cap that prevents volatilization to the atmosphere, controls contaminant migration via run-off and leaching to groundwater, and limits dermal contact is an engineering control.

Institutional and engineering controls serve as AULs because they restrict the use of a property. Institutional controls cannot be used to attain the background or Statewide health standards (35 P.S. §§ 6026.302(b)(4) and 6026.302(e)(3)). Engineering and/or institutional controls may be used to maintain all three standards. *Attaining* a standard refers to steps or actions taken to complete the requirements, and therefore demonstrate attainment, of an Act 2 standard. *Maintaining* a standard refers to steps or actions taken to ensure the requirements of a standard that have already been completed continue to be met in the foreseeable future. Table III-7 provides a decision matrix of postremediation care requirements for each Act 2 standard.

Example of attaining vs. maintaining a cleanup standard: A property with a discharge of regulated substances to the groundwater is able to *attain* the SSS under current conditions because drinking water is supplied by the municipality. The SSS is then *maintained* in the future by implementing an environmental covenant stating that groundwater is not to be used on the property without treatment approved by the Department.

4. Postremediation Care Plan

The postremediation care plan should include the following:

- The reason(s) that the postremediation care plan is necessary (See 25 Pa. Code §§ 250.204(g), 250.312, 250.411(d), and 250.708).

- A schedule of operation and maintenance of the controls. Include a description of the planned maintenance activities and frequencies at which they will be performed and future plans for submission of proposed changes.

- Information regarding the submission of monitoring results and analysis, or as otherwise approved by the Department, that demonstrates the effectiveness of the remedy. Include a description of the planned monitoring activities and frequencies at which they will be performed. Monitoring activities in this case may include inspection and reporting requirements related to engineering controls.

- The proposed method for reporting any instances of nonattainment of the selected standard(s).

- The proposed measures to be taken to correct nonattainment conditions as they occur. A postremediation care plan containing any language proposing any potential future changes to the remedy will require the approval of the Department at the time of the proposed change.

- Information regarding the maintenance of records at the property where the remediation is being conducted for monitoring, sampling and analysis. Include the name, address and telephone number of the person or office to contact about the site during the postremediation care period. This person or office shall keep an updated postremediation care plan during the postremediation care period.

- Documentation of a plan to maintain the mitigated ecological resource, report of success or failure of the mitigation measure, and demonstration of sustaining the measures up to five years from final report approval.

- If requested by the Department, documentation of financial ability to implement the remedy and the postremediation care plan.

5. Postremediation Monitoring

In some situations, postremediation monitoring may be required as part of the postremediation care plan. For example, postremediation monitoring is conducted to determine any changes in groundwater quality after attainment of a standard(s). Unless otherwise instructed by the Department, analytes to be included are those which were monitored during assessment and remediation monitoring. All monitoring activities should incorporate quality control and quality assurance provisions consistent with the Chapter 250 regulations and policies.

Well locations for postremediation monitoring are generally selected from existing monitoring wells used in the characterization and remediation phases. Where a source of contamination is removed prior to impacting groundwater, postremediation monitoring should continue at locations that will detect any residual contamination in the unsaturated zone that might migrate to the groundwater.

a) Duration

In most cases, postremediation monitoring requirements will be developed on a case-by-case basis. The factors determining the duration of postremediation monitoring are the same factors that determine whether a postremediation care plan is necessary.

b) Frequency

As stated in Section 250.204(g) of the regulations, postremediation monitoring will take place on a quarterly basis unless otherwise approved by the Department. The interval between sampling events should be short enough to allow for response and correction of any problems that may cause nonattainment at the point of compliance.

Factors that could influence the need for an alternative postremediation monitoring schedule include site size, groundwater velocity, contaminant characteristics and the vulnerability of a site to pulses of contaminant migration during precipitation events.

c) Cessation of Postremediation Monitoring

Postremediation monitoring may be terminated when monitoring provisions set forth in the postremediation care plan are met, the engineering controls are no longer needed, and it can be documented by fate and transport analysis that the standard will not be exceeded in the future.

6. Postremediation Care Attainment

Remediators can end postremediation care if they can demonstrate through a documented fate and transport analysis that the selected standard(s) will be met, and will continue to be met in the future, after removal of engineering controls. An amendment to the postremediation care plan shall be submitted for approval by the Department. The postremediation care plan shall be amended whenever changes in operating plans or facility design, or events that occur during postremediation care, affect the currently approved postremediation care plan.

F. One Cleanup Program

In March 2004, PA DEP and EPA Region 3 entered into a Memorandum of Agreement (MOA) that outlines a procedure where sites remediated according to the LRP may also satisfy requirements of several federal laws: the Resource Conservation and Recovery Act (RCRA) (42 U.S.C. § 6901, et seq.), the Comprehensive Environmental Response Compensation Liability Act (CERCLA) (42 U.S.C § 9601, et seq.), and the Toxic Substances Control Act (TSCA) (15 U.S.C. § 2601, et seq.).

1. Purpose

DEP and EPA sought to promote the One Cleanup Program initiative by working together to achieve cleanups that protect human health and the environment by making greater use of all available authorities and selecting the optimum programmatic tools to increase the pace, effectiveness, efficiency, and quality of cleanups. In effect, entering into the One Cleanup Program can provide a remediator with a "one-stop shop" for state and federal standards guiding the cleanup of brownfield sites.

2. Provisions and Applicability

EPA has reviewed and evaluated the LRP and has determined that the LRP, as implemented under the MOA, includes each of the four elements of a state response program listed in CERCLA Section 128(a)(2):

- Timely survey and inventory of brownfield properties.
- Oversight and enforcement authorities adequate to ensure that a response action will protect human health and the environment.
- Mechanisms and resources to provide meaningful opportunities for public participation.
- Mechanisms for approval and a requirement for verification and certification that the response activity is complete.

The One Cleanup Program applies only to remediation of properties conducted pursuant to Act 2 provisions. As determined by PA DEP and USEPA, the following properties are not eligible to enter in the program:

- Permitted hazardous waste management units.
- Properties proposed in the Federal Register to be placed on the National Priorities List.
- Properties that have been placed on the National Priorities List.
- Properties that have been permitted under the SWMA and the PA Clean Streams Law for which cleanup standards are different than those of the LRP.

3. Implementation

Under the MOA, DEP and EPA have agreed to work in a coordinated manner to avoid possible duplication of efforts at properties, while ensuring that remediation of properties continues in a timely fashion. DEP will notify EPA when properties are being addressed under the LRP via written documentation for properties in Comprehensive Environmental Response, Compensation and Liability Information System (CERCLIS) that are being addressed under the LRP.

Participation in the One Cleanup Program entails some additional notification and public involvement requirements upon submittal of the NIR and cleanup plan (see Section II.A.3(a)).

For all RCRA Corrective Action Facilities being remediated under the LRP, the remediator will provide EPA with copies of reports. DEP and EPA will work in teams to accomplish cleanup goals in an appropriate and efficient use of both agencies' resources. EPA will review reports submitted to DEP under the LRP to determine if the site data meets RCRA Corrective Action obligations. If EPA determines that the site characterization or final decision is not sufficient to characterize the nature and extent of contamination, the EPA and DEP intend to work together to resolve the matter. If EPA determines the proposed cleanup objectives and corrective measures are sufficient, EPA plans to proceed with remedy selection procedures, including providing opportunity for public comment and review. Once the remedy is implemented and EPA determines that the media cleanup measures are met and corrective measures are satisfied, EPA will, where appropriate, acknowledge that the remediator has completed its Corrective Action obligations.

RCRA facilities enrolled in the One Cleanup Program may be subject to UECA requirements (Section III.E.2 of this TGM). As such, a model covenant for any activity and use limitations which may be in effect for these facilities is located on the DEP website on the 'One Cleanup Program' webpage.

4. Benefits

In summary, by entering into the One Cleanup Program, site owners or operators may be able to satisfy federal RCRA obligations and obtain liability relief under the Act 2 program. Interested parties can review the historic MOA, RCRA Corrective Action Baseline Facilities that have entered the One Cleanup Program, and other useful information on the PA DEP website on the One Cleanup Program tab.

Any owner, operator, or remediator interested in entering the One Cleanup Program should consult with their assigned DEP Project Officer about opportunities and eligibility requirements.

G. Data Quality and Practical Quantitation Limits

1. Data Quality Objectives Process, Sampling, and Data Quality Assessment Process

An important issue regarding sampling and statistical analysis is the quality assurance (QA) management considerations associated with these activities. Steps for the QA management process, in general, can be divided into three phases: planning, implementation and assessment. During the planning phase, a sampling and analysis plan is developed based on Data Quality Objectives (DQO). The implementation phase includes sampling execution and sample analysis. The assessment phase includes Data Quality Assessment (DQA) (See 25 Pa. Code § 250.702(a)).

To help remediators design scientific and resource-effective sampling programs, EPA provides guidance on developing DQO (EPA 1993). The DQO process allows a person to define the data requirements and acceptable levels of decision errors, before any data are collected. The DQO process should be considered in developing the sampling and analysis plan, including the QA plan.

As stated in the EPA guidance (EPA 1993), the DQO process includes the following seven steps:

- State the problem.
- Identify the decision.
- Identify inputs to the decision.
- Define the spatial and temporal boundaries of the decision.
- Develop a decision rule.
- Specify limits on decision errors.
- Optimize the design for obtaining data.

Step 4 of the DQO process, defining the spatial and temporal boundaries of the decision, is particularly important, because it prevents pooling and averaging data in a way that could mask potentially useful information. Activities in this step include:

- Define the domain or geographic area within which all decisions must apply. Some examples are property boundaries, operable units, and exposure areas.
- Specify the characteristics that define the population of interest. Identification of multiple areas of concern—each with its own set of samples and descriptive statistics—will help to reduce the total variability if the areas of concern (AOCs) are defined so that they are very different in their contaminant concentration profiles. For example, the top 2 feet of soil are defined as surface soil. Another example is to define contaminated soil that has been impacted by SPL as SPL-impacted soil.

- When appropriate, divide the population into strata that have relatively homogeneous characteristics. This helps to reduce the variability in each data set.

- Define the scale of decision making. The scale of decision making is the smallest area, volume, or time frame of the media in which decision errors are to be controlled. This is also the unit that will be assumed to generate a "statistical unit" of possible measurements which allows the assessment and control of decision errors. Examples are remediation units, exposure units, and hot spots.

- Determine the time frame to which the study data apply. It may not be possible to collect data over the full time period to which the decision will apply. Therefore, a decision should be made regarding the most appropriate time frame that the data should reflect.

- Determine when to collect samples. Conditions at the site may vary due to seasons, weather or other factors. Therefore, a decision should be made regarding the most appropriate time period to collect data that will reflect the conditions that are of interest.

- Identify any practical constraints on data collection, such as seasonal or meteorological conditions, unavailability of personnel, time, or equipment.

At the completion of the DQO process, information obtained from the DQO process can be used to develop a sampling and analysis plan, including a QA/QC plan.

After the environmental data have been collected and validated in accordance with the sampling and analysis plan (including the QA/QC plan), data must be assessed to determine whether the DQOs are met. This is the DQA process. EPA has developed guidance on DQA (EPA, 1996).

The DQA process involves the following five steps (EPA, 1996):

- Review the DQOs and sampling design.

- Conduct a preliminary data review.

- Select the statistical test.

- Verify the underlying assumptions of the statistical test.

- Perform the statistical hypothesis test and draw conclusions that address the data user's objectives.

A properly implemented DQA process can help to determine if planning objectives were achieved. The discussions in the statistics Section (III.B) will address key statistical issues that are pertinent to Act 2 and are encountered during these DQO and DQA processes.

2. Preliminary Data Review

Preliminary data review should be performed whenever data are used. By reviewing the data both numerically and graphically, one can learn the “structure” of the data and identify limitations for using the data. Graphical methods include histograms, probability plots, box charts, and time-series plots to visually review the data for trends or patterns. Calculations of summary statistics are typically done to characterize the data and make judgments on the central tendencies, symmetry, presence of outliers, etc. These statistical methods are defined and explained in more detail in the statistical section of this guidance. (Section III.B)

Chemical concentrations should initially be compared to laboratory blank concentrations. If the blank samples contain detectable levels of common laboratory contaminants, then the sample results should be considered as positive results only if the concentrations in the sample exceed 10 times the maximum amount detected in the blank. If the concentration is less than 10 times the blank contaminant level, it is concluded that the chemical was not detected in the sample and the blank-related chemical concentration is considered to be the quantitation limit for the chemical in that sample. If all samples contain levels of a common laboratory contaminant that are less than 10 times the level of contamination noted in the blank, then completely eliminate that chemical from the set of sample results. Some common laboratory contaminants include acetone, 2-butanone (methyl ethyl ketone), methylene chloride, toluene, and phthalate esters. This evaluation is typically done during the laboratory data review process and anything that meets the criteria to be included in data evaluation will typically be marked with a “B” qualifier. The “B” flag is placed on data that is considered valid but could be affected by the presence of the same compound in the blank sample.

If the blank samples contain constituents other than common laboratory contaminants, then the sample results should be considered as positive results only if the concentrations in the sample exceed five times the maximum amount detected in any laboratory blank. As with the common laboratory contaminants, if the concentration is less than five times the blank constituent level, it is concluded that the constituent was not detected in the sample and the blank-related chemical concentration is considered to be the quantitation limit for the chemical in that sample. Again, if all samples contain levels of a constituent other than common laboratory contaminants that are less than five times the level of contamination noted in the blank, then completely eliminate that chemical from the set of sample results. As with common laboratory contaminants, this evaluation is typically done during the laboratory data review process, and anything that meets the criteria to be included in data evaluation will typically be marked with a “B” qualifier.

The details describing the five and 10 times the blank concentration evaluation is described in many EPA laboratory methods.

3. Practical Quantitation Limit (25 Pa. Code § 250.4)

Practical quantitation limit (PQL), as defined in Act 2 (35 P.S. § 6026.103), is the lowest limit that can be reliably achieved under normal laboratory conditions. Many of the SW-846 (EPA’s hazardous waste test methods) analysis methods previously listed estimated quantitation limits (EQL) or method detection limits (MDL) to ensure that laboratories were providing the data required to meet the needs of the data-user. However, as technology has improved, the need to define a minimum value to be reached has been reduced. The EQL was the limit set at the time the method was written as an estimated value that could be detected using the given method. MDL is a value that is calculated using statistics on laboratory data to provide the lowest value that can be detected. The MDL is instrument-specific.

Some laboratory methods do continue to list EQL and/or MDL values; however, most laboratories can now consistently achieve reporting limits (RL) or limits of quantitation (LOQ) that are much lower than the EQL or MDL values defined in the method. These RLs and LOQs are the lowest value that can be reliably quantified given a specific method. Detections that fall between the RL and the MDL are “J” values. This indicates that it is above the level that the instrument can reliably identify (MDL), but is below the value that can be reliably quantified (RL) and is an estimate. “J”-flagged values are valid data and can be used for screening, etc.

For the purposes of Act 2, if a laboratory’s RL value is above a constituent’s corresponding MSC value due to a technological issue, remediators should contact their regional project officer to discuss how to proceed. It is important to note that PQL values should not be used for screening data (e.g. for a risk assessment or a VI evaluation) and only apply for the purposes of attaining the standard.

H. Site-Specific Human Health Risk Assessment Guidance

1. Introduction

This Section provides general guidelines on the methodology of risk assessment and the risk assessment report for human health evaluation under Act 2. Regulations regarding risk assessment are in Chapter 250, Subchapter F. This section of the guidance document does not address issues related to ecological risk assessment. Ecological risk assessment is addressed in Section III.I.

Prior to performing a risk assessment, it is important to clearly define the problem that is to be addressed, the objectives of the study, and how the results will be used to meet these objectives. This initial step is critical to ensure a successful outcome (accurate, protective, timely, cost-effective evaluation) and that the level of effort is commensurate with the scope of the problem.

Risk assessment procedures have been well defined in various EPA guidance documents. The process does not need to be reiterated in this document. Instead, certain key issues pertinent to site-specific evaluations under Act 2 are discussed subsequently.

For risk assessment issues not directly addressed in this document, remediators may consult the most recent EPA and ASTM guidelines, such as those listed on Table III-11, for additional guidance. For petroleum release sites, the risk assessment methodology in ASTM E 1739-95 (2015) (Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites) may be consulted for further guidance.

A suggested outline for the risk assessment report is provided in Section II.B.3(g)(v) of this manual. The outline is intended to provide guidance on minimum requirements for the report.

2. When to Perform a Risk Assessment

Remediators selecting the site-specific standard established by Section 304 of Act 2 (35 P.S. § 6026.304) should submit a risk assessment report to the Department for review and approval unless no present or future complete exposure pathways exist as demonstrated in the fate and transport analysis in the site-specific remedial investigation. The exposure scenarios (e.g., residential, industrial, recreational), which will define the exposure pathways, must be based on site-specific land use considerations (see 35 P.S. §§ 6026.301(a)(3) and 6026.304(1)(2)). The pathways, which describe the mechanism by which receptors may be exposed to a source, are also site-specific. Detailed guidance on land use determination and identification of exposure scenarios and pathways are addressed in Section III.H.3(b)(i) of this document and references cited therein. A risk assessment only needs to be performed if complete exposure pathways for human receptors exist under current or potential future conditions. If engineering or institutional controls that are to be implemented will eliminate all exposure pathways, a risk assessment report is not required (see 25 Pa. Code § 250.405(b)).

A baseline risk assessment report is not required if the Department, in its remedial investigation report or cleanup plan approval, determines that a specific remedial alternative that eliminates all pathways, other than a no-action remedial alternative, can be implemented to attain the site-specific standard (25 Pa. Code § 250.405(c)). A baseline risk assessment is an evaluation of risk prior to, or in the absence of, a remedial measure. When the remedial measure has been completed, a residual risk assessment that evaluates risks posed by postremediation contamination, if present, is required in order to demonstrate attainment of the site-specific standard.

3. Risk Assessment for Human Health (25 Pa. Code § 250.602(c))

A risk assessment for human exposure from contaminated sites consists of the following four steps:

(1) Site characterization

(2) Exposure assessment

(3) Toxicity assessment

(4) Risk characterization that evaluates if the risks meet the human health protection goals specified in Subsections 304(b) and (c) of Act 2.

The following discussions address key issues pertinent to these four steps of risk assessment for human exposure:

a) Site Characterization [§ 250.602(c)(1)]

i) Chemicals of Concern

The initial steps of the site characterization are to review the analytical data and to select the chemicals of concern that are identified in distinct areas of contamination at the site. Under Act 2 there are two possible situations in determining the chemicals of concern in a baseline risk assessment under the site-specific standard: (1) strictly using the site-specific standard, or (2) a combination of standards using site-specific and Statewide health, site-specific and background, or all three standards. These situations are discussed separately below.

In the first situation of using only the site-specific standard, the chemicals of concern can be screened using the EPA Regional Screening Level (RSL) screening procedures. The purpose of this screening procedure is only for potential reduction of the number of chemicals carried through the risk assessment. Those chemicals on the site whose maximum concentration exceeds the RSL values for carcinogenic effects (10^{-6}) or the RSL values (HQ=0.1) for noncarcinogenic effects should be retained in the risk assessment. Chemicals on the site at maximum concentration below the RSL values for carcinogenic effects or the RSL values for noncarcinogenic effects may be dropped from the risk assessment unless other contaminant-specific or site-specific considerations suggest that the inclusion of these constituents in the risk assessment is more appropriate to determine the total risk of the site. Chemicals that are not retained in the risk assessment may be considered having minimal influence on total risk. (Note that it is not permissible under the SSS to perform screening using SHS MSCs.)

The second situation uses a combination of the site-specific standard with one or both of the other two standards. The chemicals of concern to be addressed in the risk assessment should include those chemicals that cannot be addressed using either the SHS or the background standard. The chemicals of concern identified for evaluation in the risk assessment may then be screened using the same RSL screening procedures mentioned above.

Three other factors should be considered when deciding to retain constituents for the risk assessment. Specifically, these factors include the constituent’s toxicity, mobility and persistence. Toxicity is a driving force when determining if exposure to a site poses any adverse impact to human health or the environment. Some constituents may be frequently detected at a site, but may be considered relatively innocuous or toxicologically inert. These constituents should not be retained for the risk assessment. In contrast, some constituents may be infrequently detected, but may be relatively more toxic than most constituents. Regardless of the constituent’s frequency of detection, its presence (assuming it is not anomalous) may deem it necessary to be retained as a constituent of concern.

The mobility of a constituent dictates what receptors on and off site may be potentially affected and consequently whether the constituent should be retained in the assessment. Physical and chemical properties of a compound control its transport and fate in the environment. For example, these attributes determine whether a constituent will readily volatilize into the air or be transported via advection or diffusion through the soil, groundwater and surface water. These characteristics also describe a chemical’s tendency to adsorb onto soil/sediment particles, in turn altering its mobility through the environment.

Finally, the persistence of a chemical in the environment determines whether further receptors would be impacted. The persistence of a chemical in the environment depends on factors such as microbial content of soil and water and the ability of these organisms to degrade the chemical. In addition, chemical and photochemical degradation may contribute to the elimination of a particular compound. Although the parent compound may be eliminated, the byproducts of the degradation of that compound must also be considered and evaluated. These chemical-specific factors will also be used to determine whether a constituent and its byproducts are retained for the risk assessment.

In general, liability protection is not afforded under the site-specific standard for those chemicals that are not identified as contamination at a site and for which attainment has not been demonstrated.

ii) Conceptual Site Model

Development of a conceptual site model is an important step in identifying additional data needs in site characterization and in defining exposure. A conceptual site model identifies all potential or suspected sources of contamination, types and concentrations of contaminants detected at the site, potentially contaminated media, potential exposure pathways and receptors. Many components of exposure (such as the source, receptors, migration pathways and routes of exposure) are determined on a site-specific basis. The conceptual site model provides a systematic way to identify and summarize this information to ensure that potential exposures at the site are accounted for accurately.

The conceptual site model may be graphical, tabular or narrative but should provide an accurate understanding of complete exposure pathways for the site. Examples of conceptual site models may be found in EPA, ITRC, or ASTM guidance documents. It is recommended that the development of the conceptual site model be coordinated with the regional project officer to ensure that potential pathways and receptors are adequately and appropriately addressed prior to performing the assessment.

b) Exposure Assessment [§§ 250.603 and 250.604]

The exposure assessment determines or estimates (qualitatively or quantitatively) the magnitude, frequency, duration and routes of exposure. The assessment is typically performed in three steps:

(1) Characterization of the exposure setting including:

- the physical setting
- potential exposed populations

(2) Identification of complete exposure pathways which includes:

- sources and receiving media
- fate and transport in the release media
- exposure points and exposure routes

The information on sources, fate and transport (including biodegradation), exposure points and exposure routes are then integrated to determine the potential exposure pathways. Complete pathways exist when all components are present. Information for complete pathways should be summarized.

(3) Quantification of exposure of the receptor including:

- environmental concentration
- intake

The exposure assessment process is well defined in various guidance documents, as cited in Section III.H.4, and is not reiterated here. This section discusses some key issues pertaining to performing the site-specific exposure assessments.

i) Exposure Scenarios and Exposure Pathways

Exposure Pathways: The exposure pathway describes the mechanism by which receptors (individuals, populations, and ecological receptors) may be exposed to the source. Pathways consist of a source, receptor, route of exposure and a transport mechanism, if the exposure point is not the same as the source. The analysis of the fate and transport of the chemical can help to predict future exposures, to link sources with currently contaminated media, and to identify exposure pathways. The intent of the fate and transport analysis at this stage is to identify media that are receiving or may receive site-related chemicals. Further guidance on fate and transport analysis can be found in Section III.A of this guidance document.

As discussed above, the conceptual site model is useful in defining potential exposure pathways. However, only complete pathways should be advanced through the assessment process. The effects of engineering or institutional controls that are to be implemented, which will eliminate exposure pathways, must be considered for the conceptual model development. The EPA provides guidance referenced in Section III.H.4 of this manual on potential pathways for given land use scenarios.

Realistic current and future land use scenarios (e.g., residential, industrial, agricultural, etc.) provide the basis for selecting the controlling exposure scenarios/pathways. Guidance on land use considerations can be found in the EPA OSWER Directive: *Land Use in The CERCLA Remedy Selection Process* (1995) as well as earlier EPA guidance on exposure assessments as referenced above. Sources and types of information that may aid in determining the reasonably anticipated future land use include, but are not limited to:

- Current land use.
- Zoning laws.
- Zoning maps.

- Comprehensive community master plans.
- Local land use authorities.
- Local officials.
- Population growth patterns and Bureau of Census projections.
- Accessibility of site to existing infrastructure (such as transportation and public utilities).
- Institutional controls currently in place.
- Site location in relation to urban, residential, commercial, industrial, agricultural and recreational areas.
- Federal/State land use designation (such as state parks).
- Historical or recent development patterns.
- Cultural factors (such as historical sites).
- Natural resources information.
- Stakeholder input - allows for all affected parties to define land use.
- Location of onsite or nearby wetlands.
- Proximity of site to a floodplain.
- Proximity of site to critical habitats of endangered or threatened species.
- Geographic and geologic information
- Location of wellhead protection areas, recharge areas, and other areas identified in the state’s Comprehensive Groundwater Protection Program.

These types of information should be considered when developing the assumptions about future land use.

Some direct pathways, such as direct ingestion of soil or groundwater and direct inhalation of volatiles and/or particulates from soil, are fairly well established and can be used routinely where they have been identified as complete pathways. At issue would be defining appropriate exposure factors (such as intake rate for the given population) since these factors exhibit a range of possible values. Typically, the choice of factors (high-end exposure vs. average exposure) is defined by the level of conservatism desired.

Dermal contact (with soil or groundwater), on the other hand, is less well defined, particularly in terms of estimating intake (the mass of substance in contact with the body per unit body weight per unit time) and, more importantly, absorbed dose (intake multiplied by an absorption factor to account for mass actually in the body). This pathway is best addressed at a site-specific level when identified as relevant. Although there is some guidance (EPA, 1991c), professional judgment may play a significant role in estimating dermal exposure. The rationale behind these judgments (and indeed professional judgments wherever they are used) and, as far as possible, documented evidence in support of these judgments should be clearly provided.

