Potable Water Sampling Work Plan Update

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

April 26, 2023

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POTABLE WATER SAMPLING WORK PLAN UPDATE

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ACRONYM LIST

ºC	degrees Celsius
CCHD	Columbiana County Health District
COC	Chain of Custody
DERR	Division of Environmental Response and Revitalization
DQO	Data Quality Objective
DWS	Drinking Water Standard
FSOP	Field Standard Operation Procedure
GIS/GPS	Global Information System/Global Positioning System
HASP	Health and Safety Plan
ID	Sample Identification
IDW	Investigation-derived waste
JSA	Job Safety Analysis
MCL	Maximum Contaminant Levels (USEPA)
ug/L	micrograms per liter
µS/cm	microSiemens per centimeter
mg/L	milligrams per liter
MS/MSD	Matrix Spike/Matrix Spike Duplicate
mV	milliVolts
NSRC	Norfolk Southern Railway Company
NTU	Nephelometric Turbidity Units
OAC	Ohio Administrative Code
ODH	Ohio Department of Health
OEPA	Ohio Environmental Protection Agency
PADEP	Pennsylvania Department of Environmental Protection
PFAS	Per- and Polyfluorinated Substances
Plan Update	Potable Water Sampling Work Plan Update

PPE	Personal Protective Equipment
PWS	Public Water System
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
Responders	NSRC, its consultants, or contractors
RSL	Regional Screening Levels (USEPA)
SOP	Standard Operating Procedure
SVOC	Semi-Volatile Organic Compound
US EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

Revision	Description	Date
0	Issued for internal review	Report Date
1	Update of Documentation	March 3, 2023
2	Update of Documentation	March 5, 2023
3	Update of Documentation	March 27, 2023
4	Update of Documentation based on 3/31/23 comments	April 3, 2023
5	Updated	April 5, 2023
6	Updated	April 19, 2023
7	Updated	April 26, 2023

1.0 INTRODUCTION

On February 3, 2023, a derailment occurred near the North Pleasant Drive crossing in East Palestine, Columbiana County, Ohio. 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 continue 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 certain additional removal activities to protect human health and the environment.

This Potable Water Sampling Work Plan Update (Plan Update) has been developed to monitor drinking water 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 work plan will be conducted in accordance with the Quality Assurance Project Plan (QAPP), 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.

A Potable Water Sampling Plan was submitted to the Potable Water Working Group, which consists of Ohio Environmental Protection Agency