Some indirect pathways are also best addressed on a site-specific basis because of the inherent uncertainty associated with defining the transport from the source to the receptor. In the case of vapor intrusion into a trench, for example, actual data from direct measurements, i.e., a monitoring approach, would be preferred to the use of models which have been shown to be imprecise. Vapor intrusion into an enclosed space is discussed in detail in Section IV of this manual.

Other indirect pathways (e.g., soil leaching to groundwater and subsequent ingestion of groundwater) can be addressed by simple analytical models. Although site-specific data inputs to these models are typically favored as producing a more realistic estimate of exposure, site-specific data may not be accessible. The use of a combination of default and site-specific parameters may be used provided the rationale for the choice of values is included.

<u>Receptors and Human Exposure Factors:</u> Receptors should be defined on a site-specific basis taking into account future land use considerations. Guidance on potential receptors for given land use are provided in EPA guidances (EPA 1989a, 1991a,b). Care should be taken to identify potential sensitive subpopulations (e.g., children) as appropriate for site-specific conditions.

Section 250.603 of the regulations specifies requirements to select exposure factors. A risk assessment may use site-specific exposure factors in accordance with EPA's Final Guidelines for Exposure Assessment, 1992 (57 FR 22888-22938) or exposure factors used in the development of the SHSs identified in Subchapter C of the regulations. Site-specific exposure factors shall be clearly justified by supporting data (see 25 Pa. Code § 25.603(b)).

Human exposure factors may be divided into receptor physiologic parameters (e.g., body weight, skin surface area); contact rate (e.g., consumption of water, soil ingestion rate); and time activity patterns (e.g., time spent indoors/outdoors, time spent at work). Some of these variables, particularly the physiologic parameters, have been well characterized but others such as time/activity patterns are less well documented. All parameters are subject to variability (true heterogeneity) and/or uncertainty (ignorance about a measurement). Thus, a range of values may be available for any given parameter. The choice will depend to some extent on the problem and the level of conservatism desired. Typical sources for these parameters are the EPA Exposure Factors Handbook (2011) and the American Industrial Health Council (AIHC) Exposure Factors Sourcebook (AIHC, 1994).

<u>Fate and Transport Parameters and Models:</u> Constituents of concern can both migrate (via leaching, advection, dispersion) and transform (via biodegradation, hydrolysis, photolysis) in the environment. These migration and transformation processes must be considered when determining environmental concentration under indirect exposure (see 25 Pa. Code §§ 250.204(a), 250.312(a), 205.408(a). A range of fate and transport models (from simple analytical to complex numerical) are available to account for these processes. However, the level of site-specific data needed to make proper use of the models also increases with the level of sophistication of the model (i.e., the increase of model technical capabilities). A tiered approach, based on level of model complexity, is best, i.e., using the least resource intensive method to achieve the objective of the evaluation. The selected model should adequately represent the physical setting (e.g., the geometric configuration of hydrogeological systems, soil profiles, river widths and depths, etc.) and migration and transformation processes that affect the problem. Input parameter values should be representative of field conditions. The choice of model and input parameters will need to be justified as appropriate for given site-specific conditions. Justifications should include why a model is appropriate when limitations of the selected model are considered. In addition, some measure of model validation may be required. This may be as simple as corroborating the conservative assumptions with field measurements. For guidance on selection of groundwater models refer to Section III.A of this manual.

The use of monitoring methods may also be appropriate for defining environmental fate, as in the case of natural attenuation. All supporting data should be provided to support such an evaluation. For specific guidance regarding the use of monitoring methods, check EPA, ITRC, and other references listed in III.H.3(f).

<u>Generic vs. Site-Specific Considerations:</u> In general, risk assessments should be based upon realistic exposure scenarios using current or planned future land use, incorporating any changes from early response actions known or planned. Site-specific information on exposure pathways,

receptors and exposure factors, including actual data, should be used to the maximum extent possible.

However, not all exposure parameters need to be site-specific. Certain generic human physical parameters (e.g., body weight) that do not vary significantly in the general human population, and thus from site to site, are such exceptions. Default values, from single point estimates to distributions for these parameters, are available from such sources as the EPA Exposure Factors Handbook (EPA, 2011) and the AIHC Exposure Factors Sourcebook (AIHC, 1994). Default values of single point estimates for these parameters are also available from Subchapter C of the regulations.

Factors affecting the choice of exposure scenario (land use), complete exposure pathways, the distribution of contaminants in the media, the characteristics of the media, and the activity patterns and demographics of the surrounding populations should be considered, whenever possible, as site-specific. For example, if the planned future land use is industrial, the appropriate population would be adults and default physiological information may be obtained from the above named sources. However, if the concern is for a residential land use, children may be the population of concern. Default physiological information is still available from the above sources but the actual values would be different because the site-specific considerations dictate a different land use and receptor population.

It is possible that a sensitive subpopulation may be of concern (e.g., pregnant women, subsistence fishermen) in certain situations. Some data for these populations may be available from national or regional surveys incorporated in the above sources, but in some instances the data may need to be generated. The choice of data should be supported in the peer review literature and proved to be appropriately applied. For information generated on a site-specific basis, proper QA/QC measures should be exercised and the data should be generated with the understanding of the regulatory agency as to how the information will be used.

ii) Exposure Characterization

Exposure characterization is the quantification step in the process. In the forward calculation of risk, both the environmental concentration and the intake must be determined. In the reverse calculation of site-specific standards, an acceptable concentration is derived based on intake and a predetermined level of risk.

<u>Exposure Point Concentration:</u> This is the concentration expected to be contacted over the exposure period. Since risk assessments are typically performed for a chronic exposure scenario, i.e., the contact period is long (typically 30-70 years), an upper confidence limit on the mean is used. It is important, therefore, to assess the potential fate of the material in the environment to provide the best estimate of its environmental

concentration over time. In some instances, short-term exposure is to be evaluated, in which case some other metric (e.g., maximum concentration) may be more appropriate. EPA OSWER Directive 9285.7-081 provides guidance on the concentration term.

Intake: Three types of variables are associated with defining intake: chemical related variables, i.e., the concentration term and its associated fate and transport parameters; variables that describe the exposed population such as physiologic parameters, contact rate and time/activity patterns; and an assessment-determined variable, i.e., the period over which the exposure is averaged.

Since most exposure factors exhibit both variability and uncertainty, EPA encourages the development of a range of exposure (and risk) descriptors. The use of probabilistic analysis (such as Monte Carlo simulations) is one way to account for variability and uncertainty. However, these evaluations are resource intensive and may be inappropriate for simple sites. Deterministic evaluations, i.e., point estimates, are useful alternatives. If single point estimates are developed, it is recommended that a most likely exposure (MLE) be quantified in addition to the typical high-end exposure (comparable to the reasonable maximum exposure or RME used in the generation of the SHSs). In this way, a range of exposures can be provided as context for risk management decisions. Thus, even within the site-specific evaluation, a tiered approach may be useful (i.e., from point estimates to ranges) depending on the level of sophistication required to address the problem at hand.

iii) Good Exposure Assessment Practices

As a fundamental practice, the methods and data used in the exposure assessment should clearly support the conclusions within the known and stated bounds of uncertainty. Documentation is a core principle of a good exposure assessment. Hawkins, Jayjock and Lynch (1992) provided eight general practices that make for good exposure assessments. Burmaster and Anderson (1994) further defined good practice as it relates to probabilistic assessments. It is suggested that exposure assessments be consistent with these practices as appropriate.

c) Toxicity Assessment [Section 250.605]

The purpose of toxicity assessment is to collect and weigh the available evidence regarding the potential for particular contaminants to cause adverse effects in exposed individuals and to provide an estimate of the relationship between the extent of exposure to a contaminant and the increase likelihood and/or severity of adverse effects.

The carcinogenic and noncarcinogenic (systemic) effects of each chemical of concern at the site should be evaluated.

For toxicity assessment, the person should use appropriate toxicity values from one of the following sources, in the order indicated:

i) Integrated Risk Information System (IRIS)/Office of Pesticide Programs (OPP) Human Health Benchmarks for Pesticides;

ii) United States Environmental Protection Agency, National Center for Environmental Assessment (NCEA) Provisional Peer-Reviewed Toxicity Values (PPRTV).

iii) Other sources

   (a) Health Effects Assessment Summary Tables (HEAST)

   (b) Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles.

   (c) California EPA, California Cancer Potency Factors and Chronic Reference Exposure Levels.

   (d) EPA criteria documents, including drinking water criteria documents, drinking water health advisory summaries, ambient water quality criteria documents and air quality criteria documents.

If no toxicity values are available from the sources identified above, the person may develop, for the Department's review in the risk assessment report, toxicity values from appropriately justified surrogates or chemical-specific toxicity values with consideration of the following:

- Available data should first be evaluated to determine the likelihood that the agent is a carcinogen. If the chemical is determined to be likely or possibly a human carcinogen, then a toxicity value (slope factor) should be calculated based on the most recent and available information from peer reviewed journals. EPA has developed its most recent approach for defining carcinogens and developing slope factors in the Proposed Guidelines for Carcinogen Risk Assessment (EPA, 1996b). This approach should be applied when determining whether a chemical is a carcinogen and determining its slope factors.

- A toxicity factor should also be developed for the potential noncarcinogenic effects based on the most recent and available information from peer reviewed journals. A reference dose is the toxicity value used most often in evaluating noncarcinogenic effects. EPA's Risk Assessment Guidance for Superfund describes the protocol for developing reference doses. Depending on the exposure duration anticipated at the site, a chronic reference dose would be developed for exposure expected to last 7 to 70 years; a subchronic reference dose would be calculated for exposure less than 7 years (EPA, 1989a).

- The toxicity value must be based on peer reviewed literature that includes all relevant sources of data and must be a balanced description of both positive and negative findings on the toxicity of the chemical, the weight of evidence supporting the toxicity value, and the main sources of uncertainty of the toxicity value documented in the risk assessment report's uncertainty section.

  The toxicity of lead is not easily defined by the above approach. EPA has developed the Integrated Exposure Uptake Biokinetic (IEUBK) Model to determine cleanup numbers for children exposed to lead in soil under a residential exposure scenario. For adult exposure in either the residential or nonresidential scenario, the IEUBK model does not apply and other models, such as EPA's adult lead model, have been developed to determine the effects of lead on adults and pregnant women. This model or others, as appropriate, may be used to determine site-specific cleanup numbers.

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d) Risk Characterization

The risk characterization section summarizes the toxicity and exposure assessments into either a quantitative estimate of risk or the development of cleanup concentrations, if needed, for each of the chemicals of concern at the site. The objectives of the risk assessment that were described in the introductory paragraphs of this section should again be defined, and a description of how the results of the report meet those objectives should be provided. The report should exemplify the values of clarity, transparency, reasonableness and consistency as stated in the Policy for Risk Characterization at the Environmental Protection Agency (EPA, 1995b).

The conceptual model for the site should be described and, for each complete pathway, the total cancer risk and non-cancer hazard quotient should be defined. In addition, a cleanup concentration for that pathway should be determined if necessary. In developing cleanup numbers for the site, cumulative excess risk (across all exposure pathways and all chemicals of concern) to exposed populations, including sensitive subgroups, shall not be greater than 1 in 10,000 for known or suspected carcinogens. The risks associated with carcinogens should be cumulative if the same individuals are exposed to these carcinogens consistently. For noncarcinogens (systemic toxicants), cleanup standards shall represent the level to which an exposed human population could be exposed on a daily basis without appreciable risk of deleterious effect. Where several systemic toxicants affect the same target organ or act by the same method of toxicity, the hazard index shall not exceed one (see 25 Pa. Code § 250.402(b)(2)). The risks associated with systemic toxicants also should be cumulative in the toxicity assessment if these toxicants affect the same target organ or act by the same method of toxicity.

To evaluate the short-term and long-term effectiveness of a selected remedy, both the potential risk associated with implementation of the remedy and the risk associated with exposure to the remediated media must be evaluated. The algorithms that were defined in the exposure assessment should be used to characterize these potential risks.

The risk characterization associated with short-term effectiveness considers the exposure of workers at the site and the exposure of receptors in the vicinity surrounding the site to migrating media during the implementation of the selected remedy. A comparison of a focused list of remedial alternatives may help predict the risks associated with the implementation of the selected remedy or whether the implementation of alternatives may have any significant impact to human health and the environment.

The risk characterization associated with long-term effectiveness demonstrates whether the selected remedy attains the remedial objectives (site-specific cleanup standards) and whether postremedial risks achieve the acceptable levels of risk. There may be times when a specific cleanup level for one constituent may not be attained, but the overall postremedial risk may be within acceptable levels. Evaluation of the postremedial risk is based on a prediction of what the postremedial exposure concentrations would be. For example, a cap would eliminate exposure to surface soils, rendering the risk from surface soils to be negligible. If bioremediation is considered, the remedial objective would be the concentration that provides the basis for characterization of the postremedial risk. If the calculated postremedial risk is within the acceptable range, the selected remedy would be considered a viable solution.

e) Uncertainty Analysis

An often-forgotten component of the risk assessment process is the characterization of uncertainty. Uncertainty represents ignorance (or lack of perfect knowledge) about poorly characterized phenomena or models (Burmaster and Anderson, 1994). The concept is important and indeed implicit in the risk-based approach, but it is often ignored in practice. For example, the SHSs are acknowledged to be conservative, and one of the rationales for being conservative is to account for the uncertainty inherent in developing the standards. In the site-specific evaluation, it is recommended that a tiered approach to addressing uncertainty be used. In applying the tiered approach, the level of effort should be commensurate with the magnitude of the decision to be made.

At an initial level, point estimates of exposure and risk (or site-specific standards) may be developed that describe both the high-end individual (RME) and a mid-range individual (MLE). If the level of risk is below the level of regulatory concern, the analysis need go no further. At a minimum a qualitative evaluation of the uncertainty should be included indicating what the most uncertain and most sensitive parameters are and their likely impact on the results. It is important to put in perspective any uncertainties inherent in the toxicity assessment as well as the exposure assessment.

At some middle level of effort, statistical estimates (experimental estimates, population variability, estimation error) should be listed and the impact of these on the results discussed. A more formal sensitivity analysis may be performed to rank the input parameters on the basis of their contribution to the uncertainty.

At the highest level of effort, methods to quantitatively address variability and uncertainty (including but not limited to probabilistic analysis) should be used to carefully determine the overall precision of the risk estimates as they relate to scenarios, models and inputs.

Probabilistic Analysis: Typically, risk assessments have used a deterministic (single point) approach to estimating risk. However, risk is defined as a probability of injury or damage. Further, exposure-related variables are generally recognized as having a range of possible values. Thus, probabilistic analysis is a useful tool for estimating risk since it can account for both variability and uncertainty.

However, probabilistic analysis is resource intensive and may be inappropriate for simple evaluations. Therefore, it is suggested that probabilistic analysis be used as part of a tiered approach to risk assessment in the site remediation process. Guidance relating to how to perform probabilistic analysis can be found in a number of the references listed in Section III.H.4 including the Burmaster document as well as the EPA Risk Assessment Guidance for Superfund.

If an uncertainty analysis includes Monte Carlo simulations, the person should consider the following guidelines as described in EPA’s Guiding Principles for Monte Carlo Analysis (EPA, 1997) to ensure high quality science:

- The purpose and scope of the assessment should be clearly articulated in a “problem formulation” section that includes a full discussion of any highly exposed or highly susceptible subpopulations evaluated (e.g., children, the elderly, etc.). The questions the assessment attempts to answer are to be discussed, and the assessment endpoints should be well defined.

- The methods used for the analysis (including all models used, all data upon which the assessment is based, and all assumptions that have a significant impact upon the results) should be documented and easily located in the report. This documentation should include a discussion of the degree to which the data used are representative of the population under study. Also, this documentation should include the names of the models and software used to generate the analysis. Sufficient information should be provided to allow the results of the analysis to be independently reproduced.

- The results of sensitivity analyses should be presented and discussed in the report. Probabilistic techniques should be applied to the compounds, pathways, and factors of importance to the assessment, as determined by sensitivity analyses or other basic requirements of the assessment.

- The presence or absence of moderate to strong correlations or dependencies between the input variables should be discussed and accounted for in the analysis, along with the effects these have on the output distribution.

- Information for each input and output distribution should be provided in the report. This includes tabular and graphical representations of the distributions (e.g., probability density function and cumulative distribution function plots) that indicate the location of any point estimates of interest (e.g., mean, median, 95th percentile). The selection of distributions should be explained and justified. For both the input and output distributions, variability and uncertainty should be differentiated where possible.

- The numerical stability of the central tendency and the higher end (i.e., tail) of the output distributions should be presented and discussed.

- Calculations of exposures and risks using deterministic (e.g., point estimate) methods should be reported if possible. Providing these values will allow comparisons between the probabilistic analysis and past or screening level risk assessments. Further, deterministic estimates may be used to answer scenario specific questions and to facilitate risk communication. When comparisons are made, it is important to explain the similarities and differences in the underlying data, assumptions, and models.

- Since fixed exposure assumptions (e.g., exposure duration, body weight) are sometimes embedded in the toxicity metrics (e.g., reference doses, reference concentrations, unit cancer risk factors), the exposure estimates from the probabilistic output distribution are to be aligned with the toxicity metric.

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I. Site-Specific Ecological Risk Assessment Guidance

1. Introduction

The objectives of the site-specific ecological risk procedure are to:

- Evaluate the threat posed by regulated substances to species and habitats of concern through a series of steps which progressively focus the assessment with an emphasis on developing site-specific empirical data and a weight-of-evidence.

- Compile a site-specific weight-of-evidence to determine if a substantial impact has occurred to species or habitats of concern.

- Develop the information necessary to determine what remedial action, if any, could be taken to reduce substantial impacts, if present, without causing greater injury to species or habitats of concern than no further action or less disruptive remedial alternatives.

The Department recommends the use of EPA's interim final guidance on Ecological Risk Assessment Guidance for Superfund (EPA, 1997), with some modification, as the process for designing and conducting site-specific ecological risk assessments. To accommodate the provisions of Act 2, points of emphasis and specific modifications of the EPA process are detailed in this document. In addition, other EPA guidance on ecological risk assessment and specific ASTM standards for ecological risk procedures and methods should be utilized as appropriate to achieve the objectives noted above. This approach contains the same fundamental concepts and components found in the Statewide health ecological screen. However, the Statewide health ecological screen cannot be applied to sites attaining the site-specific standard because that process assumes all of the SHS MSCs have been met. If a site is directed to the site-specific ecological risk assessment process in Step 8 of the Statewide health ecological screen, Steps 3 through 8 of the site-specific ecological risk assessment process as described in Section III.I.2 of this guidance should be applied to the evaluation.

2. Ecological Risk Assessment Process

The EPA ecological risk assessment process is comprised of eight steps. At the end of Steps 2 and 7, the qualified investigators determine whether a substantial impact has resulted from regulated substances. The initial screen (Steps 1 and 2) is necessary for all sites which are to attain the site-specific standard.

a) Step 1 - Fundamental Components

The following items should be evaluated carefully in the context of site-specific conditions:

- Environmental Setting and Site History.

- An evaluation of wetlands via the wetlands mapping tool (national wetlands inventory, NWI) provided by the US Fish and Wildlife Service may be used to help investigate the environmental setting.

- Remediators may use the Pennsylvania Natural Diversity Inventory (PNDI) Environmental Review Tool to search for habitats and species of concern. The PNDI search tool can be accessed at the Pennsylvania Natural Heritage Program's Pennsylvania Conservation Explorer website.

- Site Visits - evaluate receptors and chemical migration pathways.

- Contaminant Fate and Transport - emphasize gradients of contamination.

- Preliminary Ecotoxicity Evaluation - focus on probable site-specific toxicity mechanisms to species or habitats of concern.

- Preliminary Exposure Pathway Analysis - potential for completed pathways to impact species or habitats of concern.

- Review of similar case studies to assist in the Preliminary Problem Formulation (EPA, 1992; EPA, 1997).

- If any habitats or species of concern are identified; separate areas of concern shall be distinguished where relatively distinct risk scenarios are apparent. These areas of concern should be based on an evaluation of distribution patterns of regulated chemicals, habitat changes along contaminant migration pathways, and changes in species of concern across a site.

- Choose a limited number of species or habitats of concern for assessment endpoints (EPA, 1992; Suter, 1993; EPA, 1997).

b) Step 2 - Preliminary Exposure Estimate and Risk Assessment

If complete exposure pathways are identified, the regulated party has the option to evaluate the exposure and risk to selected assessment endpoints (Step 1) by either:

- Community-based analysis such as Rapid Bioassessment Protocols for fish or aquatic macroinvertebrates (EPA, 1989) or

- Hazard Quotient Method (EPA, 1997) with emphasis on representative exposure conditions and toxicity data that most directly relate to the assessment endpoints selected in Step 1. Refer to the EPA website for the Region 3 BTAG (Biological Technical Assistance Group) screening tables and the SSL (Soil Screening Levels) tables, as well as the NOAA website for the SQuiRT (Screening Quick Reference Tables) ecological screening values.

In addition, the uncertainty associated with either of these approaches should be discussed.

i) Decision Point

It is important that the qualified investigator understand that the Scientific/Management Decision made at the end of the preliminary risk calculation will not set a clean-up goal. Instead, one of the following will be decided:

- The ecological risk assessment should be continued to develop a site-specific clean-up goal, or to reduce uncertainty in the evaluation of risk and impact;
- The preliminary screening is adequate to determine that no substantial ecological risk exists; or
- There is substantial impact (de manifestis) and proceed to remediation that can eliminate or reduce exposure to an acceptable level (Suter, et al., 1995).

All steps are the same from this point whether the site started with the Statewide Ecological Screen or Steps 1 and 2 of this process (flow chart, Figure III-11). The qualified investigator shall follow the steps of the EPA Guidance but take into account factors noted below which shall be emphasized in Pennsylvania under Act 2.

c) Step 3 - Problem Formulation: Assessment Endpoint Selection and Testable Hypotheses

Identify Constituents of Potential Ecological Concern (CPECs) with particular emphasis on Table 8 in Appendix A of the regulations.

Further develop Assessment Endpoints that shall be based on evaluation of keystone species and ecological dominants that influence the ecosystem’s structure and function as they relate to species or habitats of concern (EPA, 1992; Suter, 1993; EPA, 1997).

The conclusion of this step should integrate the available information into a determination of which exposure pathways are most likely to result in a substantial ecological impact (see Statewide Ecological Screen for discussion) to habitats or species of concern. Only these prioritized pathways are evaluated in detail in the following steps of the process. All hypotheses should be focused on the prioritized pathways and selected assessment endpoints.

d) Step 4 - Problem Formulation: Conceptual Site Model, Measurement Endpoint Selection, and Study Design

The focus in this step should be on the prioritized exposure pathways identified in Step 3, emphasizing development of a study design which will determine if there is a causal relationship between a regulated substance and any substantial ecological impact that may be detected at a site.

Regarding bioaccumulation and tissue studies, the regulated party has the option of:

- Utilizing bioaccumulation factors reported in the literature which are most relevant to habitats or species of concern at the site; or
- Measuring bioaccumulation directly through tissues analysis and environmental media analysis.

Note that bioconcentration or bioaccumulation in and of itself is not evidence of environmental injury or a substantial ecological impact. Tissue levels should be related to a toxicity effect in a species of concern in order to be considered relevant in the evaluation.

Since the habitats and species of concern are readily identified and evaluated through field studies, the investigator should emphasize population/community evaluations over less direct measures of potential impact such as laboratory toxicity testing, literature references, or media chemistry, recognizing that a combination of these evaluations is usually conducted. In addition, laboratory toxicity testing should only be conducted with species that may potentially inhabit or survive at the subject site.

The conclusion of this step should describe the measurement endpoints (EPA, 1992; Suter, 1993; EPA, 1997) for the prioritized exposure pathways and provide a clear outline of the study design.

e) Step 5 - Site Assessment for Sampling Feasibility

Ensure that the measurement endpoints are present in sufficient quantity or abundance so that sampling and analysis can be collected across a gradient of contamination and include a representative reference area.[1] If necessary, the measurement endpoints should be modified to ensure the study objectives can be met (EPA, 1997).

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[1] Reference area is defined as an area not contaminated by regulated substances originating on the site and used for comparison to the site (EPA, 1997). In addition, a reference area should be near the site and have similar geochemical, physical, and biological conditions, but be uncontaminated with regulated substances from the subject site (i.e., unimpacted by the site).

f) **Step 6 - Site Investigation**

Only persons qualified and experienced in ecological assessment[2] methods can direct field activities or make modifications of methods in the field.

g) **Step 7 - Risk Characterization**

The chemical data should be presented in a manner which illustrates the contamination gradients at the site and areas of substantial environmental impact distinguished, based on the site-specific weight-of-evidence. Hazard quotients and/or population/community analysis data should be summarized on figures with the analytical data. The uncertainties associated with either of these approaches shall be discussed.

Similar to Step 2 of this process, one of two conclusions shall be reached for the site or separate areas of concern within the site (if applicable, see Step 1), based on the site-specific weight-of-evidence. The conclusion shall be:

- There is no substantial ecological impact; or
- There is a substantial ecological impact, and remediation options shall be evaluated (Step 8).

h) **Step 8 - Risk Management**

Risk management is a balancing of factors (Figure III-11). Consistent with current and intended future use, the risk manager should consider the following in determining whether to remediate or allow natural attenuation processes to complete the recovery:

- Only differences of greater than 20% in the density of species of concern or greater than 50% in the diversity and habitats of concern should be regarded as potentially substantive impacts (Suter, 1993; Suter, et al., 1995).
- Where substantive impacts are determined, an evaluation of the risk reduction and restoration options should be completed, taking into account:
    1. Environmental injury caused by any remedy should not exceed the injury caused by regulated substances;
    2. The primary source of the regulated substance release has been or will be removed or controlled;

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[2] Qualified and experienced means: a certified ecologist or hold a college degree in ecology or environmental sciences or natural resources and at least five years of experience conducting ecological field work and risk assessments.

3. That at many sites, risks to native terrestrial organisms are likely to be low because the current or intended future use is for human activity (such as residential, industrial or commercial land use) and consequently the probability of habitats of concern existing on the site is low;

4. Natural physical and chemical attenuation mechanisms act on the released regulated compounds resulting in degradation or sequestration and consequent reduced bioavailability of remaining chemical residuals;

5. The substantial acclimation capacity of natural populations to exposure to low or moderate concentrations of chemical residuals;

6. That most remedial actions cause substantial injury to areas of concern beyond the toxicological impacts, as well as impacts to previously unimpacted areas along the perimeter of the remediation area; and

7. That natural systems are self-organizing, and an attempt to manage these processes to produce a particular result requires long-term management, and even then can result in undesirable results.

- Implementation of the selected remedy that will reduce the risks and restore the structure and function of the impacted ecological system to a condition which is capable of sustaining species and habitats of concern without substantial adverse effect from residual regulated substances.

- Sources of regulated substances will be removed and natural attenuation/acclimation processes in relatively small areas will mitigate impacts naturally to the point that they are no longer substantive.

- The restoration objective is to return the substantially impacted ecological system to a structure and function which is capable of sustaining species and habitats of concern without adverse effects, consistent with planned future use of the site within a reasonable time frame. The restoration objective is not to return to pre-stressed conditions but something that is similar structurally and functionally.

3. References

EPA. 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers. EPA/444/4-89-001.

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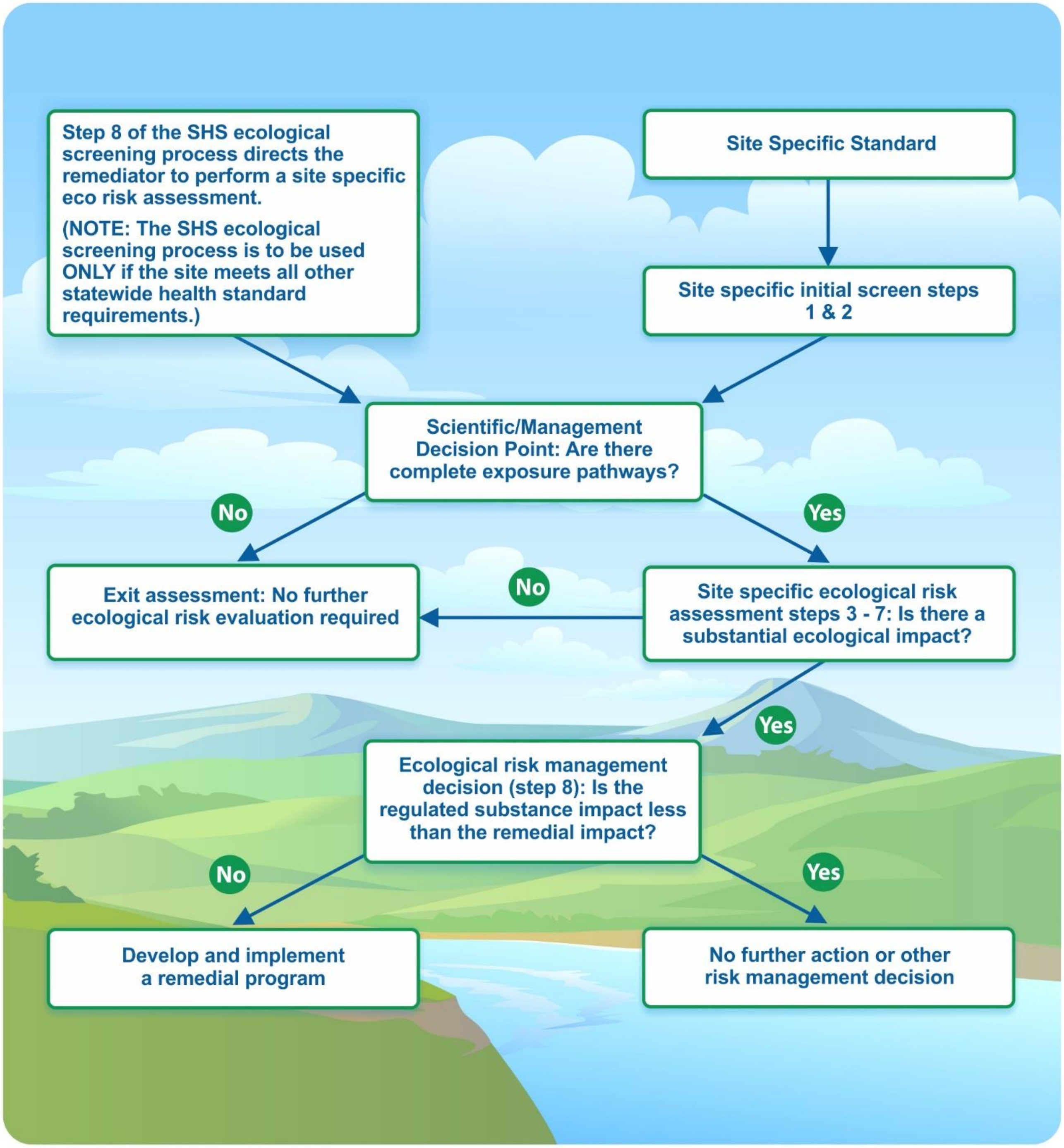
Figure III-11: Site-Specific Ecological Risk Assessment Procedure



Appendix A

Groundwater Monitoring Guidance

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APPENDIX A: GROUNDWATER MONITORING GUIDANCE

When groundwater is an affected medium, monitoring it is an extremely important part of site characterization, fate and transport assessment, and ultimately, demonstrating attainment of a cleanup standard at Act 2 sites. Taking this under consideration, the Groundwater Monitoring Guidance identifies technical considerations for performing detailed yet concise hydrogeologic investigations and groundwater monitoring programs at Act 2 sites. The purpose of this guidance is to ensure consistency within the Department and to inform the regulated community of DEP's technical recommendations and the basis for them.

The methods and practices described in this guidance are not intended to be the only methods and practices available to a remediator for attaining compliance with Act 2 regulations. The procedures used to meet requirements should be tailored to the specific needs of the individual site and Act 2 project and based on the history, logistics, and unique circumstances of those sites. The guidance is not intended to be a rigid step-by-step approach that is utilized in all situations. The Department recommends that site remediators consult with DEP Regional Office staff for assistance in evaluating and understanding site characterization information for a more efficient Act 2 cleanup.

A. Overview

1. Introduction

Monitoring of groundwater quality is an important component in the application of and compliance with Act 2 of 1995, the Land Recycling and Environmental Remediation Standards Act (Act 2, 35 P.S. §§ 6026.101-2026.908). The goal for monitoring groundwater quality is to obtain reliable data and information that is representative of aquifer characteristics, groundwater flow direction, and physical and chemical characteristics of the groundwater.

Before beginning a hydrogeologic investigation at an Act 2 site, a conceptual site model (CSM) should be developed based on site geology and hydrogeology and the characteristics of the release. The CSM should estimate distribution of predominant geologic units, flow conditions, location of aquifers and aquitards (if known), water table surface and other pertinent hydrogeologic factors present at the site. Coupled with hydrogeologic properties at the Act 2 site, the CSM should consider the type of contaminant which has been released and its physical properties (e.g., petroleum-based or solvent-based, weathered vs. fresh, etc.), the manner of release to the environment, and the volume of the release as can best be determined.

Typical groundwater quality monitoring at Act 2 sites may include:

- Background monitoring: relating to determination of background conditions in accordance with the Act 2 background cleanup standard (e.g. establishing if a groundwater contaminant is naturally occurring, an areawide problem typically resulting from historic, areawide releases, or from an upgradient source). The results of background groundwater monitoring will form a basis against which future monitoring results will be compared to established background values for specific regulated substances of concern, develop groundwater quality trend analyses, or remediation effectiveness under Act 2 when the background cleanup standard is selected.

- Site Characterization: During site characterization, groundwater monitoring wells may be installed and sampled at an Act 2 site throughout the area(s) of contamination, as well as in areas not affected by the release of any regulated substance. Some of the data collected at the monitoring well locations may include groundwater elevations, which are then used to calculate groundwater flow direction and hydraulic gradient, permeability of aquifer materials, porosity of the aquifer, the types of regulated substances present and their concentrations, and the spatial variation in concentration, both horizontally and vertically. A fate and transport assessment most likely should be implemented during this phase of the Act 2 investigation.

- Attainment monitoring: Attainment monitoring of groundwater is performed to demonstrate that the selected Act 2 cleanup standard has been attained at the Point of Compliance (POC). Refer to Section II.B of this guidance for additional information on this concept. Attainment monitoring is also utilized to determine the effectiveness of groundwater cleanup activities.

- Postremedial monitoring: Postclosure monitoring is conducted to determine any changes in groundwater quality after the cessation of a regulated activity or activities. This monitoring may also be part of a postremedial care plan, such as periodic monitoring of sentinel wells. Analytes most likely to be included are those which were monitored during site characterization and/or attainment monitoring.

2. References

Alaska Department of Environmental Conservation, September 2013, Division of Spill Prevention and Response Contamination Sites Program, Monitoring Well Guidance.

B. Monitoring Well Types and Construction

1. Objectives of Monitoring Wells

Monitoring wells should be located and constructed to provide the controlled access necessary to characterize the groundwater at an Act 2 site. Wells should be constructed by a driller who is licensed by the Commonwealth of Pennsylvania (Act 610 of 1956, 32 P.S. § 645.12, and 17 Pa. Code Chapter 47). Drillers do not need to be licensed to install piezometers, temporary well points, or in-situ sampling probes.

Monitoring wells should effectively achieve one or more of the following objectives:

- Provide access to the groundwater system for collection of water samples.
- Measure the hydraulic head at a specific location in the groundwater flow system.
- Provide access for conducting tests or collecting information necessary to characterize the chemical properties of aquifer materials or their hydrologic properties.

While achieving these objectives, the groundwater monitoring system should also preserve the conditions of the subsurface that is penetrated, but not monitored. For example, a well designed to monitor a bedrock aquifer should be designed and installed with minimal or no impact to the flow system in the unconsolidated material overlying the bedrock.

Although monitoring (or observation) wells may be used to measure water levels and then determine the configuration of the water table, or other potentiometric surface, the focus of this appendix is groundwater quality monitoring. Specifically, this appendix provides guidance for the monitoring of groundwater at Act 2 sites.

2. Types of Groundwater Monitoring Systems

Groundwater monitoring systems range from the simple to the complex. Each system has its own value and use in the monitoring environment. Various types of groundwater monitoring systems are described below. General recommendations for the construction of single-screened wells and open boreholes are shown in Figures A-1 and A-2. Site-specific circumstances may require modifications to the recommended construction details.

<u>Open boreholes</u> - These boreholes are typically drilled into competent bedrock with the casing extending completely through the overburden (unconsolidated material) and into the competent rock below. Note that a vertical conduit is created which may intercept active groundwater flow zones (controlled by primary porosity and secondary porosity; i.e. fractures, bedding planes, solution cavities) previously not in contact with each other, potentially resulting in cross contamination. Recommended installation details are shown in Figure A-1.

Figure A-1: Recommended Construction of an Open Borehole Well

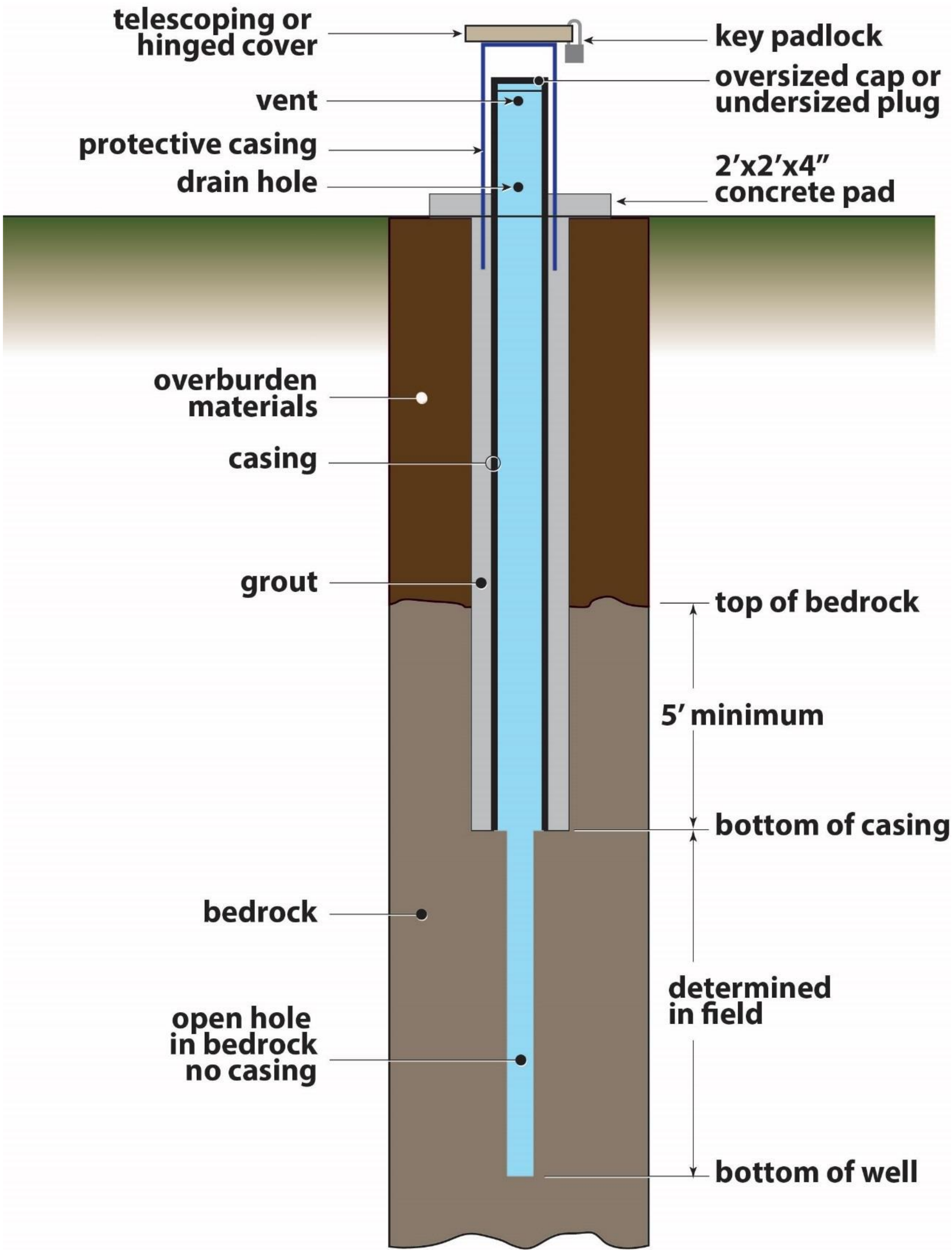


Figure A-2: Recommended Construction of a Single-Screened Well

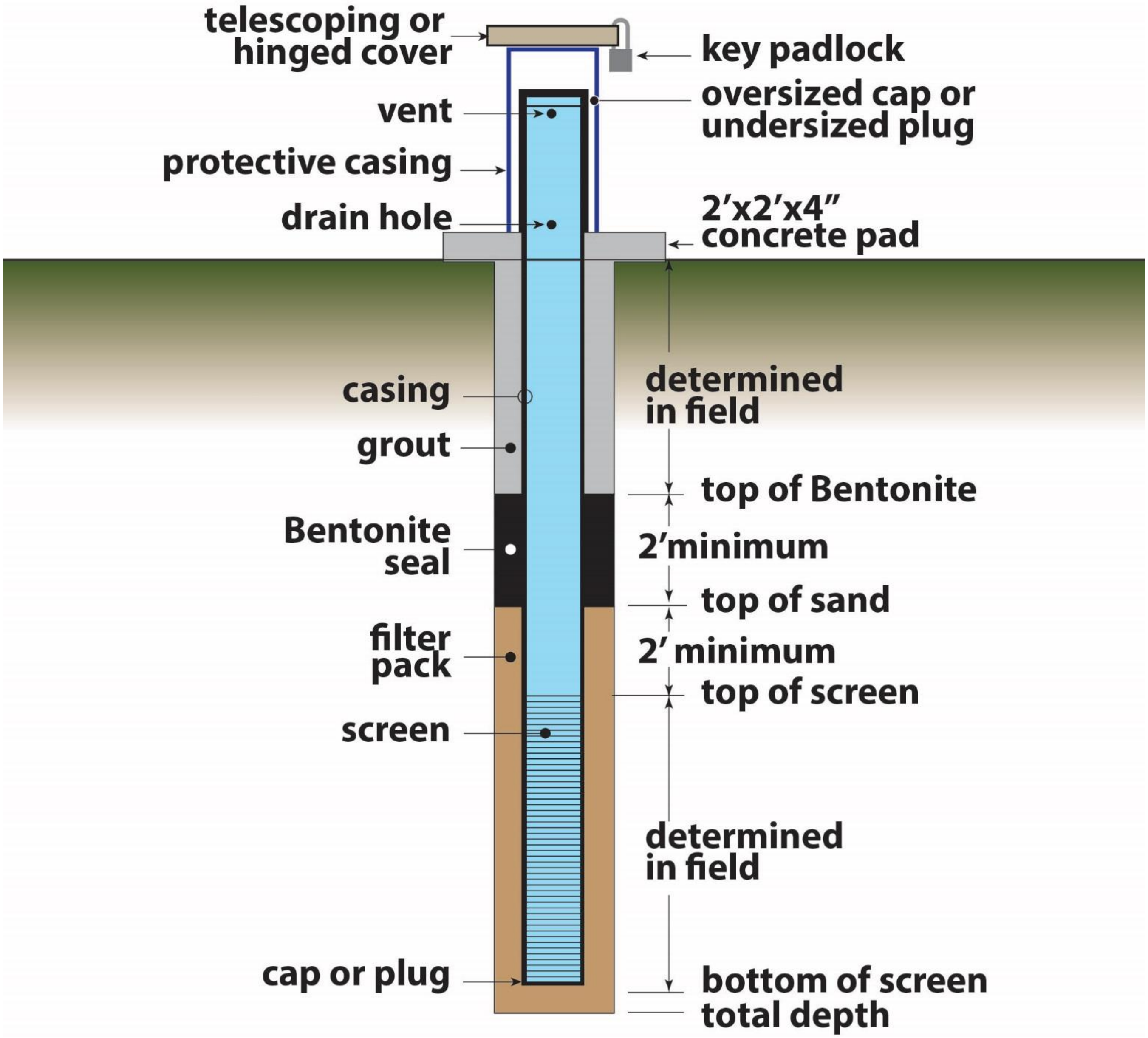
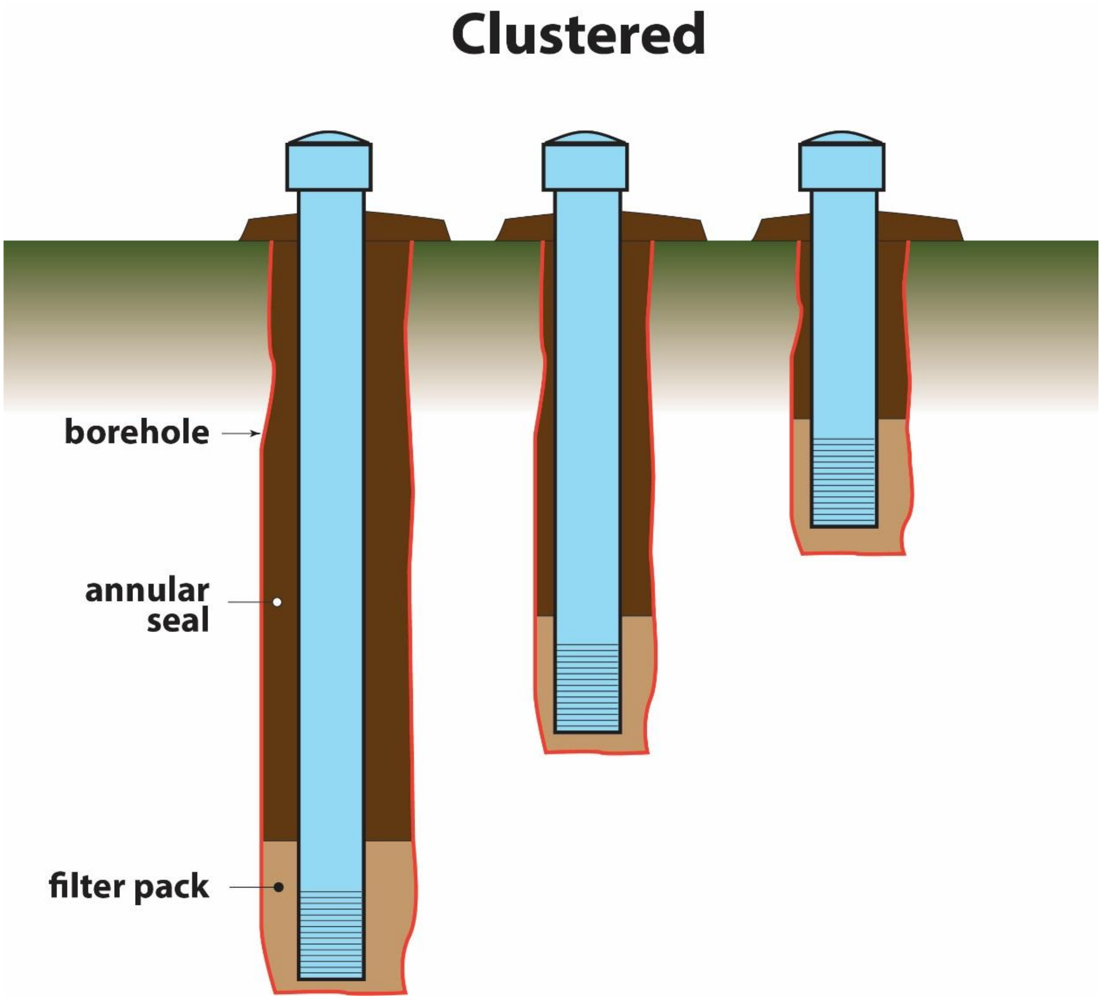


Figure A-3: Example of a Well Cluster



Single screened wells - These wells consist of a prefabricated screen of polyvinylchloride plastic, stainless steel, etc., that is inserted into an open borehole. Clean sand or gravel is placed around the annular space of the screen for the entire vertical distance of the screen length and slightly higher past the connecting screen and well casing. Recommended installation details are shown in Figure A-2.

Well clusters - Well clusters, or a well nest, consist of the construction of open boreholes or screened monitoring wells in a specific location, with each well monitoring a different depth or zone of groundwater. An example of a well cluster is shown in Figure A-3.

Well points - Well points are usually short lengths (i.e., 1-3 feet) of screen attached to a hardened metal point so that the entire unit can be driven, pushed, or drilled to the desired depth for monitoring. (This method is usually limited to shallow, unconsolidated formations.)

Piezometers - These are small diameter wells, generally non-pumping, with a very short well screen or section of slotted pipe at the end that is used to measure the hydraulic head at a certain point below the water table or other potentiometric surface.

3. Choice of Monitoring System

The type of monitoring system chosen depends on the objectives of monitoring at the site. Once the target zones, or areal locations and depths that are the most likely to be impacted by the release are defined, monitoring is often adequately accomplished by using open rock boreholes or single-screened wells that monitor the entire saturated thickness, or a large portion of the target zone.

Where contamination has been detected and definition of vertical contaminant stratification is desired, wells that monitor more discrete intervals of the target zone, or individual aquifers, usually need to be constructed. In this case, well clusters such as shown in Figure A-3 will often be the construction design of choice, although open holes that monitor a short vertical interval or single water-bearing zone also may have application. As the flow beneath the site is better understood, the monitoring system typically will target more specific depths and locations.

Well points, or in-situ sampling probes (direct push technology), can be valuable reconnaissance tools for preliminary site characterizations, or for determining the locations of permanent monitoring wells (see EPA, 1993 and ITRC, 2006). However, in-situ sampling probes can miss a light nonaqueous phase liquid (LNAPL) on the water table and may have problems penetrating coarse sands and gravel (where contamination may be located). Other potential problems include very slow fill times in clayey sediments and significant capture of fines in the sample.

Special well construction will be needed to monitor for certain types of contaminants. **For example, if an LNAPL is a concern, the well screen should be open, bridging the top of the water table and within the zone of fluctuation, so that the LNAPL contaminants will not be cased-off.**

4. Minimum Construction Standards

To properly meet the objectives listed in Section B.1, monitoring wells should be designed and constructed using minimum standards in each of the following categories.

1) Materials

2) Assembly and installation

3) Well development

4) Recordkeeping and reporting

Figure A-4: Examples of Target Zones

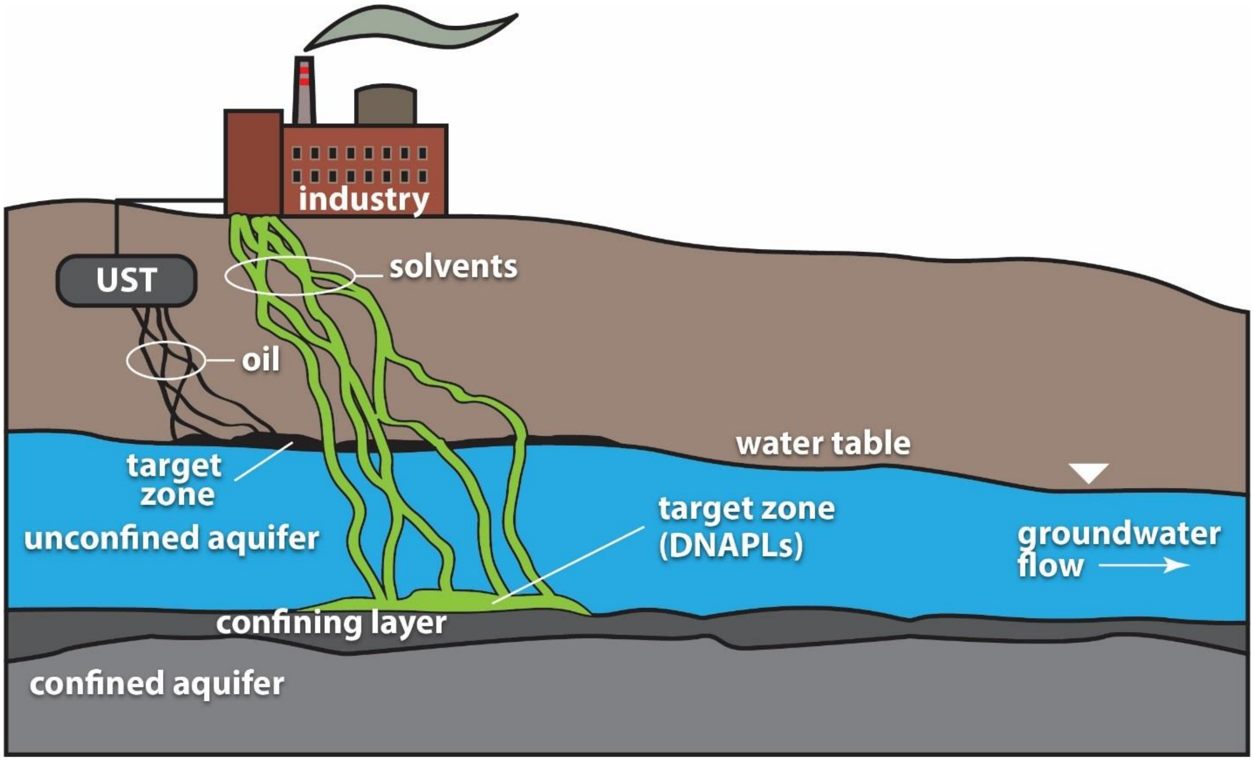
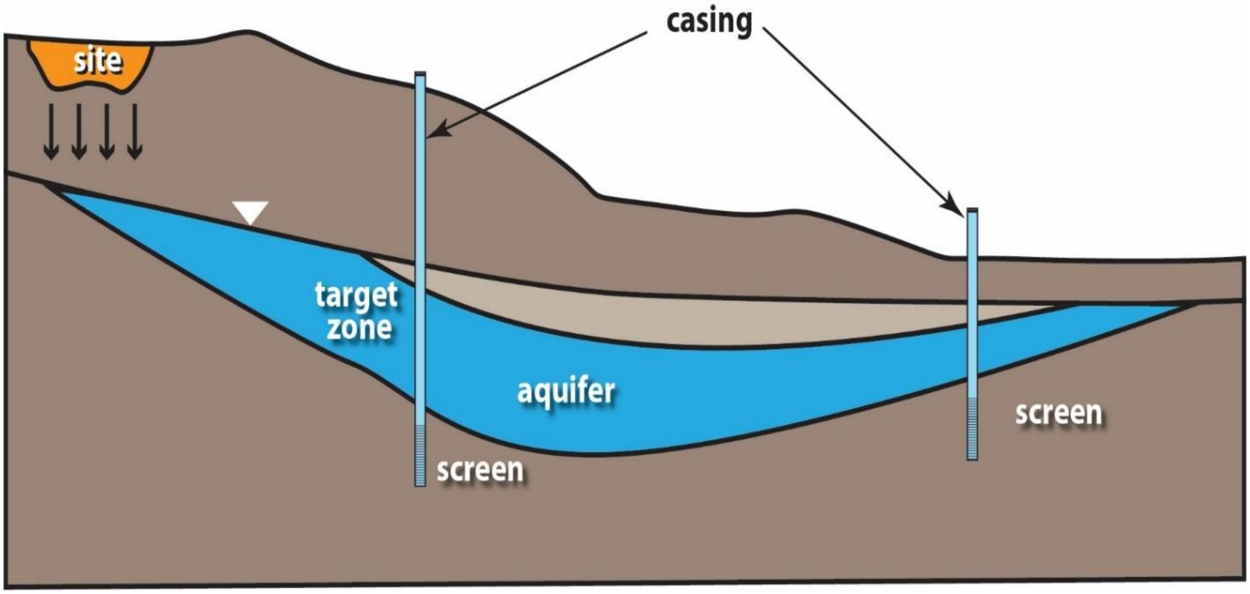


Figure A-5: Monitoring Well Screens Placed Too Deeply Below the Target Zone to Detect Contamination



Different standards and practices may be necessary depending upon the monitoring objectives of an individual site. Monitoring wells constructed to meet multiple objectives should employ the standards of the most rigorous objective. For instance, a well point may be suitable for monitoring hydraulic head, but may not be optimum for collecting samples. Therefore, a well proposed to monitor head and collect water samples should be designed as a conventional, screened well and not as a well point. In addition, construction methods, materials, and well development of each point in the plan must not compromise the objective of other monitoring wells in the well system.

a) Materials

Materials that are used in construction of a monitoring well should not contaminate the groundwater being monitored. A list of materials should include, but not be limited to, the drilling tools and equipment, casing, riser pipe, well screen, centralizers (if needed), annular sealant, filter pack, and drilling fluids or additives. All materials should be of adequate size and of competent strength to meet the objectives of the monitoring point. All materials introduced into the boring should be free of chemicals or other contaminants that could compromise the monitoring well or other downgradient wells. Practices must be employed to minimize the potential for contamination of the materials during storage, assembly, and installation. Specific cleaning procedures should be employed in situations where the materials might introduce contaminants to the groundwater system. Well screens and risers should be coupled using either water-tight flush-joint threads or thermal welds. Solvent welded couplings are not recommended for monitoring well construction.

b) Assembly and Installation

Equipment and techniques should be used that create a stable, open, vertical borehole of large enough diameter to ensure that the monitoring well can be installed as designed, while minimizing the impact on the zone(s) being monitored. When drill cuttings and groundwater removed during construction will likely be contaminated, procedures commensurate with the type and level of contamination should be followed for the handling, storage, and disposal of the contaminated material. Whenever feasible, drilling procedures that do not introduce water or other liquids into the borehole should be utilized. When the use of drilling fluids is unavoidable, the fluid should have as little impact on the constituents of interest as possible. If air or other gas is used as the drilling fluid, the compressor should be equipped with an oil air filter or an oil trap.

The well screen and riser assembly should be installed using procedures that ensure the integrity of the assembly. If water or other ballast is used, it should be of known and compatible chemistry with the water in the boring. Unless designed otherwise, the assembly should be installed plumb and in the center of the boring. Centralizers of proper spacing and diameter can be used. Depending upon the physical environment, the well should be finished as a secure stick-up or flushmount at the discretion of the project geologist. Either completed type of well should be securely capped to prevent the entry of foreign material.

Installation of the filter pack, sealants, or other materials in the annular space should be done using tremie pipes or other accepted practices. Protective casing and locking well caps must be installed, and any other necessary measures must be taken to ensure that the monitoring well is protected from vandalism and accidental damage. To reduce misidentification, all monitoring wells constructed in developed areas, or in any location where they may be mistaken for other structures (such as tank-fill tubes, drains, and breather tubes), should have a locking cap conspicuously labeled “Monitoring Well” (preferably by the well-cap manufacturer). In addition, locks for the monitoring wells should use a key pattern different from locks on other structures at the site. It is also advisable that the well identification number be placed on both the inside and outside of the protective casing.

c) Well Development

After installation, groundwater monitoring wells should be developed to:

- Correct damage to the geological formation caused by the drilling process;
- Restore the natural water quality of the aquifer in and around the well;
- Optimize hydraulic communication between the geologic formation and the well screen; and
- Create an effective filter pack around the well screen.

Well development is necessary to provide groundwater samples that represent natural undisturbed hydrogeological conditions. When properly developed, a monitoring well will produce samples of acceptably low turbidity (less than 10 Nephelometric Turbidity Units (NTUs) as recommended by U.S. EPA, 2013). Low turbidity is desirable as turbidity may interfere with subsequent analyses, especially for constituents that sorb to fine-grained materials, such as metals (CEPA, 2014). Well development stresses the formation and filter pack so that fine-grained materials are mobilized, pulled through the well screen into the well, and removed by pumping.

Well development should continue until as much of the fine-grained materials present in the well column have been removed as possible. It is important to record pumping rates utilized during well development. Purging and sampling rates should not exceed the maximum pumping rate used during well development. When it is likely that the water removed during development will be contaminated, procedures commensurate with the type and level of contamination should be utilized and documented for the handling, storage, and disposal of the contaminated material. Development methods should minimize the introduction of materials that might compromise the objective of the monitoring. If air is used, the compressor should have an oil air filter or oil trap.

Repeated well development may be conducted as necessary at the discretion of the project geologist, especially if clogged screens or biofouling are evident.

d) Recordkeeping and Reporting

Because interpretation of monitoring data from a monitoring well is spatially dependent on both the activity being monitored and other monitoring wells in the system, records and samples of the materials used to construct and drill the monitoring well should be kept. Following construction, accurate horizontal and vertical surveys should be performed. The surveys should be completed by personnel knowledgeable in land surveying techniques. A permanent reference point should be made by notching the riser pipe. Whenever possible, all reference points should be established in relation to an established National Geodetic Vertical Datum (NGVD). Monitoring well locations should be surveyed to ±1 linear foot, and monitoring well elevations should be to the nearest .01 foot. Elevations of the protective casing (with the cap off or hinged back), the well casing, and the ground surface should be surveyed for each monitoring well (see Nielsen, 1991). DEP-permitted facilities are generally required to record the latitude and longitude for each monitoring well (this also is recommended for non-permitted facilities).

A groundwater monitoring network report should be prepared. This report should include copies of the well boring logs, test pit and exploratory borehole logs; details on the construction of each monitoring point; maps, air photos or other information necessary to fully describe the location and spatial relationship of the points in the monitoring system; and a recommended decommissioning procedure consistent with the applicable regulatory program and the well decommissioning procedures recommended in Section E of this appendix.

Monitoring well logs should be prepared and should describe, at a minimum, the date of construction; the thickness and composition of the geologic units (identification of stratigraphic units should be completed on the well log using the Unified Soil Classification System); the location and type of samples collected; the nature of fractures and other discontinuities encountered; the nature and occurrence of groundwater encountered during construction, including the depth and yield of water-bearing zones; headspace of photoionization detector (PID) readings collected; any observations of contamination (e.g. NAPL); and the static water level upon completing construction.

A well completion plan should also be included in the monitoring network report. Each plan should include information on the length, location, slot size, and nature of filter pack for each screen; type, location and quantity of material used as annular seals and filler; description of the type and effectiveness of well development employed; and notes describing how the well, as constructed, differs from its original design and/or location.

The reports described above do not relieve the driller from the obligation to submit, for each well drilled, a Water Well Completion Report to the Department of Conservation and Natural Resources (DCNR), Bureau of Topographic and Geologic Survey, as required by Act 610 (the Water Well Drillers License Act).

5. Direct Push Technology

Direct Push Technology (DPT) devices are investigative tools that drive or ‘push’ small-diameter rods into the subsurface via hydraulic or percussive methods without the use of conventional drilling. DPT has been in use in the environmental industry for more than two decades and its utilization as a tool for performing subsurface investigations in Pennsylvania and many other states has grown concurrently with its evolving technology.

Monitoring wells installed using DPT could either be field-constructed, similar to conventionally drilled and installed wells, or installed using pre-packed well screens. The pre-packed well screen assemblies consist of an inner slotted screen surrounded by a wire mesh sleeve which acts as a support for filter media (sand). The sand is packed between the slotted screen and the mesh. It is important to note that only DPT pre-packed wells are considered suitable for Act 2 sites, due to quality assurance concerns regarding field-construction and associated problems placing the filter pack around the screens of small-diameter wells.

a) Advantages of DPT

Depending on site conditions, DPT offers an attractive alternative to conventional auger drilling and split spoon sampling. The smaller size of DPT rigs enables well installation and sampling in areas not accessible to traditional large auger rigs.

As DPT methods utilize a smaller diameter boring than conventional drilling, less solid waste is generated. Similarly, less liquid waste will be generated from smaller diameter monitoring wells. Because less waste is generated, worker exposures are reduced.

Overall, there is minimal disturbance to the natural formation using DPT in comparison with auger drilling.

From an economic standpoint, DPT has several advantages versus conventional drilling. In relation to project schedule and budget, the time-effectiveness of DPT installation may enable the remediator to investigate more areas of a site than traditional hollow stem auger (HSA) drilling would allow and in a shorter time. Fewer well construction materials may enable a remediator to install additional monitoring points on a limited budget.

Most importantly, short-term and long-term groundwater monitoring studies conducted by others have produced results demonstrating that water samples collected from DPT installed wells are comparable in quality to those obtained from conventionally constructed wells.

b) Disadvantages of DPT

DPT cannot completely replace the use of conventional drilling/monitoring well installation as limitations of the technology are evident in certain situations. DPT is only useful at generally shallow depths (less than 100 feet below surface grade) and in unconsolidated formations. DPT is not suitable for formations containing excessive gravel, cobbles, boulders, etc., or for bedrock drilling due to the obvious lack of augering capabilities.

DPT may be utilized for monitoring well installation below confining layers or as 'nested' wells with extreme caution. DPT utilizing only a macrocore barrel and drive rods may not provide for the advancement of casing to keep the borehole open and seal off each separate zone of saturation, which therefore can potentially allow for the mixing of separate zones of saturation when the push rods are withdrawn from the borehole. Therefore, DPT may be utilized for this purpose only if the project geologist can ensure that the threat of cross-contamination from separate zones of saturation above clean zones of saturation will not occur.

If large volumes of aqueous sample are required, DPT installed monitoring wells may not be suitable due to the small diameter of the well screen.

Since DPT causes smearing and compaction of the borehole sides, proper well development techniques are vital to ensure that natural hydraulic permeabilities are maintained. Several studies have demonstrated that hydraulic conductivities can vary by an order of magnitude lower for wells installed by DPT versus wells installed by conventional HSA. For this reason, DPT-installed wells may not be suitable for aquifer characteristics testing, nor for efficient groundwater recovery. Great care needs to be taken to ensure adequate well development when using DPT for well installations.

6. References

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C. Locations and Depths of Monitoring Wells

1. Importance

The locations and depths of monitoring wells are the most important aspects of a groundwater monitoring network. A monitoring point that is misplaced, or not constructed properly to monitor constituents with unique physical characteristics, is of little use and may misrepresent the quality of the groundwater migrating to or from a site. On the other hand, a properly positioned and constructed monitoring well that detects the earliest occurrence of contamination could save both time and money spent on cleanup of a site. It is important to note that the placement and construction of a groundwater monitoring network at an Act 2 site shall be conducted by a professional geologist licensed in Pennsylvania (25 Pa. Code §§ 250.204(a), 250.312(a), and 250.408(a)).

2. Approach to Determining Monitoring Locations and Depths

Different approaches and efforts for determining the location and depth of wells may be necessary based on the type of monitoring to be done. However, before well locations are chosen for any type of monitoring, the existing data should be evaluated. This can reduce the costs of implementing the monitoring program and can help to make appropriate choices for three-dimensional monitoring locations.

The most efficient way to accomplish the location and depth of monitoring wells for an Act 2 study is to formulate a CSM, or conceptual groundwater flow model. A conceptual groundwater flow model is the illustrative delineation and formulation of the important controlling components of groundwater flow and thus contaminant transport from recharge areas to discharge zones or withdrawal points. Without a proper conceptualization of groundwater flow, a groundwater model can give spurious results. On the other hand, a well-developed conceptual model may allow groundwater flow to be accurately approximated without using computer modeling or complex analytical procedures. The groundwater conceptual model is an important tool in the study of groundwater flow on both a local and even larger scale. The goal of the conceptual model is to represent the controlling aspects of groundwater flow at the site being investigated. Important controlling components of groundwater flow can include geological characteristics, geologic structural and stratigraphic relationships, anisotropy, calculated groundwater flow directions and recharge and discharge relationships.

Information may be obtained through site visits, site records and previous studies, interviews with present and past workers, aerial photographs, scientific publications on the local and regional hydrogeology, geophysical surveys, borings, wells, aquifer tests, etc. If enough information is available, the designer can determine the groundwater flow paths and design a complete monitoring network. However, actual testing of aquifer parameters and borehole geophysics provides the best information to evaluate placement and construction of monitoring wells, especially in newly established sites or facilities where little site information is available.

a) Background Monitoring

The determination of background water quality is paramount in understanding the effect of an activity or site on groundwater quality. Often, insufficient site information is available so that initial well locations may depend on casual observations and assumptions regarding groundwater flow. If subsequent information shows that monitoring wells are misplaced, new wells should be installed.

b) Site Characterization Monitoring

Appropriately placed monitoring wells are necessary to detect groundwater quality at an Act 2 site. The more that is known about the history of operations at the site, (potential) contaminant flow paths, and the constituents that may have been discharged to the environment, the more likely that monitoring wells installed during the site characterization phase of the investigation will be optimally placed and constructed to monitor the impact on groundwater quality. Monitoring well locations should be concentrated in those areas that will most likely first be impacted by the known discharges on the site, which typically will be located within or comprise the uppermost aquifer. As groundwater data is collected, additional monitoring wells may need to be installed to fully characterize the groundwater contaminant plume(s) present. The greater the complexity of the hydrogeology and the spread of contamination, the more monitoring wells that may be necessary to characterize the contamination.

c) Attainment and Postremedial Monitoring

Any number of wells, including all installed during the site characterization phase, may be used for attainment monitoring. These wells will demonstrate attainment of the chosen cleanup standard at the POC. The impact of any remediation conducted at the Act 2 site on the groundwater flow paths (e.g. pumping the aquifer) should be considered for placement of attainment monitoring wells. Postremedial monitoring would likely be conducted in the same wells as attainment monitoring to monitor for any residual rebound occurring in the aquifer after remediation activities have been completed.

3. Factors in Determining Target Zones for Monitoring

The prime requirement for a successful monitoring system is to determine the “target” zones - the spatial locations and depths that are the most likely areas to be impacted by the site being investigated. The dimensions of target zones depend on the vertical and horizontal components of flow in the aquifers being monitored, the size of the Act 2 site, the potential contaminants released, and the distance that contamination may have traveled from the facility since being released. Figure A-4 shows how different target zones could be formed based on these factors.

Horizontal and vertical components of groundwater flow are best determined by constructing planar and cross-sectional flow nets based on the measurement of water levels in piezometers. Where the vertical components of flow are negligible, wells, rather than piezometers, drilled into the aquifer to about the same depth, will allow preparation of a contour map of water levels representing horizontal flow. This should be adequate to prepare a planar flow net and determine the target zone.

With regard to upgradient wells, target zones (as defined above) do not exist. Upgradient wells should be drilled to depths that are screened or open to intervals similar to that of the downgradient wells, or to depths that yield water that is otherwise most representative of the background quality of the water being monitored by the downgradient wells. In other words, upgradient wells should be installed within the same hydrogeologic aquifer to the respective downgradient wells.

The numerous site details to consider when establishing target zones may be grouped into either groundwater movement or the spatial distribution of contamination.

a) Groundwater Movement

In what direction is groundwater flowing? If flow paths are not easily determined, what will influence the direction of groundwater flow? The answers to these questions are critical to selecting target zones and the optimal locations of monitoring wells.

Using the groundwater levels from piezometers or wells at the site, the groundwater flow direction and hydraulic gradient can be determined. At least three monitoring points are needed to determine the horizontal flow direction and hydraulic gradient; however, at some sites, knowledge of the vertical component of flow may be important. This is best accomplished by using well pairs of "shallow" and "deep" piezometers or short-screened wells.

It may appear to be a simple task to place monitoring wells in downgradient positions using a map of the groundwater elevation contours, or by anticipating the flow direction based on topography or discharge points. However, at many sites, three-dimensional flow zones must be understood to install appropriate monitoring points (see Section C.5 of this appendix). Figure A-5 shows how a well can miss the vertical location of contamination at a site. Water level measurements, piezometer and well construction logs, geologic well logs, and groundwater flow direction maps should be reviewed carefully when assessing the dimensions of target zones.

i) Geologic Factors

The geology of a site can complicate the selection of the target zones for monitoring. Geologic factors can produce aquifers that are anisotropic. In an anisotropic aquifer, the hydraulic conductivity is not uniform in all directions so that groundwater moves faster in one direction than another and oblique to the hydraulic gradient. Anisotropy can result from various sedimentary or structural features such as buried channels, bedding planes, folds, faults, voids, and fractures.

In Pennsylvania, most of groundwater flow in bedrock is through fractured rocks. Fracture flow in bedrock (or hardened sediments) requires additional considerations compared to flow in unconsolidated materials. Consolidated materials may exhibit small effective porosities and low hydraulic conductivities that impede groundwater flow. However, the development of secondary porosity may allow substantial flow of groundwater through fractures, joints, voids, cleavage planes and foliations. These features tend to be highly directional, exhibit varying degrees of interconnection, and may produce local groundwater flow regimes that are much different from the regional trends.

Geologic factors influence the direction of groundwater flow by controlling the transmissivity. For example, Figure A-6 shows the effect of fractures on the spread of contamination. Although the gradient indicates flow to the north, groundwater also follows the major fractures and spreads to the northeast. Monitoring wells “1” and “2” located to the north of the site may detect contamination, but the lack of a monitoring well to the northeast will miss an important direction of migration. Common sedimentary bedding planes also could have a similar effect on groundwater flow.

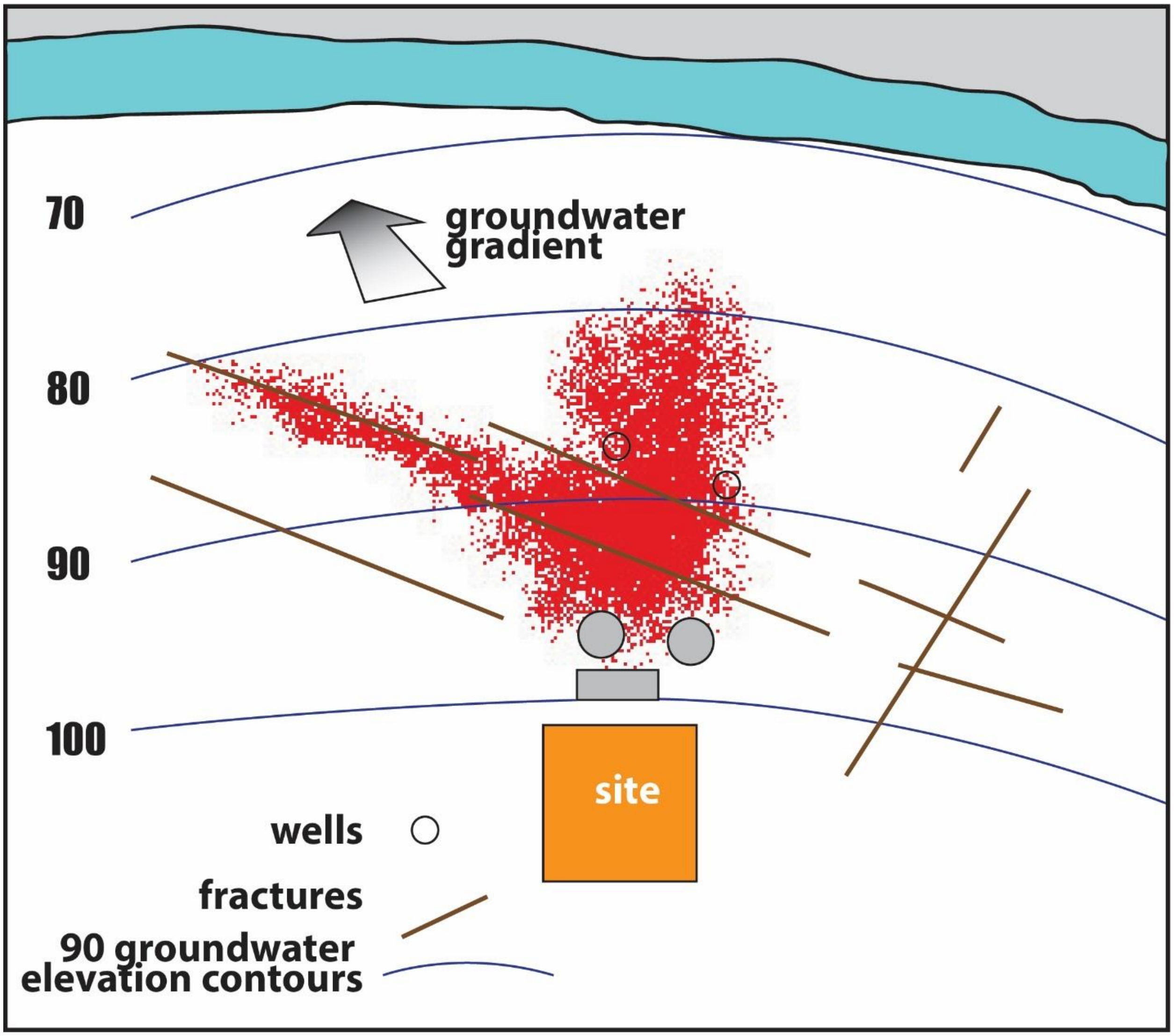
It is important to identify hydrostratigraphic intervals which may or may not be interconnected at the site when conducting a groundwater investigation. Monitoring wells should not be screened across two intervals as groundwater flow and concentrations of contaminants may differ significantly in each interval.

ii) Groundwater Barriers

The presence of hydrogeologic barriers should also be considered when locating wells in a groundwater monitoring system. A groundwater barrier is a natural geologic or artificial obstacle to the lateral movement of groundwater. Groundwater barriers can be characterized by a noticeable difference in groundwater levels on opposite sides of the barrier. Geologic faults and dikes along with tight lithologic formations such as shale and clay layers are common examples. Important types of barriers include the following:

<u>Geologic faults</u> - Fault planes that contain gouge (soft rock material) or bring rock bodies of widely differing hydraulic conductivity into juxtaposition can influence groundwater flow direction and velocity. Location of downgradient wells across fault zones or planes should not be approved until the nature of the influence of the fault zone on groundwater flow has been evaluated. One method of evaluating fault zones is to conduct pumping tests with wells on either side of the fault plane to evaluate the degree of hydraulic connection.

Figure A-6: Effect of Fractures on the Spread of Contamination



Dikes - Diabase dikes, common in southeastern Pennsylvania, can function as lithologic barriers to groundwater flow because of their very low permeability. If a dike lies between a site and a proposed downgradient well, the role of the dike should be evaluated prior to approving the well's location.

Others - Geologically "tight" layers (aquitards) or formations can function in a similar way: they can create subsurface "dams" that cause groundwater to flow in unexpected directions. Additional barriers to flow can include inclined confining beds, groundwater divides, and artesian aquifers.

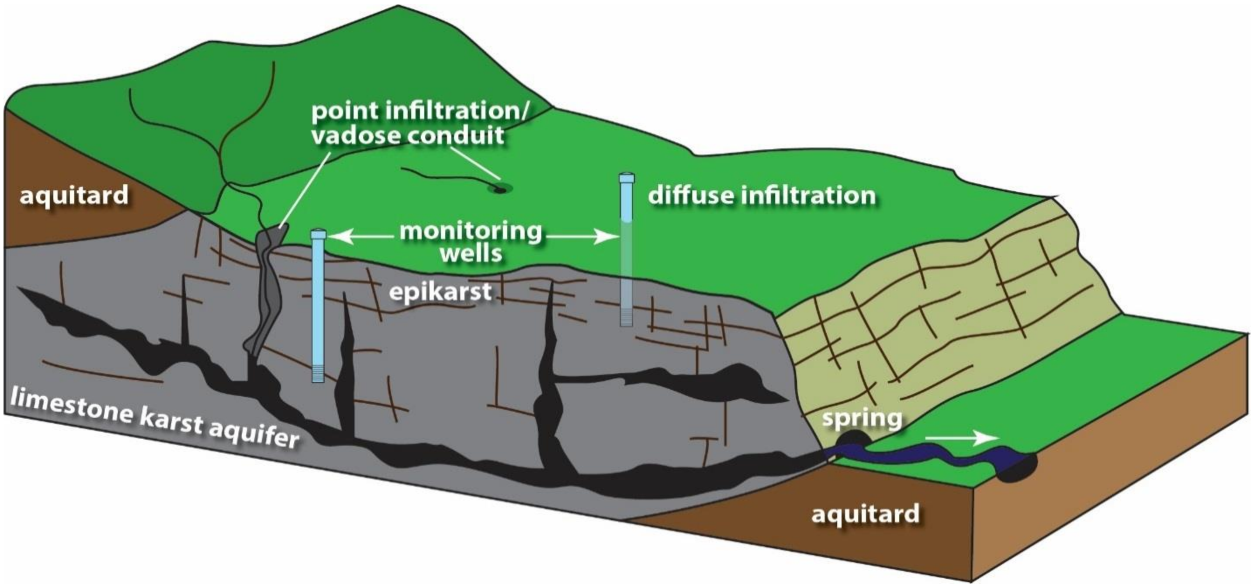
iii) Karst Terrane

Carbonate rock such as limestone and dolomite is susceptible to the formation of sinkholes, solution channels, and caverns. In Pennsylvania, almost all carbonate rock will exhibit some degree of karst development. Resulting flow patterns can be very complicated; flow depends on the degree of interconnection of the joints, fractures, and solution openings (small and large), the hydraulic gradient, and geologic barriers. The resulting anisotropic setting can make it difficult to effectively monitor and model a site in a karst area. Even a relatively small cavernous opening with its connecting drainage paths can control a significant amount of the flow from an area, and may perhaps effectively carry all the groundwater that discharges from underneath a site. In addition, karst geology has the potential to rapidly transmit groundwater over a large distance.

Groundwater flow in a karst terrane can be highly affected by precipitation events, and groundwater divides can be transient. To determine monitoring locations in limestone and dolomite areas, the remediator should investigate the degree to which the rocks are susceptible to dissolution. The more dissolution features that are recognized, the more likely that conduit flow will occur. Dissolution features may be identified through site visits, aerial photographs, geologic well logs, and geophysical techniques.

Thus, it would seem logical that monitoring locations should be based on major conduits of flow. However, Figure A-7 shows how a monitoring well can easily miss a primary conduit. It may be futile to attempt to establish the locations of such flow zones because they probably represent only a small fraction of a site. However, several procedures can be used to increase the odds of monitoring the site of concern. (Note that many of the procedures discussed here also can be used in other types of fractured rocks.)

Figure A-7: Ineffective Monitoring Wells in a Carbonate Aquifer



<u>Tracer tests</u> - Tracer tests offer the best possibility of determining where groundwater is flowing and discharging. They are conducted to establish a hydraulic connection between a downgradient monitoring point and the facility of concern. Tracer tests should be combined with a thorough inspection for the presence of local and regional springs, surface streams, and dry stream channels that could serve as discharge points for groundwater at the site. It also could be possible that groundwater beneath a site could discharge to several features, or that the flow directions could be different during flood or high groundwater stages. A determination of the point of regional base flow should also be made and possibly included as a monitoring point when possible.

It is important to understand the potential chemical and physical behavior of the tracer in groundwater. The objective is to use a tracer that travels with the same velocity and direction as the water and does not interact with solid material. It should be easily detected and be present in concentrations well above natural background quality. The tracer should not modify the hydraulic conductivity or other properties of the medium being studied. Investigations using tracers should have the approval of local authorities and the Department, and local citizens should be informed of the tracer injections.

Various types of tracers are used including water temperature, solid particles, ions, organic acids, and dyes. Fluorescent dyes are the most common type of tracer used in karst areas. These dyes are used because they are readily available, are generally the most practical and convenient tracers, and they can be adsorbed onto activated coconut charcoal or unbleached cotton. Fluorescent dyes can be detected at concentrations ranging from one to three orders of magnitude less than those required for visual detection of non-fluorescent dyes. This helps to prevent the aesthetically unpleasant result of discoloring a private or public water supply.

Fluorescein (CI Acid Yellow 73 - $C_{20}H_{10}O_5Na_2$) is one of the most widely used water-tracers in karst terrane studies because of its safety, availability, and ready adsorption onto activated coconut charcoal. It is a reddish-brown powder that turns vivid yellow-green in water, is photochemically unstable, and loses fluorescence in water with pH less than 5.5.

Rhodamine WT is another commonly used dye tracer. Rhodamine WT is a conservative dye and generally efficient tracer because it is water soluble, highly detectable (strongly fluorescent), fluorescent in a part of the spectrum not common to materials generally found in water, thereby reducing the problem of background fluorescence, harmless in low concentrations, inexpensive, and reasonably stable in a normal water environment (U.S. EPA 2013).

The toxicity of the dyes should also be considered, especially when there is a chance of private or public water supplies being affected. Smart (1984) presents a review of the toxicity of 12 fluorescent dyes. Other excellent references include U.S. EPA and the USGS (1988) and Davis and others (1985).

The mapping of outcrops and associated joints and faults can distinguish directional trends that groundwater might follow. Fracture trace analysis using aerial photographs can detect local and regional trends in fractures, closed depressions, sinkholes, stream alignments, and discharge areas. However, tracer tests are still recommended to verify where groundwater is flowing.

Additional site investigation techniques may be helpful in determining flow paths. Geophysical methods such as self-potential (a surface electromagnetic method) and ground penetrating radar can enhance the understanding of karst systems.

Effort should be made to monitor at or near the site of concern rather than depend on springs that discharge away from the site. Wells sited on fracture traces or other structural trends can be tested with tracers to see if they intercept groundwater flowing from the site. A monitoring network should not be solely dependent on water levels to establish the locations of monitoring wells in such fractured rock settings. These uncertainties and the potential traveling distances may cause monitoring in karst areas to be involved and expensive.

For more information regarding tracer tests, please refer to the USGS website on tracer studies.

iv) Deep-Mined Areas

When designing a groundwater monitoring program for a site in which coal or noncoal deep mining has occurred, it is important to consider the effect of the underlying mine on the hydrologic system.

Because of the mine workings and the associated subsidence fractures, the deep mine often acts as a large drain for the overlying water-bearing zones. Groundwater monitoring of this zone may be considered on a case-by-case basis.

Saturated zones within deep mines may be characterized as a mine pool, which is a body of water at a relatively stable elevation, or it may be a pathway for channelized water. Because of these special problems, a drilling plan should be devised that includes provisions for drilling through the coal pillar, mine void or collapsed structures. Several attempts should be made at each well location to intercept the pool, saturated zone and/or mine void.

Well construction requires the placement of a grout basket or plug attached to the riser pipe that is placed above the zone to be monitored. This helps to seal the bentonite grout.

b) Contaminant Distribution

In addition to normal groundwater flow (advection), the distribution of contamination is critical to the correct placement of monitoring points. This distribution is based on 1) the chemical and physical characteristics of groundwater and contaminants present that affect the migration of the monitored contaminant, and 2) its occurrence or source at the site. For example, the density of a contaminant is one of the most important factors in its distribution in the aquifer, and especially for determining the depth of a target zone (see Section C.5 of this appendix). Petroleum hydrocarbons tend to remain in shallow groundwater. Chlorinated VOCs tend to migrate deeper into the aquifer, sometimes following structural features that may be contrary to groundwater flow direction. These factors are extremely important to consider when designing a groundwater monitoring network.

Isoconcentration maps can be useful in plume interpretation and for placement of groundwater recovery wells. Also, the remediator should keep in mind the relationship of the flow lines with the activity’s location or potential sources of contamination.

4. Areal Placement of Wells

For establishing the target zones, the remediator should consider the topics of groundwater movement and contaminant distribution that were discussed above. For the initial placement of wells at a site where little information is available, the downgradient well positions are typically assumed to be downslope. In apparent flat-lying sites, drainage patterns can be used to estimate the flow direction. The site boundary that is closest to a body of water is a likely choice for downgradient well locations. An upgradient well is typically placed upslope.

As more information is obtained about the site, groundwater gradients will be more accurately defined. Upgradient and downgradient monitoring points may need to be added or moved. However, even well-defined groundwater flow direction maps should be evaluated carefully when choosing the target zones for upgradient and downgradient wells. Because of structural controls in fracture flow described in Section C.3.a, groundwater can move obliquely to the regional gradient. Some monitoring points may need to be moved as target zones are refined.

In general, when comparing sites, intervals between monitoring wells probably should be closer for a site that has one or more of the following:

- a small area
- complicated geology such as folding, faulting, closely spaced fractures, or solution channels
- heterogeneous lithology and hydraulic conductivities
- steep or variable hydraulic gradient
- high seepage velocity
- had liquid contaminants
- tanks, buried pipes, trenches, etc.
- low dispersivity potential

Sites without these features may have well interval distances that are greater. See also Section C.6 on the number of wells.

Reconnaissance tools and screening techniques such as surface geophysical techniques and soil gas studies can help to locate plumes before wells are drilled and thus help to determine optimal well locations. Methods for selecting sample locations range from random yet logical picks to probability sampling (such as a grid pattern). Random sampling is very inefficient. When selecting many monitoring points in an area where little is known, such monitoring points should be placed in a grid or herringbone pattern.

5. Well Depths, Screen Lengths, and Open Intervals

The first zone of saturation is typically an unconfined or water-table aquifer, which is recharged from direct infiltration of precipitation. Impacts to the aquifer under unconfined conditions are more easily evaluated than under confined or semi-confined conditions. The shallowest aquifer should be the target zone for chemicals and substances that are less dense than water.

Sites with confined aquifers that have the potential to be impacted will need to be evaluated in combination with the unconfined aquifer. Such a situation would require more detailed vertical and discrete zone monitoring.

Once the subsurface geometry of the monitoring target zone is determined, decisions can be made with respect to the depth and screen lengths of individual wells that will be used. Groundwater monitoring networks should monitor the entire saturated thickness of the target zone, or a very large percentage of it. If large vertical intervals of the target zone are unmonitored, chances are dramatically increased that groundwater contamination may go undetected or be underestimated if detected.

Choosing the length of the open interval in a monitoring well is in many respects a balancing act. Shorter open intervals or screen lengths provide better accuracy in determining hydraulic head at a specific point in the flow system. If a sufficient number of shorter well screens or open intervals are stacked or clustered vertically so that the entire saturated thickness of the target zone is adequately monitored, they will, when taken together, provide better resolution of the vertical distribution of any contamination that may be detected. In addition, the possibility of cross-contamination is minimized. Disadvantages of shorter intervals include reduced water volume from each well and the increased cost of installing, sampling, analyzing, and interpreting the data from the more numerous sampling points, which can be considerable.

Some disadvantages also are likely for longer screen lengths or open intervals. Resolution of hydraulic head distribution in the aquifer decreases, contamination entering the well at a specific point may be diluted by other less contaminated water, and there is less certainty regarding where water is entering the well.

It would be preferable from a strictly technical point of view to monitor the entire saturated thickness of any target zone with a number of individual, shorter-screened wells drilled to different depths that, together, monitor the entire target zone. However, the remediator/hydrogeologist designing the project must decide if the increased cost over single, longer-screened wells is justified for background and compliance monitoring. The goal is to establish screens and open intervals that will detect any contamination emanating from any portion of the site as quickly as possible. A Pennsylvania-licensed professional geologist should make all decisions related to the construction of monitoring wells at Act 2 sites.

Care should be taken when monitoring target zones in bedrock formations. In this case, by geologic necessity, the portion of the target zone which is monitored will be determined by the location and number of water-producing fractures that are intercepted by the well. Care must be taken not to drill wells too deeply below the target zone in search of a water-producing fracture.

Where multiple aquifers exist, such as an unconsolidated aquifer overlying a bedrock aquifer, or where two permeable aquifers are separated by a confining layer, the target zones within each aquifer should be monitored separately.

The specific gravity of a contaminant and whether it will most likely be introduced to the environment as a free phase or in a dissolved phase also will influence how a well is constructed. In conducting monitoring for an LNAPL or a petroleum-based dissolved contaminant, such as gasoline, wells should be constructed with screens, or open intervals, that intercept the water table surface at all times of the year during periods of both high and low water table elevations. LNAPL can then accumulate into a distinct layer and flow into the monitoring well. For materials that exhibit specific gravities greater than water (such as many chlorinated solvents), it is desirable, though not always possible, to locate subsurface boundaries on which such contaminants might accumulate if released to the environment in a free phase.

6. Number of Wells

The number of wells needed depends on site-specific factors. In general, the spacing of background or upgradient wells should be adequate to account for any spatial variability in the groundwater quality. Downgradient wells should be positioned to adequately monitor the activity and any other variability of the groundwater quality. Compliance wells should be considered downgradient wells and positioned as close to the downgradient boundary of the site. The estimate of the separation distance will depend on the extent and type of activity, the geology, and the potential contaminants (see also Section C.4 on the Areal Placement of Wells).

7. Well Yield

Monitoring wells should produce yields that are representative of the formation in which they are drilled. Wells located in anomalously low-yielding zones are undesirable for several reasons. First, flow lines tend to flow around low-permeability areas rather than through them. In effect, this results in potential contaminants bypassing low-permeability areas, consequently not being detected in representative concentrations. In addition, by the time a potential contaminant shows up in a very low-yielding well that is unrepresentative of the formation, other potential contamination may have traveled extensively downgradient beyond the monitoring well. Therefore, in settings where well yields are variable, the best monitoring wells will be those that are open to the highest permeability flow lines that are potentially more likely to be contaminated by the site.

The best information regarding representative yield for the target zones selected for any site should come from the wells and borings used in the investigation to characterize the groundwater flow system for the site. Borehole geophysics can be a valuable tool for determining the location of higher-yielding zones and the presence of contaminants. For more detailed descriptions of borehole geophysical techniques and devices, see EPA (1993) Chapter 3 - Geophysical Logging of Boreholes, and Nielsen (1991). Additional regional hydrogeologic information may be obtained from:

- The Pennsylvania Bureau of Topographic and Geologic Survey (BTGS)

- The United States Geological Survey (USGS)

Water Resource Reports have been published by the USGS and BTGS for select counties and areas in Pennsylvania. Many of these reports are available electronically on their respective websites.

In Pennsylvania, there are three general hydrogeologic settings that merit special discussion from a well-yield perspective.

a) Fractured Rock

In aquifers composed of fractured bedrock, groundwater flow is generally restricted primarily to the fractures. If a well fails to intersect any fractures or a very few small fractures in this setting, the well will not detect potential contamination, or it will be inefficient in detecting potential contamination. For this reason, wells that fail to intersect fractures in the target zone that are representative of the formation should be approved with caution, and wells that are essentially dry are not acceptable. Such wells should be relocated nearby and another attempt made to obtain a better yield when it is determined that it is likely that more representative yields can be obtained. Likewise, wells drilled below the proper target zone, strictly to increase yield, are not reliable for site characterization purposes.

b) Heterogeneous Unconsolidated Formations

Low permeability, clay-rich formations with interbedded or lenticular, higher permeability sand or gravel units can present a significant challenge to designers and installers of monitoring wells. Wells need to be located so that they are open to any high permeability zones within the target zone that are hydraulically connected to the site being monitored. These wells will produce a higher yield than wells drilled exclusively into the clay-rich portions of the site.

c) Areas of Uniformly Low Yield

Certain geologic formations and hydrogeologic settings are characterized by exhibiting naturally low yield over a wide area. Other geologic formations may exhibit low yield locally in certain settings such as ridge tops, steeply dipping strata, or slopes. In these settings, a permanent or seasonal perched water table or shallow flow system may develop on the relatively impermeable bedrock that may or may not be hydraulically connected to the bedrock system. Depending on the permeability of the soils and unconsolidated material overlying the solid, less permeable bedrock, the shallow groundwater flow can express itself as a rather rapid “subsurface storm flow” or a more sluggish, longer-lasting condition in poorly drained soils.

It is important to be sure that the shallow systems are part of the target zone of the site being monitored. In these cases, the shallow system may constitute the most sensitive target zone for monitoring a facility. While wells drilled into the bedrock system may be needed to monitor for vertical flow of contaminants, the importance of sampling monitoring wells or springs in the shallow intermittent flow system should not be underestimated, although the usual periodic monitoring schedules may not always be necessary in these settings. If the systems are intermittent, one must be aware of when they are active (e.g. in Spring or after significant or extended precipitation events) and be prepared to monitor the systems at that time. Monitoring can be conducted in wells, springs that are properly developed, or in some cases, by sampling man-made underdrain systems that are constructed to collect the shallow flow system in some cases.

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D. Groundwater Sampling Techniques

1. Importance of Sampling Technique

Proper sampling procedures which result in a representative measure of groundwater quality are critical to any monitoring program. The accuracy of the sample analysis in the laboratory is dependent upon the sampling methodology in the field. A laboratory cannot generate reliable data if the sample was collected improperly. Therefore, taking precautions and selecting the correct sampling methods are imperative to produce accurate and representative analyses.

Some of the reasons groundwater samples may not be representative of aquifer conditions include the following:

- The sample was taken from stagnant water in the well. Water standing in a well and exposed to the atmosphere may undergo a gas exchange (oxygen and carbon dioxide), allowing chemical reactions to occur. Biological organisms capable of driving reactions might also be introduced. Obviously, such altered waters will no longer be representative of the water within the aquifer and therefore should be purged prior to sample collection.

- The sample was not collected at the appropriate time. The sample should be collected as soon as possible after purging is completed. This reduces the possibility of chemical reactions occurring because of gas exchange and temperature variations. In addition, if the well is pumped too long, the sample may be comprised of water far from the well site and not be representative of groundwater chemistry for the site being monitored.

- The sample contained suspended or settleable solids. Groundwater is generally free of suspended solids because of the natural filtering action and slow velocity of most aquifers. However, even properly constructed monitoring wells will often fail to produce samples that are free of sediment or settleable solids (turbidity). When samples containing suspended solids are analyzed for metals, this sediment is digested (dissolved) in the laboratory prior to performing the analysis. Consequently, any of the metals present in the sediment (primarily iron, manganese, and aluminum) will be included in the results of the analysis of the water that includes these metals. The analysis of the water samples containing sediment will result in certain analytes, such as these metals, being reported at higher levels than the actual levels in groundwater.

In addition to common metals, other metals such as lead, chromium, arsenic, and cadmium, which occur naturally in trace amounts may also show up in the analysis. Additionally, the sediment content of the monitoring wells will often vary across a site, so that samples collected from the same well at different times can vary in sediment content. This problem can make analysis of monitoring well data for metals where samples have not been filtered to remove turbidity an almost futile exercise.

- Release of carbon dioxide during pumping increased the pH, allowing many metallic ions to come out of solution (i.e. iron, manganese, magnesium, cadmium, arsenic, selenium, and boron). Pumping can also cause volatilization of VOCs. This emphasizes the importance of conducting field measurements such as pH, specific conductance, temperature, etc., within the well before the sample is brought to the surface.

- Chemical changes occurred from oxidation of the sample during sampling. Dissolved oxygen is usually very limited within aquifers. Bringing the sample to the surface allows oxygen to dissolve within the water sample. Oxidation also can occur in the pump, or it can be caused by water cascading into a well installed in “tight” formations. Depending on the chemical makeup of the sample, the addition of dissolved oxygen may allow chemical reactions to occur. Some of the changes that can be expected include oxidation of: 1) organics, 2) sulfide to sulfate, 3) ferrous iron and precipitation of ferric hydroxide, 4) ammonium ion to nitrate, and 5) manganese and precipitation of manganese dioxide or similar hydrous oxide. In cases where oxidation would be expected to impact chemical quality, precautions should be employed to reduce oxidation potential (e.g. minimize agitation during purging and sample collection, minimize the length of time the sample is exposed to air, fill the sample container completely to the top, and promptly chill the sample).

- The sample was not preserved correctly. Increases in temperature will allow certain chemical reactions to occur. Certain metals, especially iron, may coat the inside of the sample container. If the sample is not properly preserved for shipment to the laboratory, the sample arriving at the lab may be quite different chemically from the sample which was collected in the field.

- The sample was contaminated by residues in sampling equipment. Residues may cling to the sampling equipment if it is not properly cleaned or decontaminated. Those residues may become mobile in successive samples, yielding unreliable results. This becomes critical when the analytes being sampled are in the parts per billion or parts per trillion range. As a result, all sample pumps, tubing, and other associated materials should be properly decontaminated prior to sampling at each monitoring well location.

- The sample was contaminated by the mishandling of bottleware. Care should be taken to avoid contamination by mishandling bottleware, whether in the field or during transport. All sample bottleware and coolers should be stored and transported in clean environments to avoid potential contamination. In addition, care should be taken when storing and transporting bottleware that already contains a preservative. For example, the preservative may leak from a sample bottle or be altered by extreme heat or cold.

- The sample was contaminated by residuals on the hands of the sampler. To avoid contamination that may result from bare skin, protective sampling gloves should be worn during sample collection. New gloves should be worn for each well location.

DEP recommends utilizing a consistent sampling methodology throughout the monitoring program.

2. Sample Collection Devices

The most common devices available for the collection of water from monitoring wells include bailers, suction-lift pumps, air-lift samplers, bladder pumps, submersible centrifugal pumps, and passive samplers. Each has its advantages and disadvantages, as shown in Table A-1, and should be considered before selecting the sample collection device.

3. Sample Collection Procedures

The following are general procedures that should serve as a framework for sampling groundwater. These procedures should be modified as necessary for each situation encountered in the field and to conform to monitoring objectives. In addition, appropriate health and safety measures should always be taken before, during, and after sampling.

a) Protective Clothing

Protective clothing should be worn as dictated by the nature of the contaminants. Different types of protective clothing are appropriate for different contaminants. Protective sampling gloves should always be worn during sample collection to ensure a representative sample and to protect the sampler.

b) Water Levels

Every effort should be made to determine and record the static water level of the well prior to purging. Static water levels should be recorded in each well prior to any well purging when part or all of a groundwater monitoring network is sampled in one event. Water level measurements should also be measured and recorded during well purging to document associated drawdown.

c) Field Measurements

In most cases, field measurements should be taken before and during the sampling to gauge the purging of the well and to measure any changes between the time the sample is collected compared to when it is analyzed in the laboratory. Measurements in the field also provide a record of actual, onsite conditions that may be useful for data analysis. The following measurements and observations are often determined in the field:

- pH
- Eh
- water level (static and purged)
- temperature

- specific conductance
- dissolved oxygen
- acidity/turbidity
- climatic conditions

The specific techniques for obtaining each of these measurements depend upon the instruments used. The operator should carefully read and follow the manufacturer's instructions, including those for equipment maintenance and calibration. A record of the calibration and maintenance checks should be kept. Field measurements should always be made with properly calibrated instrumentation.

d) Purging

The purpose of purging a well prior to sampling is to remove stagnant water from the well bore and assure that the sample is representative of the groundwater in the geologic formation. Stagnant water in the well bore results from the water's contact with the casing and atmosphere between sampling events. What might seem to be a relatively simple and straightforward procedure, purging technique has been the subject of considerable scientific investigation and discussion.

There are two basic approaches to purging a well. The first is to use dedicated equipment in which the water is pumped from a fixed position in the well. This technique eliminates the possibility of cross-contamination, but tends to purge only the well section, or screen section opposite of the purge pump. (This is especially a concern when purge rates are much lower than the yield of the water-bearing zone supplying water to the purge pump.)

The second basic approach is to use a transportable pump and purge from the water surface, or preferably by gradually lowering the pump in the well as stagnant water is evacuated. This technique is considered as being more reliable in terms of evacuating the entire well bore. However, the disadvantage is that the equipment must be decontaminated between wells, which in turn increases the potential for cross-contamination.

It is important to recognize the impact of equipment location in relation to the well and other sampling equipment. Often purging and sampling equipment require the use of generators to power pumps and other equipment. The engines of vehicles and generators produce exhausts which contain VOCs as well as various metals and particulates. If engines or generators need to be operating while sampling, they should be located upwind from the well and sampling equipment since water contacting these exhausts has been shown to contaminate samples with various compounds.

Table A-1: Advantages and Disadvantages of Different Sampling Devices

	ADVANTAGES	DISADVANTAGES
Bailer	Portable Simple to use No need for an electrical source	Difficult to ascertain where within the water column the sample is collected Allows for oxidation of the sample Disturbance of the water column by the sampler Impractical for removing large volumes of water
Suction-lift Pump	Allows sample to contact only Teflon (less decontamination) Very portable Simple to use for shallow applications Flow rates easily controllable	Limited to shallow groundwater conditions (approximately 30 feet) Causes sample mixing, oxidation, and allows for degassing Not ideal for collection of gas-sensitive parameters
Air-lift Sampler	Suited for small diameter wells	Causes extreme agitation Significant redox, pH, and specie transformations Plastic tubing source of potential contamination
Bladder Pump	Provide a reliable means for highly representative sample Mixing and degassing minimized Portable Noted by EPA as an excellent sampling device for inorganic and organic constituents	Somewhat more complex than other samplers Turbid water may damage the inner bladder Water with high suspended solids may damage check valves

	ADVANTAGES	DISADVANTAGES
Submersible Centrifugal Pump	Higher extraction rates	Considerable agitation and turbulent flow Potential to introduce trace metals from the pump materials
Passive Samplers	Low cost Easily deployed Minimal purging and water disposal Able to monitor a variety of analytes	Some devices are incompatible with certain analytes. May have sample volume limitations. Results may differ from conventional methods.

An excellent summary of purging methods and techniques is given by Herzog et al. (in Nielsen, 1991). The following discussion is based in part on that summary. Four techniques for determining the volume of water to be purged from a well are discussed. These techniques include criteria based on:

- Numbers of well bore volumes
- Stabilization of indicator parameters
- Hydraulic and chemical parameters
- Special problems with low-yielding wells

By far, the most common choices have been to base the purging volume on either a certain number of well volumes, or stabilization of chemical and physical parameters, or some combination of these two.

An alternative approach, also described below, eliminates purging the well altogether by using passive sampling devices.

i) Criteria Based on the Number of Bore Volumes

The purging of three well volumes was universally accepted at one time and ingrained in monitoring practice. However, Herzog et al., provides references from numerous studies which conclude that anywhere from less than one to more than 20 bore volumes might variously be purged from wells prior to being acceptable for sampling. Herzog, et al. conclude:

"It is obvious that it is not possible to recommend that a specific number of bore volumes be removed from monitoring wells during purging. The range of suggested volumes is too large and the cost of improper purging is too great to permit such a recommendation.”

DEP recommends that if the borehole volume technique is going to be used, the number of borehole volumes required for each well should have a technical or scientific basis, such as stabilization of indicator parameters (see following section) conducted at least once for each well during initial sampling events, rather than being based on some arbitrary criterion such as “three well volumes.”

When purging is based on some set number of borehole volumes, the borehole volume calculation should take into account the entire original borehole diameter, corrected for the porosity of any sand or filter pack, and not be based just on the innermost casing diameter.

ii) Criteria Based on Stabilization of Indicator Parameters

Stagnant water in a well bore differs from formation water with respect to many parameters. Field measurement of indicator parameters such as temperature, pH, specific conductance, dissolved oxygen, and Eh has been used as the criteria for determining the amount of water to purge and when to sample a well. These parameters are measured in the purge water during purging until they reasonably stabilize. DEP encourages the use of this method.

DEP recommends that all of the above indicators be measured during the initial and first few sampling events for the monitoring well. The data should then be reviewed to determine which indicator parameters are the most sensitive indicator that stagnant water has been evacuated from the well. The most sensitive parameters will be those showing the greatest changes and longest times to achieve stabilization. During the initial sampling, the purging time should be extended beyond what initially appears to be stabilization as a check to ensure that the parameter stability is maintained.

iii) Low Flow Purging

Another purge method using the stabilization of indicator parameters is low-flow (minimal drawdown) well purging. This technique is based upon placing the pump intake at the screened interval, or in the case of fractured rock, the water-bearing zone of interest. The well is pumped at a very low rate, commonly less than 0.5 liters per minute, while producing less than 0.1 meters of drawdown. Pumping continues until various indicator parameters stabilize. The objective is to produce minimal drawdown and less stress upon the aquifer while obtaining a sample from the aquifer interval of interest. Lack of definitive well construction or water-producing interval information negates the use of this purge method.

Low-flow purging often creates much less purge water. Some purge water contains various substances which cannot be disposed of on the ground necessitating disposal. In these cases, low-flow purging can greatly reduce the costs of disposal. In addition, purge time is often substantially less. Set-up is usually more complex, and costs may therefore be higher than when using other purge methods.

Indicator parameters typically include temperature, pH, redox potential, conductivity, dissolved oxygen (DO), and turbidity. These common stabilization parameters are often used to indicate that the water coming from the pumped interval is aquifer water. Although often not very sensitive to changes between borehole and aquifer water, temperature and pH are usually included because they are easy to measure, and the data is commonly used for other field analysis reasons. The minimum number of parameters to measure should include pH, conductivity, and dissolved oxygen. Stabilization is indicated after three successive readings taken at 3- to 5-minute intervals. Indicator parameters should show a change of less than ± 0.1 for pH, ± 3% for conductivity, ± 10% mv for redox potential, and ± 10% for turbidity and dissolved oxygen. The stabilization rates put forth are a guideline. Experience may dictate the need for more or less tolerance in particular wells or situations.

If a well has a history of water quality data produced using a different well purging method, the result should be compared with the new low-flow purge results. Significant variation in data will require justification of continued use of the low-flow purge method. Depending upon the situation, purge methods may need to return to the original method.

iv) Special Problems of Low-Yielding Wells

Low-yield wells present a special problem for the sampler in that they may take hours, or even days, to recover after purging so that there is enough water to sample. This waiting period not only increases the cost of sampling, but also allows changes in water quality to occur between the time the sample water enters the casing and the time it is collected. This is especially problematic when sampling volatile constituents.

In practice, very low-yield wells are commonly pumped dry and sampled the following day if necessary. This practice is believed to result in water being sampled that is not representative of the aquifer being sampled from the well due to the loss of volatiles and oxygenation of the water during the waiting period. This results from pumping the well dry and exposing the formation to the atmosphere. While there does not appear to be any method uniformly agreed upon to eliminate these concerns, the following considerations are suggested:

- Purge in such a way that the water level does not fall below the well screen.

- Evaluate the use of larger diameter wells that may deliver the required amount of sample water more quickly than small diameter wells.

- If full recovery cannot be achieved within two hours, collect the required amount of water as it becomes available, collecting samples for parameters in order of decreasing volatility.

v) No-Purge Methods

Passive samplers offer an alternative to traditional purge methods. Commonly used technologies include polyethylene (or passive) diffusion bags (PDBs) and HydraSleeves^{TM}. Some sampler types operate through diffusion of contaminants into the device; others collect a discrete grab sample. A key advantage of passive samplers is that no purge water is generated that requires treatment or disposal. Other advantages include reduction of field sampling time and potentially less variability in sample results. It should be noted that passive sampling methods that detect only the presence or absence of contaminants may be utilized for characterization, but are not recommended for attainment sampling. Additionally, if the screening investigation indicates that regulated substances are present, and if the aquifer recharge rate is reasonable, conventional grab sampling should be performed to obtain quantitative data on contaminant concentrations as part of a complete characterization effort.

Some important limitations should be evaluated when considering the use of passive samplers. The well construction, hydraulic properties of the aquifer, and contaminant type and distribution should be known and discussed with DEP prior to engaging in a full-scale sampling program (see the references for further information).

- No-purge sampling methods rely on adequate groundwater flow through the well screen. If the seepage velocity is low or the screen is fouled, then the exchange rate of water in the well could be slow, the water may be stagnant, and the sample may not be representative of groundwater in the formation.

- Some devices are incompatible with certain analytes. For example, most VOCs readily diffuse through polyethylene, but some (such as MTBE) do not. Polyethylene diffusion bags cannot be used to sample semi-volatile organic compounds (SVOCs) or inorganics.

- Because passive samplers collect from a discrete interval, results may be sensitive to the depth at which the device is placed. If flow is stratified in the formation or localized at bedrock fractures, or if the contaminant is density-stratified in the water column, then deployment depth is important. Some sampler types allow multiple devices to be arrayed vertically on a tether, allowing the remediator to better determine an optimal depth.

Passive samplers will not necessarily produce results equivalent to purge methods. Ideally, a consistent purge and sampling methodology will be used for all wells in the site network from the beginning of characterization until the end of attainment. If a change in the sampling method is being proposed midway through a monitoring program, then sufficient side-by-side testing with the current approach should be performed and discussed with DEP to determine if the change in method is appropriate.

vi) Summary on Purging

The following general statements can be made with respect to purging:

- Every groundwater monitoring plan should contain a section discussing how wells will be purged.
- It is often desirable to use the same device for sampling that was used for purging. In this case the purge pump can be set within the screened section of the well or across from the yielding zone being monitored.
- If different devices are used for purging and sampling, purging should begin at the static water surface and the device should be lowered down the well at a rate proportional to water stored in the well bore. Because of the better mixing of water in wells with multiple yielding zones, this technique is considered preferable for sampling wells with multiple yielding zones where a composite sample of water in the yielding zones is desired (see Section C.5 on Well Depths, Screen Lengths, and Open Intervals).
- Where the same device is used to sample and purge a well, it should be established that the sampling device will not change the quality of the groundwater it contacts.
- In sampling for some analytes, such as volatile organics, it is critical that the discharge be reduced to approximately 100 ml/minute to minimize degassing and aeration (Barcelona et al., 1984). Flow control should be achieved by means of an electric current using a rheostat rather than by valving or other flow restrictors.
- Purging should be completed without lowering the water level in the well below the well screen or water-bearing zone being sampled.

Never purge a well at a rate or in a way that causes water to cascade into the well bore, resulting in increased degassing and volatilization.

e) Management of Purge Water

The first step in the management of monitoring well purge water is to minimize its generation. Consideration should be given to techniques that minimize the amount of purge water produced, such as low-flow or low-volume purging, or a no-purge method. Purge water should be handled in a way that is environmentally compatible with the volume generated, the type and concentration of confirmed or suspected contaminants, and the specific site conditions. A procedure that can be used is outlined in Table A-2. The procedure is designed to ensure that potentially contaminated purge water is disposed properly without contaminating other environmental media.

The following items should be considered when handling purge water:

- Purge water should be containerized until it is characterized by laboratory analysis. Containers with purge water comingled from multiple wells should use the highest concentration seen in any one of the wells from which the comingled purge water was produced, unless the comingled purge water is sampled.

- Purge water that has been characterized with no detections (i.e., with analytical results less than method detection limits (MDLs)) may be handled as uncontaminated groundwater under Table A-2.

- Purge water that has been characterized with detections of constituents that do not exceed the Act 2 Residential, Used Aquifer Groundwater MSCs may utilize any of the actions described in the contaminated groundwater section of Table A-2. Discharging to the ground surface to return water to the impacted groundwater plume (re-infiltration) under action (d) is an option if it does not create runoff. Discharge to a surface water, wetland, storm drain or paved surface that drains to a channel or stormwater conveyance requires a permit or other appropriate regulatory authorization.

- Purge water that has been characterized with detections of constituents that exceed the residential used aquifer MSCs should be managed as contaminated groundwater utilizing one of the actions described in (a), (b), (d), or (e) of Table A-2. If action (e) is utilized, one of the approved methods is as follows (for organic constituents only):

    – Place up to 20 gallons/well of contaminated purge water onto the ground surface of the site in a controlled manner for re-infiltration after treatment with portable engineered carbon adsorption units designed and operated to remove the organic contaminants to levels below residential used aquifer MSCs according to the following:

- Re-infiltration may only occur within the area of groundwater contamination exceeding Act 2 residential, used aquifer MSCs;

- Placement on site should not create runoff that will enter surface water, wetlands, storm drains or other water conveyances to surface water;

- All contaminants should be capable of being treated by carbon adsorption;

- Carbon adsorption units should be designed to provide contact time for the amount of carbon at the expected levels of raw water contamination to reach residential used aquifer MSCs;

- A sample should be collected to demonstrate the unit has functioned as intended. Samples should be collected at the beginning and end of the filtration cycle; and

- Purge water should contain no free product.

f) Private Wells

If a well is a private water supply, sample as close to the well as physically practical and prior to any treatment or filtering devices if possible and practical. If sample collection must be from a holding tank, allow water to flow long enough to flush the tank and the lines; when the pump in the well is triggered and turned on, verification of tank flushing is provided. If a sample that passes through a treatment tank must be taken, the type, size, and purpose of the unit should be noted on the sample data sheet and in the field log book.

g) Filtering

When possible, avoid collecting samples which are turbid, colored, cloudy or contain significant suspended matter. Exceptions to this include when the sample site has been pumped and flushed or has been naturally flowing for a sufficient time to confirm that these conditions are representative of the aquifer conditions.

Unless analysis of unfiltered samples for “total metals” is specifically required by program regulation or guidance, all samples for metals analysis should be field-filtered through a 0.45-micron filter prior to analysis. Filtering samples for SVOC analysis is not appropriate to be conducted in the field as SVOCs have been known to adhere to certain materials used during the filtration process.

Table A-2: Procedure for the Management of Well Purge Water from Groundwater Sampling

TYPE OF GROUNDWATER	ACTION
Purge Water – Shown to not exceed the Act 2 residential, used aquifer groundwater standards contained in Tables A-1 and A-2 of 25 Pa. Code Chapter 250.	Purge water may be placed on the ground surface (onsite) provided precautions are in place to avoid erosion or runoff. Discharge to a surface water, wetland, storm drain or paved surface is prohibited without a permit or other appropriate regulatory authorization.
Purge Water – Shown to exceed the Act 2 residential, used aquifer groundwater standards contained in Tables A-1 and A-2 of 25 Pa. Code Chapter 250.	Management of purge water may proceed with one of the following options: a) Convey directly into an on-site treatment plant or leachate collection system for final treatment. b) Transport to off-site treatment facility. c) Place in a temporary storage unit onsite for analysis to determine the final disposition. d) De minimis quantities may be treated and placed on the ground surface onsite provided the type and concentration of contamination(s) will not adversely impact surface water or wetlands, or further contaminate soil or groundwater. The treatment unit must be rated to remove the identified contaminants and must be operated and maintained to ensure contaminant removal to Act 2 residential used aquifer standards. e) Other methods approved by DEP (may require a permit for specific site conditions).
Purge Water where water quality is not determined	Purge water that is not characterized needs to be containerized until laboratory analysis is complete. Containers with purge water comingled from multiple wells should use the highest concentration seen in any one of the wells from which the comingled purge water was produced, unless the comingled purge water is sampled. Following analysis of purge water, it may be treated as one of the two categories above.

h) Sample Preservation

Perform sample preservation techniques onsite as soon as possible after the sample is collected. Complete preservation of samples is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. For this reason, samples should be analyzed as soon as possible. However, chemical and biological changes occurring in the sample may be slowed significantly by proper preservation techniques.

Chemical changes generally happen because of a shift in the physical conditions of the sample. Under a fluctuation in reducing or oxidizing conditions, the valence number of the cations or anions may change; other analytes may volatilize or dissolve; metal cations may form complexes or precipitate as hydroxides, or they may adsorb onto surfaces.

Biological changes can also alter the valence of a constituent. Organic processes may bind soluble material into the cell structure, or cell material may be released into solution.

Methods of preservation are relatively limited and are generally intended to: 1) retard biological activity, 2) retard hydrolysis of chemical compounds and complexes, 3) reduce the volatility of constituents, and 4) reduce sorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, freezing, and selecting the type of material used to contain the sample.

The best overall preservation technique is refrigeration at, or about, 4°C. Refrigeration primarily helps to inhibit bacteria. However, this method is not always applicable to all types of samples.

Acids such as HNO_3 and H_2SO_4 can be used to prevent precipitation and inhibit the growth of bacteria. Preservation methods for any specific analysis should be discussed with the accredited laboratory that is analyzing the samples.

i) Decontamination of Sampling Devices

All non-disposable and non-dedicated equipment that is submerged in a monitoring well or contacts groundwater will need to be cleaned between sampling additional wells to prevent cross-contamination. Generally, the level of decontamination is dependent on the level and type of suspected or known contaminants. Extreme care should be taken to avoid any decontamination product from being introduced into a groundwater sample.

The decontamination area should be established upwind of sampling activities and implemented on a layer of polyethylene sheeting to prevent surface soils from contacting the equipment. The following steps summarize recommended decontamination procedures for an Act 2 site:

- Wash with non-phosphate detergent and potable water. Use bristle brush made from inert material to help remove visible soil;

- Rinse with potable water - pressure spray is recommended;

- If collecting samples for metals analysis, rinsing with 10% hydrochloric or nitric acid;

- Rinse liberally with deionized/distilled water –pressure spray is recommended;

- If collecting samples for organics analysis, rinsing with solvent-grade isopropanol, acetone, or methanol (should not be a solvent of potential interest to the investigation);

- Rinse liberally with deionized/distilled water – pressure spray is recommended;

- Air-dry;

- Wrap with inert material (such as aluminum foil) if equipment is not being used promptly.

j) Field Sampling Logbook

A field logbook or field sampling forms should be completed and maintained for all sampling events. The following list provides some examples of pertinent information that should be documented:

- date/time of sample collection for each well

- well identification

- well depth

- presence of immiscible layers and detection method (i.e., an interface probe)

- thickness of immiscible layers, if applicable

- estimated well yield (high, moderate, or low)

- purging device, purge volume, and pumping rate

- duration of well purging

- measured field parameters (see 4.3.3)

- sample appearance

- description on any abnormalities around the wellhead (standing/ponded water, evidence of vandalization, etc.)

- description of any wellhead materials that were or need to be replaced (sanitary well cap, well lid or well lid bolts, locking devices, etc.)

k) Chain-of-Custody

A chain-of-custody record provides a legal document that traces sample procession from time of collection to final laboratory analysis. The document should account for all samples collected that require laboratory analyses and provide the following information:

- sample identification number
- printed name and signature of sample collector(s)
- date/time of collection for each sample
- sample media type (i.e., groundwater)
- thickness of immiscible layers, if applicable
- well identification
- type and number of containers for each sample
- laboratory parameters requested for analyses
- type(s) of preservatives used
- carrier used, if applicable
- printed name and signature of person(s) involved in the chain of possession
- date/time samples were relinquished by the sampler and received by the laboratory
- presence/absence of ice in cooler or other sample holding device
- special handling instructions for the laboratory, if applicable

4. References

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E. Well Decommission Procedures

1. Introduction

Unsealed or improperly sealed wells may threaten public health and safety and the quality of the groundwater resources. Therefore, the proper abandonment (decommissioning) of a well is a critical final step in its service life.

Act 610, the Water Well Drillers License Act (32 P.S. § 645.1, et seq), includes a provision for abandonment of wells. This legislation makes it the responsibility of a well owner to properly seal an abandoned well in accordance with the rules and regulations of DCNR. In the absence of more stringent regulatory standards, the procedures outlined in this section represent minimum guidelines for proper decommissioning of wells and borings. These procedures may be applicable for, but not limited to, public and domestic water supply wells, monitoring wells, borings or drive points drilled to collect subsurface information, test borings for groundwater exploration, and dry wells (drains or borings to the subsurface).

Proper well decommissioning accomplishes the following: 1) eliminates the physical hazard of the well (the hole in the ground and the wellhead protruding above surface grade when applicable); 2) eliminates a pathway for the introduction and migration of contamination; and 3) prevents hydrologic changes in the aquifer system, such as the changes in hydraulic head and the mixing of water between aquifers. The proper decommissioning method will depend on both the reason for abandonment and the condition and construction details of the boring or well and the specific threat of existing and potential contamination sources near the well bore.

An unused and decommissioned well could be the conduit for spread of contamination. The lack of well decommissioning and a poorly sealed well could both result in the spread of contamination into previously uncontaminated areas for which the well owner or contractor may be responsible.

2. Well Characterization

Effective decommissioning depends on knowledge of the well construction, site geology, and hydrogeology. The importance of a full characterization increases as the complexity of the well construction, site geology, and the risk of aquifer contamination increases. Construction information for wells drilled since 1966 may be available from the DCNR BTGS PaGWIS database. Additional well construction data and information describing the hydrologic characteristics of geologic formations may be available from reports published by BTGS and the USGS. Site or program records also may exist. The well should be positively identified before initiating the decommissioning. Field information should be compared with any existing information.

Water levels and well depths can be measured with a well sounder, weighted tape measure, or downhole camera. In critical situations, well construction details and hydrogeology can be determined with borehole geophysics or a downhole camera. For example, a caliper log, which is used to determine the borehole diameter, can be very helpful in locating cavernous areas in open hole wells.

3. Well Preparation

If possible, the borehole should be cleared of obstructions prior to decommissioning. Obstructions such as pumps, pipes, wiring, and air lines must be pulled. Well preparation also may involve “fishing” obstacles out of the borehole. An attempt should be made to pull the casing when it will not jeopardize the integrity of the borehole. Before the casing is pulled, the well should be grouted to near the bottom of the casing. This will at least provide some seal if the well collapses after the casing is pulled.

The presence of nested or telescoped casing strings complicates well decommissioning. Inner strings should be removed when possible, but only when removal will not jeopardize the decommissioning of the well. If inner strings cannot be removed and sealing of the annular space is required, then the inner string should be vertically split (plastic-cased wells) or cut (metal-cased wells) at intervals necessary to ensure complete filling of the annular space.

Damaged, poorly constructed or dilapidated wells may need to be re-drilled prior to application of proper decommissioning techniques. Also, in situations where intermixing of aquifers is likely, the borehole may need to be re-drilled.

4. Materials and Methods

a) Aggregate

Materials that eliminate the physical hazard and open space of the borehole, but do not prevent the flow of water through the well bore, are categorized as aggregate. Aggregates consist of sand, crushed stone or similar material that is used to fill the well. Aggregates should be uncontaminated and of consistent size to minimize bridging during placement.

Aggregate is usually not placed in wells smaller than two inches in diameter. Nominal size of the aggregate should be no more than 1/4 of the minimum well diameter through which it must pass during placement. Because aggregate is usually poured from the top of the well, care should be taken to prevent bridging by slowly pouring the aggregate and monitoring the progress with frequent depth measurements. The volume of aggregate needed should be calculated prior to placement into the well.

Aggregates may be used in the following circumstances: 1) there is no need to penetrate or seal fractures, joints or other openings in the interval to be filled; 2) a watertight seal is not required in the interval to be filled; 3) the hole is caving; 4) the interval does not penetrate a perched or confined aquifer; and 5) the interval does not penetrate more than one aquifer. If aggregate is used, a casing seal should be installed (see Section E.5.a). The use of aggregate and a casing seal should be consistent with the future land use.

b) Sealants

Sealants are used in well decommissioning to provide a watertight barrier and prevent the migration of water in the well bore, in the annular spaces or in fractures and openings adjacent to the well bore. Sealants usually consist of Portland cement-based grouts, “bentonite” clay, or combinations of these substances. Additives are frequently used to enhance or delay specific properties such as viscosity, setting time, shrinkage, or strength.

Sealing mixtures should be formulated to minimize shrinkage and ensure compatibility with the chemistry of the groundwater in the well.

To avoid the bridging of sealants in the well, sealing should be performed under pressure from the bottom upward. A grout pump and tremie pipe are preferred for delivering grout to the bottom of the well. This method ensures the positive displacement of the water in the well and will minimize dilution or separation of the grout.

If aggregate is to be placed above sealant, sufficient curing time should be allotted before placing the aggregate above the seal. Curing time for grout using Type 1 cement is typically 24-48 hours, and 12 hours for Type III cement.

General types of sealants are defined as follows:

<u>Neat cement grout:</u> Neat cement grout is generally formulated using a ratio of one 94-pound bag of Portland cement to no more than 6 gallons of water. This grout is superior for sealing small openings, for penetrating any annular space outside of the casings, and for filling voids in the surrounding rocks. When applied under pressure, neat cement grout is strongly favored for sealing artesian wells or those penetrating more than one aquifer. Neat cement grout is generally preferred to concrete grout because it avoids the problem of separation of the aggregate and the cement. Neat cement grout can be susceptible to shrinkage, and the heat of hydration can possibly damage some plastic casing materials.

<u>Concrete grout:</u> Concrete grout consists of a ratio of not more than six gallons of water, one 94-pound bag of Portland cement, and an equal volume of sand. This grout is generally used for filling the upper part of the well above the water-bearing zone, for plugging short sections of casings, or for filling large-diameter wells.

Concrete grout, which makes a stronger seal than neat cement, may not significantly penetrate seams, crevices or interstices. Grout pumps can handle sand without being immediately damaged. Aggregate particles bigger than this may damage the pump. If not properly emplaced, the aggregate is apt to separate from the cement. Concrete grout should generally not be placed below the water level in a well, unless a tremie pipe and a grout pump are used.

<u>Grout additives:</u> Some bentonite (2 to 8 percent) can be added to neat cement or concrete grout to decrease the amount of shrinkage. Other additives can be used

to alter the curing time or the permeability of the grout. For example, calcium chloride can be used as a curing accelerator.

High-solids sodium bentonite: This type of grout is composed of 15-20 percent solids content by weight of sodium bentonite when mixed with water. To determine the percentage content, the weight of bentonite is divided by the weight of the water plus the weight of the bentonite. For example, if 75 pounds of powdered bentonite and 250 pounds of granular bentonite were mixed in 150 gallons of water (at 8.34 pounds per gallon), the percentage of high-solids bentonite is approximately 20 percent [325/(1251+325)]. High-solids bentonite must be pumped before its viscosity is lowered. Pumping pressures higher than those used for cement grouts are usually necessary. Hydration of the bentonite must be delayed until it has been placed down the well. This can be done by: 1) using additives with the dry bentonite or in the water; 2) mixing calcium bentonite (it expands less) with sodium bentonite; or 3) using granular bentonite, which has less surface area.

In addition, positive displacement pumps such as piston, gear, and moyno (progressive cavity) pumps should be used because pumps that shear the grout (such as centrifugal pumps) will accelerate congealing of the bentonite. A paddle mixer is typically used to mix the grout. A high-solids bentonite grout is not made from bentonite that is labeled as drilling fluid or gel.

c) Bridge Seals

A bridge seal can be used to isolate cavernous sections of a well, to isolate two producing zones in the well, or to provide the structural integrity necessary to support overlying materials, and thus protect underlying aggregate or sealants from excessive compressive force. Bridge seals are usually constructed by installing an expandable plug made of wood, neoprene, or a pneumatic or other mechanical packer. Additional aggregate can be placed above the bridge.

5. Recommendations

The complexity of the decommissioning procedure depends primarily on the site hydrogeology, geology, well construction, and the groundwater quality. Four principal complicating factors have been identified, which include: 1) artesian conditions, 2) multiple aquifers, 3) cavernous rocks, and 4) the threat or presence of contamination. The recommended procedures for abandoning wells will be more rigorous with the presence of one or more complicating factors. The procedures may vary from a simple casing seal above aggregate to entirely grouting a well using a tremie pipe after existing casing has been ripped or perforated. Figure A-8 summarizes the general approach to well decommissioning.

a) Casing Seal

The transition from well casing to open borehole is the most suspect zone for migration of water. To minimize the movement of water (contaminated or otherwise) from the overlying, less consolidated materials to the lower water-bearing units, this zone should be sealed. Generally, this can be accomplished by filling at least the upper 10 feet of open borehole and the lower five feet of casing with sealant. The length of open borehole sealed should be increased if extenuating circumstances exist. Such circumstances would include a history of bacterial contamination, saprolitic bedrock, or possibly deep fracture zones. Water-bearing zones reported in the upper 20 feet or so of open borehole are indications of fractures and warrant the use of additional sealant. Casing that is deteriorated should be sealed along its entire length. If the casing is to be pulled, the sealant used should remain fluid for an adequate time to permit removal of the casing.

If the casing is to remain, then whenever feasible, it should be cut off below land surface. After the casing seal discussed above achieves adequate strength, the open casing should, at a minimum, be filled with aggregate. It is strongly suggested that a sealant be used in the upper two to five feet of casing.

b) Wells in Unconfined or Semi-Confined Conditions

These are the most common well types in Pennsylvania. The geology may consist of either unconsolidated or consolidated materials. When applicable, unconfined wells in non-contaminated areas may be satisfactorily decommissioned using aggregate materials up to 10-15 feet below the ground surface. Monitoring wells located at sites with no known contamination might be decommissioned in this manner. The casing seal should be installed above the aggregate. A sealant may be used over the entire depth.

c) Wells at Contaminated Sites

A decommissioned, contaminated well often mixes contaminated groundwater with uncontaminated groundwater. Complete and uniform sealing of the well from the bottom to the surface is required. Therefore, proper well preparation (Section E.3) should be accomplished before the well is sealed with a proper sealant (Section E.4.b).

d) Flowing Wells

The sealing of artesian wells requires special attention. The flow of groundwater may be sufficient to make sealing by gravity placement of concrete, cement grout, neat cement, clay or sand impractical. In such wells, large stone aggregate (not more than 1/4 of the diameter of the hole), or well packers (pneumatic or other) will be needed to restrict the flow and thereby permit the gravity placement of sealing material above the zone where water is produced. If plugs are used, they should be several times longer than the diameter of the well to prevent tilting. Seals should be designed to withstand the maximum anticipated hydraulic head of the artesian aquifer.

Because it is very important in wells of this type to prevent circulation between water yielding zones, or loss of water to the surface or annular spacing outside of the casing, it is recommended to pressure grout the well with cement using the minimum volume of water during mixing that will permit handling.

For wells in which the hydrostatic head producing flow to the surface is low, the movement of water may be stopped by extending the well casing to an elevation above the artesian pressure surface.

e) Wells with Complicating Factors at Contaminated Sites

Wells with one or more of the above complicating factors that are to be decommissioned in areas with contaminated groundwater, or in areas where the groundwater is at a high risk for future contamination, require the most rigorous decommissioning procedures. In general, the entire length of these wells should be sealed.

When the threat of contamination has been established, the elimination of a potential flowpath is critical. For example, a contaminated well in a karst terrane must be carefully sealed to avoid exacerbating the situation. In general, the entire lengths of these wells should be sealed. In some situations, a bridge seal may need to be installed, and casing may have to be perforated. In each case, a prudent method should be selected which will eliminate all potential vertical flowpaths.

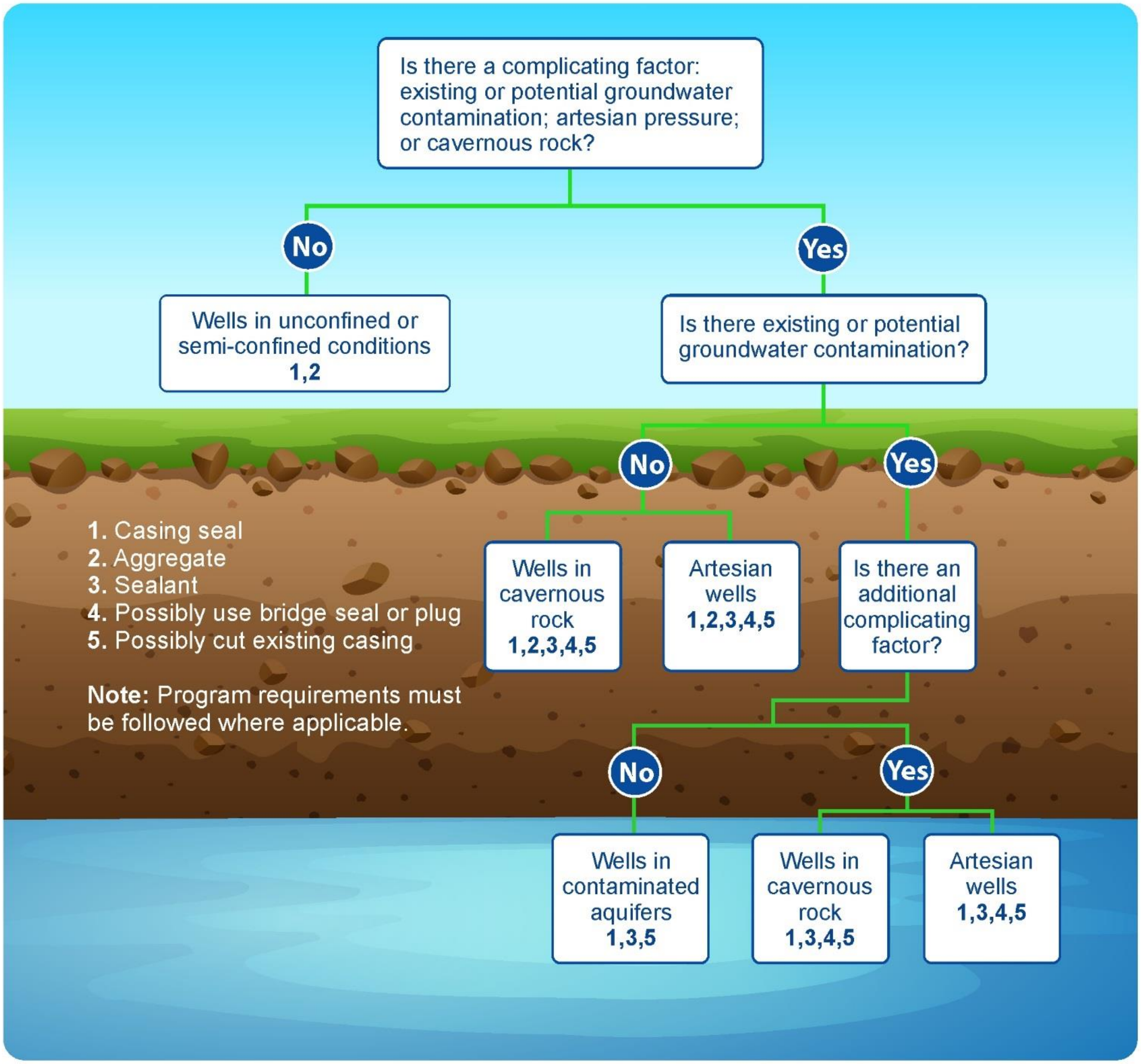
f) Monitoring Wells

Monitoring wells which are installed for an investigation, cleanup or other monitoring in a program that has no rules or regulations for decommissioning, such as the Act 2 program, should be decommissioned in accordance with the following guidelines.

Monitoring wells that were installed and continue to function as designed can usually be decommissioned in place after they are no longer needed. Exceptions would include wells whose design precludes complete and effective placement of sealant and wells in locations subject to future disturbance that could compromise the decommissioning. In such instances, all tubing, screens, casings, aggregate, backfilling, and sealant should be cleaned from the boring and the hole should be completely filled with an appropriate sealant.

Monitoring wells that are abandoned in place should be completely filled with sealant. Screened intervals can be backfilled with inert aggregate if sealant may alter the groundwater chemistry, thereby jeopardizing ongoing monitoring at the facility. Intervals between screens, and between the last screen and the surface, must be filled with sealant. Generally, sealant should be emplaced from the bottom of the interval being sealed to the top of that interval. Protective casings, riser pipes, tubing, and other appurtenances at the surface which could not be removed should be cut off below grade after the sealant has properly set. When decommissioning will be completed below the finished grade, the area of the boring should be covered with a layer of bentonite, grout, concrete, or other sealant before backfilling to grade.

Figure A-8: Summary of Procedures for Well Decommissioning



Note: Figure must be used in conjunction with the text. Reference Section A.E.

6. Existing Regulations and Standards

17 Pa. Code § 47.8 requires that the owner or consultant who is to abandon the well notify DCNR's BTGS of the intent to decommission a well at least 10 days before the well is sealed or filled.

7. Reporting

All decommissioned wells shall be reported to BTGS, along with any bureau that requires a report, on forms required by BTGS (and any other pertinent forms). If available, the original driller's log should be included, along with the details of the well decommissioning procedure. A photograph should be taken of the site, and a reference map should be made, showing the location of the decommissioned well. It also may be appropriate to survey the exact location of the well (if not already completed). Licensed drillers may use the online application WebDriller to complete the well decommissioning report.

8. References

American Water Works Association, 1990, Abandonment of Test Holes, partially completed wells and completed wells: AWWA Standard for Water Wells, pp. 25-26.

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F. Quality Assurance/Quality Control Requirements

1. Purpose

A Quality Assurance/Quality Control Plan (QA/QC Plan) is a detailed account of methods and procedures used for data collection (i.e., monitoring) activities. This plan, when properly developed and implemented, ensures that adequate control and documentation procedures are utilized, from initiation to completion of the monitoring, so that the data generated is of the highest quality and can be used for the intended purpose with confidence. A QA/QC plan is also an effective tool in assessing and assuring the completeness and adequacy of the basic monitoring plan.

2. Design

A QA/QC plan should be designed to satisfy the objectives of the monitoring project. Although the elements of each QA/QC plan described below will be similar, the intended uses of the collected data will determine the requirements associated with the monitoring activity. In most cases, there will be sufficient differences within monitoring activities for each project to require a specific QA/QC plan.

The following paragraphs describe the basic elements of a QA/QC plan. In most cases, the proper development and adherence to this format will be sufficient to ensure that the data collection meets the objectives of a project. However, in some cases it may be necessary to include additional considerations that may be unique to a specific site and/or project.

3. Elements

- Project Name or Title: Provide the project identification and location.
- Project Required by: Provide the reason(s) or requirement(s) for the project.
- Date of Requirement: Provide date the project was required, either by legal or other order.
- Date of Project Initiation: Provide date that the project was implemented.
- Project Officer(s): Provide name(s) of individual(s) responsible for managing or overseeing the project.
- Quality Assurance Officer(s): Provide name(s) of individual(s) responsible for development of and adherence to the QA/QC plan.
- Project Description: Provide the following: 1) an objective and scope statement which comprehensively describes the specific objectives and goals of the project, such as determining treatment technology effectiveness, or remediation effectiveness for specific parameters; 2) a data usage statement that details how the monitoring data will be evaluated, including any statistical or other methods; 3) a description of the location of monitoring stations and reasons for the

locations, including geologic, hydrogeologic or other considerations; and 4) a description of the monitoring analytes and frequency of sample collection, including the expected number of samples to be collected for each analyte, the sample matrix (i.e., water), the exact analytical method, reasons for selection of analytes, and sample preservation method(s) and holding time(s).

- Project Organization and Responsibility: Provide a list of key personnel and their corresponding responsibilities, including the position and/or individual in charge of the following functions: field sampling operations, field sampling QA/QC, laboratory analyses, laboratory analyses QA/QC, data processing activities, data processing QA/QC and overall project coordination.

- Project Fiscal Information: Provide an estimate in work days of the project time needed for data collection, laboratory support, data input, quality assurance and report preparation in work days.

- Schedule of Tasks and Products: Provide a projected schedule for completing the various tasks and developing the products associated with the project, such as sample collections (monthly, quarterly, etc.), data analysis/reports (quarterly, annual, biennial, etc.).

- Data Quality Requirements and Assessments: Provide a description of data accuracy and precision, data representativeness, data comparability, and data completeness.

- Sampling Procedures: Provide a description of the procedures and equipment/hardware used to collect samples from monitoring wells or other sites, including sampling containers and field preservation and transport procedures.

- Sampling Plan: A sampling plan should provide necessary guidance for the number and types of sampling QCs to be used. The following is a list of common sample QC types and the recommended minimum frequency if used. It is important to remember that all QC samples should be treated with the same dechlorination and/or preserving reagents as the associated field samples.

    – Trip Blanks - These are appropriate sample containers filled with laboratory-quality reagent water that are transported to and from the sampling site(s) and shipped with the samples to the laboratory for analysis. The intent of these samples is to determine whether cross contamination occurred during the shipping process. They are also used to validate that the sampling containers were clean. Each sampling event that uses this type of QC should have a minimum of one trip blank for each container type used.

    – Field Blanks - These are appropriate sample containers that are filled with laboratory-quality reagent water at the sampling site(s) and shipped with the samples to the laboratory for analysis. These samples are intended to determine if cross-contamination occurred during the sampling process due to ambient conditions. They are also used to validate that the sampling containers were clean. Each sampling event that uses this type of QC should have a minimum of one field blank for each sampling site and of each container type used. This type of sampling QC is most useful when sampling for VOC's.

- <u>Rinsate Blanks</u> - These are samples of laboratory-quality reagent water used to rinse the collection device, including filtration devices and filters, which contact the same surfaces as the sample. The QC samples(s) are then submitted with the field samples for analysis. This type of QC sample helps to determine if the sample collection device is contributing any detectable material to the sample. The minimum number of blanks needed, if this type of QC is utilized, is dependent upon operational considerations. A minimum of two rinsate blanks should be submitted (one before sampling and one after sampling) if multiple samples are being collected with the same decontaminated collection device. If you are using disposable sample collection devices or multiple pre-cleaned devices, then a single representative sample should suffice.

- <u>Split/Duplicate Samples</u> - This is a single, large sample that has been homogenized, split into two or more individual samples, with each sample submitted independently for analysis. This QC determines the amount of variance in the entire sampling/analysis process. This type of QC is not recommended for samples analyzed for analytes that would be adversely affected by the homogenization process (i.e. VOC's). The minimum number of this type of sampling QC, if utilized, is one per sampling event, with a rate of 5 percent to 10 percent commonly used.

- <u>Replicate Samples</u> - Comprised of two or more samples collected from the same source, in a very short time frame (i.e., minutes), with each sample submitted independently for analysis. This QC measure, like the split/duplicate sample, determines the amount of variance in the entire sampling/analysis process. The amount of variance determined by this type of QC may be larger than that of a split/duplicate sample. The use of this type of QC also presumes that the sample's materials are already homogenous. This type of QC is recommended for samples where analytes could be adversely affected by an external homogenization process (i.e. volatile organics). The minimum number of this type of sampling QC, if utilized, is one per sampling event, with a rate of 5 percent to 10 percent commonly used.

- <u>Known Samples</u> - These are reference materials that have been characterized as acceptable to the range of values for the analytes of concern. These materials are available from commercial sources. This type of QC helps determine if the analytical work is sufficiently accurate. It must be noted that improper handling or storage of this type of reference material can invalidate the materials characterization. The minimum number of this type of QC, if used, is one per subject.

  - Spiked Samples - These are split/duplicate or replicate samples that have been fortified with the analytes of concern. This QC is intended to determine if there have been changes in concentration due to factors associated with the sample or the shipping and analysis process. This type of QC is very difficult to use in a field environment and routinely is done as part of the analysis process. If this type of QC is necessary, the minimum required is one per project.

- Sample Custody Procedures: Provide information which describes accountability for sample chain-of-custody including sample collector identification, sample location identification, sample number, date and time of collection, parameters to be analyzed, preservatives and fixatives, identification of all couriers, identification of laboratory and receiver, time and date of receipt at laboratory, laboratory analyzer, and time and date of analysis.

- Calibration Procedures and Preventative Maintenance: Equipment maintenance and calibration should be performed in accordance with manufacturer's instructions. Calibration and maintenance sheets should be maintained on file for all equipment.

- Documentation, Data Reduction, and Reporting: Provide discussion on where field data are recorded, reviewed, and filed.

- Data Validation: Provide a discussion and reference to the protocols used for validation of chemical data and field instrumentation and calibration. Describe procedure for validating database fields (i.e., through error checking routines, automatic flagging of data outside of specified ranges, and manual review and spot checking of data printouts against laboratory analytical results).

- Performance and Systems Audits: Provide a description of how field staff performance is checked and how data files are verified for accuracy and completeness.

- Corrective Action: Provide a discussion on what corrections are made when errors are found and actions taken to prevent future recurrence of errors.

- Reports: Provide a list of the types and frequency of reports to be generated (i.e., performance and systems audits, compliance analyses, remediation effectiveness, etc.).

4. References

U.S. Environmental Protection Agency, May 1984, Guidance for Preparation of Combined Work/Quality Assurance Project Plans for Environmental Monitoring, (OWRS QA-1), US EPA Office of Water Regulations and Standards.

Mueller, D.K., Schertz, T.L., Martin, J.D., and Sandstrom, M.W., 2015, Design, analysis, and interpretation of field quality-control data for water-sampling projects: U.S. Geological Survey Techniques and Methods, book 4, chap. C4, 54 p.

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APPENDIX D
PFAS FIELD-SAMPLING SOP

Ohio Environmental Protection Agency

DDAGW Standard Operating Procedure

For Per- and Polyfluorinated Alkyl Substances

Sampling at Public Water Systems

Ohio EPA LOE Contractors

Revision 1.1

March 3, 2020

(Final)

Division of Drinking and Ground Waters
March 2020

1.0 INTRODUCTION

This document provides guidance for field sampling of Perfluorinated and Polyfluorinated Alkyl Substances (PFAS) in water from public water systems (PWS). This guidance applies to all Ohio EPA Level of Effort (LOE) contractors and subcontractors who collect samples for PFAS analysis.

PFAS are a class of manufactured compounds created from carbon chains bonded to fluorine atoms. The carbon-fluorine bond is one of the shortest and strongest chemical bonds known. The strength of this bond provides the unique characteristics and properties of PFAS. Including persistence in the environment, bioaccumulation, and remediation and treatment difficulties.

PFAS are used to provide water, oil and stain repellency to textiles, carpets and leather, and to create grease-proof and water-proof coatings for paper plates and food packaging. They are also used in chrome plating, Class B fire-fighting foams, and numerous other industrial processes. One of the main challenges that field staff will encounter in successfully sampling for these compounds is to fully appreciate how ubiquitous these substances are in modern life – from the seat and dashboard of the field truck, to the water-resistant boots and jackets we wear. A successful field sampling program depends on staff’s awareness of these key factors which will help minimize cross-contamination.

2.0 SCOPE

All LOE contractor personnel and subcontractors who collect or otherwise handle samples for PFAS analysis should review this SOP prior to performing any field work and should carefully adhere to the procedures set forth herein.

3.0 RESPONSIBILITES

Ohio EPA Contract Manager or Project Administrator

The Ohio EPA Contract Manager or Project Administrator shall provide the Quality Assurance Project Plan (QAPP), the PWS PFAS Sampling Program Work Plan (Work Plan) and this Sampling SOP for field activities. All deviations from the QAPP, Work Plan or Sampling SOP will be reported to the Ohio EPA Quality Assurance (QA) Officer.

Ohio EPA Quality Assurance Officer

The QA Officer is responsible for the quality control management of the entire project. The QA Officer will conduct QC field audits during the sampling process to ensure field crews are adhering to the QAPP, Work Plan and Sampling SOP.

LOE Contractor Field Supervisor

The Field Supervisor shall ensure that all samples are collected in accordance with the QAPP, Work Plan and Sampling SOP. The Field Supervisor is responsible for making logical decisions in the field that may represent changes to the Work Plan and report any Work Plan deviations to the Ohio EPA QA Officer or Ohio EPA Contract Manager.

LOE Contractor Field Personnel (Including Subcontractors)

Field Personnel are responsible for carrying out the PWS PFAS sampling according to specifications outlined in the QAPP, the Work Plan and the Sampling SOP. Field Personnel are required to notify the Field Supervisor of any deviations from the QAPP, Work Plan or Sampling SOP that they encounter in the field. The Field Supervisor should in turn notify the Ohio EPA QA Officer as soon as possible. Any changes or deviations from the QAPP, Work Plan or Sampling SOP are to be documented in field forms or log books.

4.0 FIELD PROCEDURES

General Sampling Considerations

PFAS are analyzed with detection limits that are some three orders of magnitude lower than those used for trace elements typical of water samples (e.g., ppt vs ppb). To put the parts-per-trillion (ppt) scale into context, one part per trillion is about 1 inch in 250 square miles, 1 second in 32,000 years, or 1 ounce in 7.5 billion gallons of water. This requires that field personnel be especially aware of their surroundings, equipment and that the Sampling SOP is closely followed to minimize the potential for cross contamination and analytical false positives. Attachment 1 includes a list of prohibited and acceptable products for PFAS sampling events, and Attachment 2 provides a PFAS sampling checklist.

Sampling Teams

- **Two-person sampling teams are highly recommended.** Distributing the workload to ensure attention to the Sampling SOP is easier with a two-person team. Also, having another team member present will increase awareness to conditions and actions that can adversely affect the quality of the sampling effort. Team members should watch each other’s movement and activities where possible and identify immediately if someone is observed not following protocol.
- **Work distribution for a two-person sample team**

  When sampling for PFAS, a two-person team allows one person to be a dedicated "sample" handler, and the other person the dedicated "document" handler

  - The "**Sample**" team member will:
    - Maintain an uncompromised and uncontaminated sample area
    - Be the only team member to handle/manage/label sample containers until they are filled and capped
    - Maintain coolers with ice
    - Not handle field log books, forms or non-essential sampling materials or equipment (e.g., cell phones, clipboards, hand tools, etc.) during the sampling process
    - Not wear wrist watches, wristband fitness trackers or bracelets during the sampling process (i.e., nothing around the wrists)

  - The "**Document**" team member will:
    - Maintain the sampling and field log books
    - Complete required field documentation including the chain-of-custody (COC) form, field log and sample shipping paperwork
    - Photograph sampling locations
    - Perform other tasks not directly related to sample collection and handling

Sample Site Considerations

- **Split sample site into two parts**
  - Staging Area (greater than 10 feet away from sample points, i.e., PWS taps, as far as reasonably possible as space allows)
    - This is where all non-essential items should be kept: trucks/vehicles, food, drink, handwashing area, etc.
  - Sampling Area (area within a minimum distance of 10 feet of the sampling point or large as reasonably possible as space allows)
    - Only essential materials, personnel, and equipment should be brought inside this boundary.

Personal Hygiene

- On sampling days, avoid the use of soaps, body washes, shampoos or other personal hygiene products that may contain PFAS. Do not use cosmetics, moisturizers, hand cream or similar products as these may contain PFAS.
- Many sunblock and insect repellents contain PFAS. Attachment 1 includes a list of acceptable products. To help avoid use of sunblock and insect repellents, wear long sleeve cotton shirts and wide brimmed hats.
- Always wash hands after eating, preferably with plain soap (without moisturizing lotions).
- Avoid contact with PFAS-containing products or materials prior to sampling activities. Always wash hands with non-PFAS detergent (Liquinox®, Alconox® or plain bar soap recommended) prior to sampling. Use water from the tap to be sampled for handwashing.[1] **Do not use distilled or bottled water.** Dry hands with a clean paper towel.

Field Equipment

- **Do not use waterproof field books.** Prepare field reports on loose paper on Masonite or aluminum clipboards. Avoid plastic clipboards, binders or spiral hard cover notebooks.
- **Do not use markers.** Use ballpoint pen or pencil, but no permanent markers.
- **Do not use Post-It Notes® or similar adhesive products.**

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[1] In general, dermal contact with water is not a health concern because PFAS are not readily absorbed through the skin. Using water that contains PFAS for showering, bathing, laundry or household cleaning is generally safe (see www.pfas.ohio.gov).

- **Do not use "Blue Ice"** for sample cooling or storage of food and drink.

Field Gear, Clothing, and Personal Protective Equipment

- **Disposable powderless nitrile gloves must be worn at all times and changed every time a new (different) activity is undertaken: "When in doubt, change gloves."**
- **A new pair of nitrile gloves must be donned prior to the following activities at each location:**
    - Contact with sampling bottles or the field reagent blank (PFAS-free water)
    - Sample collection and handling
    - QA/QC sample collection and handling (field reagent blanks, duplicates, matrix spike/matrix spike duplicates)
- **Do not wear synthetic, stain-resistant (stain-treated), or water-proofed (water-resistance) clothing during sampling.** Field clothing should be restricted to natural fibers (preferably cotton). Field clothing should be well-laundered avoiding the use of fabric softeners and dryer sheets. Avoid PFAS-containing clothing such as Gore-Tex®, as well as wind breakers, boots and other apparel that have been treated for water resistance. **Do not wear Tyvek® clothing.**
- **Do not wear boots containing Gore-Tex™** Most field footwear is made with some type of synthetic fiber. They are also commonly treated for water resistance to some degree. Be aware to avoid contact with your footwear in the vicinity of the sample site, and always change nitrile gloves donned when changing footwear, tightening laces, etc. Leather boots that have not been treated with PFAS-containing waterproofing are acceptable.
- If wet conditions are encountered, appropriate clothing that will not pose a risk of cross-contamination should be considered. Fabrics that have been treated with water-repellents should be avoided because they may contain PFAS. Rain gear made from polyurethane and wax-coated materials may be used.

Field Vehicle

- The field vehicle seats may be treated with stain resistant products and represent a source of cross-contamination. The seats should be covered with well-laundered cotton blankets or sheets, especially if sample containers are handled on the vehicle seats. If donning gloves while entering the vehicle, always change gloves after exiting the vehicle.
- A well laundered cotton blanket or sheet should be available for use in any area of the vehicle that samples are handled including the back of an SUV or the bed of a pickup truck.
- The field vehicles should be clean, including the bed/cap area if it is a pickup truck, or any part of the vehicle that may hold the cooler containing samples. "Clean" means no potential sources of PFAS (e.g., fast food wrappers), trash, used sampling gloves, excessive dirt or soil, or materials or equipment that are not necessary for PWS PFAS sampling.

Food Breaks

- Food packaging has historically been treated with PFAS to resist wetting, such as sandwich wrappers, paper cups, coated papers, etc. Field personnel are not to bring any food items into the sampling area for this reason. In addition, any food items must be stored separately from sampling equipment and supplies (i.e., use a designated cooler for food and drink).

- Snacks and meals are not to be eaten in the field vehicle or when sampling. Food breaks should only be taken off-site before, after or between individual PWS sampling events.
- Samplers should always wash their hands after eating lunch or snacks.

Visitors

- Due to the high risk of inadvertent cross-contamination visitors to the site should remain at a reasonable distance (at least 30 ft) from the sampling area.
- The PWS operator or designated contact should be at least 10 feet from sample tap or as far as reasonably possible, but they may fall inside the 30ft radius required for visitors.
- If approached by a member of the press, an elected official or other visitor who has questions regarding the sampling activities, politely refer them to Ohio EPA's Public Interest Center (PIC) for assistance from an authorized PIC staff member. Do not attempt to answer any questions on your own, just respond that Ohio EPA has not authorized you to do so. Ohio EPA will provide each Contractor with "Media and Citizen Inquiries" and "Elected Official Inquiries" wallet cards with the appropriate contact information. These cards may be distributed as necessary.

5.0 SAMPLE COLLECTION

Samplers should maintain awareness of all materials that physically contact the sample tap and all sampling equipment. It is important that "muscle memory" not take over and allow a procedure that might be acceptable for other sample constituents but would compromise PFAS sampling.

Laboratory

- The designated laboratory will furnish field personnel with appropriate sampling supplies, including but not limited to sample containers, quality assurance/quality control (QA/QC) containers, chain-of custody (COC) forms and PFAS-free reagent grade water as required by Method 537.1.
- Samplers are to fill the number of sample and QA/QC containers requested by the laboratory and to follow any associated instructions provided by the laboratory. Be aware that there may be some difference between laboratories, e.g., one versus two containers per sample, use of a temperature blank in the sample cooler, etc. If in doubt, contact the laboratory for instructions. If additional assistance is needed, contact the Ohio EPA QA Officer.

Sample Containers and Labels

- Sample containers will be 250 mL wide-mouth high density polyethylene (HDPE) bottles fitted with an unlined (no Teflon®) polypropylene or HDPE screw cap. Only laboratory-provided sample bottles may be used.
- Sample (and QA/QC) containers are to be pre-preserved in accordance with Method 537.1 and should appear in the bottle as a white crystalline powder.
- The laboratory will provide PFAS-free sample labels. Only labels provided by the laboratory may be used (be aware that some common "waterproof" labels may contain PFAS). Labels should be completed using ball-point pens (no permanent markers).

PWS EP and Active RS Tap Sampling Locations

- At least one PWS Entry Point (EP) tap samples will be collected, and if possible one PWS Raw Source (RS) tap sample will be collected. EP and RS tap sampling locations are defined as follows:

  - EP Tap Sampling Location: tap located after the pressure tank, treatment or chemical addition, but before the PWS distribution system
  - RS Tap Sampling Location: tap located before the pressure tank, treatment or chemical addition

System Purging for PWS EP and Active RS Tap Sampling

- Determine which wells and/or intakes are operational at the time of sampling and the wells and/or intakes that were operational in the past 24 hours. Record this information on the field form or log book. If the sources have been running for a reasonable amount of time (at least 20 minutes) no additional purging is necessary. If not, purge the source for 20 minutes.
- Flush sample taps for 2 minutes prior to collecting the sample.
  - Use a bucket to collect water during flushing to avoid spilling water on the floor of the sampling area.
  - **Do not flush the tap (the tap should be OFF) when collecting the field reagent blank (FRB).**

Tap Grab Sampling

- Prior to sampling, field staff should:
  1. Prepare the sample cooler with ice, leaving adequate room for the sample containers so that ice does not need to be removed from the cooler after the filled and bagged sample containers are returned to it. To prevent cooler leakage as the ice melts, the cooler should be lined with a large plastic bag or ice should be contained in double plastic (e.g., 1- or 2-gallon Ziplock™) bags.
  2. Inspect EP tap and RS tap sampling locations for ease of access, safety concerns and the presence of materials or conditions that may cause PFAS cross contamination to establish the sampling area and any pre-samplings tasks (e.g. moving materials or equipment to access a tap). If there appear to be logistical or safety conditions under which sampling cannot be performed, or conditions that are likely to adversely affect sample quality, include documentation of the condition in the field notes **and contact the Ohio EPA QA Officer immediately for direction before sampling.**
  3. Remove tubing or hoses from sampling taps (if possible). If the PWS representative is available, they may remove hoses and tubing for the sample team.
  4. Inspect the tap. If grease, oil, Teflon tape/paste or other foreign substances appear to be present on the tap threads, include documentation of the condition in the field notes **and contact the Ohio EPA QA Officer immediately for direction before sampling.**
  5. Take close-up photographs of the EP and RS sampling taps. The tap photos should include the completed field form (header section) for reference. Additional photos may be taken of the sampling areas at the contractor's discretion to document field sampling conditions. If notes need to be included in the photo, use a plain white paper page (8.5 x 11") and ballpoint pen or pencil. All photos should include GIS location data (latitude, longitude). Photos may be taken before or after sampling, but not during sampling.

6. Before beginning the sampling process at each site (i.e., before collecting the FRB), wash hands[2] using Liquinox®, Alconox® or plain bar soap (no moisturizers) and water from the tap to be sampled **(do not use distilled or bottled water).** Dry hands using a clean disposable (single-use) paper towel. If using bar soap, discard the bar after use, and use a new (unused) bar at the next sampling site (we don't want to potentially transport PFAS cross contamination from one site to another via the bar soap).
7. Don new nitrile gloves (multiple layering of clean gloves is acceptable).
8. Document the lot numbers from all sampling bottles and the expiration date (if applicable) for the field reagent blank (FRB, PFAS-free water) on the field form or in the field log book.
9. Complete all label of bottles using ballpoint pen or pencil at any point prior to sampling.

- Ohio EPA recommends that the "Document" team member (Section 4.0) perform tasks 1 through 7 above, and that the "Sample" team member (Section 4.0) perform tasks 6 through 9.

Sampling Procedures

- Ohio EPA recommends the use of a clean five-gallon PVC bucket to transport the sample bottles (in plastic bags) from the sample cooler to and from the sampling locations (taps). Use of the bucket will help reduce the potential for cross contamination during the sampling process, i.e., bottles can remain in the bucket and not be placed on floors or other potentially contaminated surfaces. The bucket can be placed near the tap to be sampled (i.e., within five to 10 feet), but care should be taken to avoid splashing tap water into the bucket. This bucket should never be used to capture flushed water.
- The sample bottles should remain closed until immediately prior to sample collection and be closed tightly immediately after sample collection. If possible, the sampler should hold the bottle cap during sample collection. After filling, replace the cap securely and shake to completely dissolve the preservative.
- Do not rinse the pre-preserved PFAS sample bottle with sample water prior to sample collection.
- Each PWS sample site (the PWS being sampled) is to be accompanied with an FRB, taken immediately before the EP tap sample.
- The sample sequence will be field reagent blank (FRB), EP tap, QA/QC samples (see Section 6.0) and RS tap.
- Disposal of empty bottles, paper towels, gloves and other one-time use items should occur after all samples have been completed, not during the sampling process.
- To begin the sampling sequence, obtain the FRB:

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[2] In general, dermal contact with water is not a health concern because PFAS are not readily absorbed through the skin. Using water that contains PFAS for showering, bathing, laundry or household cleaning is generally safe (www.pfas.ohio.gov)

1. **Don't flush the tap while collecting the FRB.**
2. Don a clean pair of nitrile gloves (multiple layering of clean gloves is acceptable).
3. Remove the bottles from the bag and verify the label on the empty FRB.
4. Uncap the empty FRB and the pre-filled PFAS-free water bottles.
5. Within one minute of uncapping the bottles, slowly pour the PFAS-free water from the pre-filled bottle into the empty FRB bottle, then cap the FRB bottle securely and return it to the bag. Place the bag in the cooler and dispose of the empty pre-filled bottle.

- To obtain the EP or RS tap sample:
    1. Turn on the tap. Reduce the water flow to a near-laminar stream (about 200 to 300 mL/min where possible). Taps should be flushed for 2 minutes. Use a bucket to contain the water from the tap if necessary (i.e., a sink or floor drain is not present); do not allow water to spill over the sampling area floor.
    2. Don a clean pair of nitrile gloves (multiple layering of gloves is acceptable).
    3. Remove sample bottles from bag and verify the label.
    4. Have all sample bottles within reach (again, use of a five-gallon PVC bucket is recommended to avoid placing bottles on the ground or floor). Fill each bottle to its neck, one after the other. Avoid splashing/spilling sample water out of the bottle. Cap all bottles tightly.
    5. Ensure the rim of the sample bottle does not contact the sample tap or other equipment during sample collection.
    6. Once tightly capped, shake the bottles to completely dissolve the preservative.
    7. Return bottles to the bag.
- Record label information including the sample identification, sample collection date, sample collection time and any other information the laboratory requires on the chain of custody (COC) form. The "Document" team member should be responsible for maintaining the COC.
- Bagged samples are to be stored on ice as soon as reasonably possible given the site conditions. Remove excess air from bags as the samples are packed (air acts as an insulator).
- If required (if sample bottles provided), field duplicate, laboratory fortified sample matrix or laboratory fortified sample matrix duplicate QA/QC samples should be collected after the EP tap sample following the procedures described above for EP tap sampling.
- The PWS may want to collect their own PFAS samples during Ohio EPA's sampling event. If this is the case, the PWS personnel should wait until after Ohio EPA's sampling has been completed. **Do not attempt to collect split samples with the PWS. Ohio EPA LOE contractor personnel should not handle PWS sampling containers, and PWS personnel should not handle Ohio EPA's sampling containers.**
- All sampling materials should be treated as single use and disposed following completion of sampling at each sample site.
- See Section 7.0 for shipping procedures.

6.0 QUALITY ASSURANCE/QUALITY CONTROL

The QA/QC samples required for Method 537.1 are referenced in the QAPP (Section B) and summarized below:

Field Reagent Blank (FRB)

- A field reagent blank consists of a single 250 mL bottle of PFAS-free reagent grade water with preservative. This water is to be transferred into an empty 250 mL bottle absent of preservative. The FRB should be collected immediately before the EP sample and collected per Section 5.0.

Field Duplicate (FD)

- A FD will consist of a one or more 250 mL bottles of sample water. The FD should be collected immediately after the EP tap sample and collected in the same manner as the sample in Section 5.0. Per Method 537.1, FDs will be collected at a rate of one per 20 samples. FD bottles will be provided by the laboratory as needed to meet Method 537.1 requirements.

Laboratory Fortified Sample Matrix (SM)

- A SM will consist of a one or more 250 mL bottles of sample water. The SM should be collected immediately after the EP tap sample and collected in the same manner as the sample in Section 5.0. Per Method 537.1, SMs will be collected at a rate of one per 20 samples. SM bottles will be provided by the laboratory as needed to meet Method 537.1 requirements.

Laboratory Fortified Sample Matrix Duplicate (SMD)

- A SMD will consist of a one or more 250 mL bottles of sample water. The SMD should be collected immediately after the EP tap sample and collected in the same manner as the sample in Section 5.0. Per Method 537.1, SMDs will be collected at a rate of one per 20 samples. SMD bottles will be provided by the laboratory as needed to meet Method 537.1 requirements.

Temperature Blank

- Depending on the lab, a temperature blank may accompany each cooler. A temperature blank is simply a water-filled sample bottle that accompanies each cooler. When the samples are received at the laboratory, the temperature of this blank is taken to ensure that all samples are received at 10°C or less. The temperature blank allows the laboratory to make this determination without compromising one of the samples.

Trip Blanks

- No trip blanks should be required to accompany PFAS samples.

7.0 SHIPPING

- Place all sample bags into the cooler with ice (see page 7). If using a cooler liner, squeeze the air out of the liner and tie it off tightly. Ice should not be placed outside of the cooler liner or the cooler may leak as the ice melts. If a sample cooler leaks during shipment, the shipper may stop or delay delivery to the laboratory. As an alternative to a cooler liner, ice may be contained in double-plastic bags (e.g., 1- or 2-gallon Ziplock™ bags).

- Samples must be chilled during shipment and should not exceed 10°C during the first 48 hours after sample collection per Method 537.1.
- Sample temperature must be confirmed when the samples are received at the laboratory per Method 537.1 and should be at or below 10°C.
- The samples for each site (PWS) should be listed on separate (site-specific) chains of custody (COC). Samples from multiple sites may be included in the same sampling cooler, but the cooler should include a separate COC for each site sampled.
- Same day pre-paid contract agent shipping is recommended. Note that Method 537.1 holding time for PFAS is 14 days.

8.0 DOCUMENTATION

- Ensure that the COC information and all other field documentation is complete and accurate before leaving a PWS sampling location.
- All necessary documentation for sample custody and submission to the laboratory must meet laboratory requirements.
- As described in Section 5.0, all photographs are to be provided to Ohio EPA.
- Copies of all COCs, field notes, photographs or other field sampling documentation are to be provided to Ohio EPA.

8.0 REFERENCES

AECOM, 2016 PFAS Sampling Webinar: Technical Training for Waste Site Cleanup Professionals. Chiang, D., presenter. AECOM, Aug 3, 2016.

AECOM, *Poly- and Perfluoroalkyl Substance (PFAS) Sampling and Analysis: Truths, Traps, and Consequences;* June, 2016; AECOM PFAS Client Webinar.

Aerostar SES LLC Standard Operating Procedure 002P Groundwater Sampling at Perfluorinated Compound (PFC) Sites, July 2016 (Revision 2)

Aerostar SES LLC Standard Operating Procedure 028P Field Sampling Protocols to Avoid Cross-Contamination at Perfluorinated Compound (PFC) Sites, July 2016 (Revision 2)

Fujii et al., 2013, Occurrence of perfluorinated carboxylic acids (PFASAs) in personal care products and compounding agents. Chemosphere 2013 Sep; 93(3): 538-44. 10.1016/j.chemosphere.2013.06.049. Epub 2013 Aug 6

Technical Guidance Manual for Ground Water Investigations, Chapter 10, *Ground Water Sampling*, Ohio Environmental Protection Agency, May 2012.

Tetra Tech*, Standard Operating Procedure, Field Sampling at Per- and Poly-fluorinated Compounds (PFAS) Sites*, Tetra Tech PFAS SOP.

Transport Canada, *Perfluorochemical (PFAS) Field Sampling Protocol*; Revised, May 2013; TC_PFAS_SamplingProtocol.

Attachment 1: List of Prohibited and Acceptable Products for PFAS Sampling Events

Prohibited Personal Care Products:	**Acceptable Personal Care Products:**
On the morning of sampling event, no application of cosmetics, moisturizers, hand creams or related products or use of shampoos, soaps or body washes that may contain PFAS	PFAS-free sunscreens: • Alba Organics Natural Sunscreen™ • Yes to Cucumbers™ • Aubrey Organics® • Jason Natural Sun Block® • Kiss My Face® • Baby sunscreens labelled “free” or “natural” PFAS-free insect repellants: • Jason Natural Quit Bugging Me® • Repel Lemon Eucalyptus Insect Repellant® • Herbal Armor™ • California Baby Natural Bug Spray® • BabyGanics® • Avon Skin So Soft Bug Guard Plus SPF 30 Lotion®
Prohibited Field Clothing & PPE:	**Acceptable Field Clothing & PPE:**
New cotton clothing or water-resistant, waterproof or stain-treated synthetic clothing or boots; Gore Tex™ or Tyvek®	Natural fiber clothing (preferably cotton), well laundered without the use of fabric softeners; boots made with polyurethane, PVC or leather treated only with PFAS-free conditioner or waterproofing
Synthetic water-resistant or waterproof rain gear	Polyurethane or PVC rain gear
Prohibited Field Equipment & Supplies:	**Acceptable Field Equipment & Supplies:**
Teflon™ or unapproved low-density polyethylene (LDPE) materials (*LDPE sampling bags are acceptable*)	Stainless steel, silicon, acetate, polypropylene or high-density polyethylene (HDPE) materials
“Blue ice” or other synthetic ice substitutes	“Wet” ice
Waterproof field books or field forms (*e.g.*, Rite in the Rain©), spiral hard cover notebooks or adhesives (*e.g.*, Post-It Notes®)	Untreated (PFAS-free) paper field forms
Plastic clipboards or binders	Aluminum or Masonite® clipboards
Markers	Ball-point pens and pencils
LDPE or glass sample containers or containers with Teflon-lined caps	HDPE or polypropylene sample containers, sample container with unlined polypropylene caps
Decon 90™	Alconox® or Liquinox®
All food and drink are prohibited during sampling activities with the exception of bottled water and hydration drinks (e.g., Gatorade, Powerade).	

Attachment 2 – PFAS Equipment Checklist

Paperwork/Materials

- Business Cards
- Ohio EPA PIC inquiry cards
- Maps
- Site addresses & contact information
- COC forms, field forms, log books
- UPS/FedEx overnight air bill forms

Field Clothing/PPE

- Field Crew is wearing well-worn cotton clothing (synthetic fabric should be avoided)
- All safety boots made from poly/PVC or leather (not treated with PFAS waterproofing)
- Wet weather gear only made of polyurethane or PVC only
- Cotton covers for field vehicle seats

Cross Contamination Check List

- Field crew has not used PFAS-containing cosmetics, moisturizers, hand cream, sunscreen, insect repellant or related products on day of sampling.
- Field crew is not wearing clothing laundered with fabric softener/dryer sheets
- No Gore-Tex or Tyvek clothing/boots
- No Teflon or unauthorized LDPE materials
- No blue ice/chem gel packs
- All sample materials made from SS, HDPE, acetate, silicon, or polypropylene
- No waterproof books/labels/paper on site
- No plastic clip boards, or spiral hard cover notebooks on site
- No adhesives (Post-It Notes) on site
- No aluminum foil or fast food wrappers

Handwashing & Field Decontamination

- Alconox, Liquinox or plain bar soap (no moisturizers) only

Food

- No food or drink in sampling area; food and drink should only be available in or outside the staging area

Disposables/Field Equipment

- Powderless nitrile gloves
- Sample table
- 25’ garden hose (5/8” diameter)
- Tool kit (wrenches/drivers)
- 5-gallon PVC buckets
- Garbage bags for waste/coolers
- Sample cooler liners (large plastic bags)
- Sampling bags
- Paper towels
- Ice
- Sample & QA/QC bottles
- Ball point pens or pencils for labeling
- Field log book/loose-leaf papers (appropriate material)
- Clipboard (aluminum w/cover)
- Clear poncho for rain/snow sampling cover (polyurethane or PVC only)

APPENDIX E
PFAS FIELD SAMPLING PROTOCOL CHECKLIST

Stantec

PFAS Field Sampling Protocol Checklist

Project name: ______________________________ Project Number: ________________
Project Manager: ______________________________ Date: ________________
Field Personnel ______________________________

Checklist 1.

Complete prior to mobilizing to Site. **Do not sample if you answer no to any of the following items under Checklist 1.**

Field Gear

Did you refrain from wearing water-resistant, water proof, or stain-resistant clothing?	Yes ☐ No ☐
Were your clothes laundered with minimal soap, no fabric softener or scented products, and rinsed before drying?	Yes ☐ No ☐

Personnel Hygiene

Did you refrain from using shampoo, conditioner, body gels, scents, cosmetics or hand creams on the day of sampling?	Yes ☐ No ☐
Did you wash your hands and rinse with PFAS-free water prior to doning powderless nitrile gloves for sampling?	Yes ☐ No ☐

Checklist 2.

Complete during/after sampling.

Field Gear

Were gloves changed prior to and following these activities: Yes ☐ No ☐

- Removing/putting on steel-toed boots/fire retardant clothing
- Decontamination of re-usable sampling equipment
- Handling any QA/QC samples (field blanks, trip blanks, etc.)
- Putting labels on PFAS sample containers

Did you use a pencil/ball point pen for all field notes and labeling sample bottles?	Yes ☐ No ☐
Did you record field notes on separate non-coated sheets of paper?	Yes ☐ No ☐

Personnel Hygiene

Did you refrain from collecting samples within 30 feet of a washroom or port-a-potty?	Yes ☐ No ☐

Food Considerations

Did you refrain from using paper bags and did not bring food on site in any paper packaging (i.e. fast food that uses any form of paper packaging)?	Yes ☐ No ☐
Did you avoid eating food within 10 metres of the sampling locations?	Yes ☐ No ☐

Signature (field personnel) ______________________________ Date ________________

Signature (project manager) ______________________________ Date ________________

APPENDIX F
EXAMPLE FIELD FORMS

LOW-FLOW GROUNDWATER SAMPLING FIELD DATA SHEET **GAUGE & SAMPLE**

PROJECT NUMBER:________________________ DATE: ____________________ WELL ID: __________________
FACILITY NAME: Norfolk Southern – East Palestine, Ohio TEMPERATURE: ____________ ºF
FIELD PERSONNEL:__________________________________ WEATHER:______________________________

FIELD MEASUREMENTS:

A. Depth to Static Water Level from top of casing: __________ FT.

B. Depth to Free NAPL from top of casing (Thickness, if present: _________ FT.): N/A FT.

C. Total Depth of Well from top of casing: __________ FT.

D. Depth of Screened Interval from top of casing: __________FT.

PURGING METHOD: Low Flow Flow rate (mL/min): ________ WATER QUALITY METER: YSI S/N:_________________

PUMP TYPE (circle): Submersible, Bladder, or Peristaltic

OBSERVATIONS: TUBING INLET DEPTH: ______________ feet below TOC

Time	**Volume Removed (G)**	**Depth to Water (ft below TOC)**	**Color (visual)**	**pH ± 0.2**	**Conductivity (mS/cm) ± 3%**	**Turbidity (NTU) ± 10% or <10**	**Dissolved O_2 (mg/L) ± 0.3 mg/L**	**Temperature (°C) ± 0.5% °C**	**ORP (mV) ± 20mV**

Flow rate for purging and sampling should not exceed 500mL/min. Total drawdown in well should not exceed 0.30 ft.
Read parameters every 5 minutes. Sample well when the changes between three consecutive readings are each within the following ranges:
pH ± 0.2 unit Conductivity ± 3% Turbidity ± 10% or if <10 NTU then 3 consecutive readings <10 NTU is stable
Dissolved O_2 ± 0.3 mg/L Temperature ± 0.5°C ORP ± 20 mV

SAMPLES COLLECTED:

Sample ID & Date	Time	Number of Containers	Preservative	Analytical Parameter
______________	_________	(4) 40 mL VOAs	Ascorbic acid & HCL	524.2
		(2) 40 mL VOAs	Unpreserved	8015
______________	_________	(2) 1 L Amber	Unpreserved	8270
		(2) 1 L Amber glass	Sodium Sulfite & HCL	525.2

COMMENTS: Start Pump @ **Stop Pump @** **Pump run time:**

Total purged:

Signature: ________________________

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ESFF2.08 - WELL DEVELOPMENT / PURGING

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Project Name: ______________________________ Project Number: ______________________________
Project Manager: ______________________________ Date: ______________________________
Field Personnel: ______________________________ Weather: ______________________________

Monitoring Location ID: ______________________________ **Location Description:** ______________________________

Inital Water Level (mBTOC): ____________ **Total Depth (mBTOC):** ____________ **Height of Water (m) =** Total depth (mbrp) - initial water level (mbrp) = __________ **m**
Well Diameter (inches): ____________ x 0.0127 = **Well Radius (m):** ____________ **One Well Volume =** 3.14 * well radius (m) * well radius (m) * height of water (m) * 1000 = __________ **litres**
(for 1.25" diameter well, 1 m of water = 0.8 L, for 2" diameter well, 1 m of water = 2 L)

SAMPLING METHOD: ☐ Low-Flow (Peristaltic Pump) ☐ Watterra Manual ☐ Watterra Hydrolift ☐ Submersible Pump (Model ________________) ☐ Bailer ☐ Other ______________________________

Time	Intake Depth (mBTOC)	Total Volume Removed (L)	Water Level after volume removed (mBTOC)	Temperature (°C) +/- 0.5	Specific Conductance (µS/cm or mS/cm) +/- 3%	Conductivity (µS/cm or mS/cm) +/- 3%	pH (Std. Units) +/- 0.2	Oxid./Red. Potential [ORP] (mV) +/- 20 mV	Turbidity (NTU) +/- 10% or <10	DO meter reading (mg/L) Note: Titration prefered for WRM projects the greater of +/- 10% or 0.2 mg/L	Comments
					circle appropriate units						
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											

Dissolved Oxygen Titration Analysis: DO Bottle #: N/A
Time of Sample Collection:
Number of Bottles: N/A
Sample Identification: N/A
Which bottles were field filtered?: N/A

General Comments / Well Recovery (low, medium, high) / Well Conditions

Quality Control: This form is complete (__) & legible (__).

check (_ √_)

Signatures: ______________________________ ______________
(field personnel) (date)

Signatures: ______________________________ ______________
(project manager) (date)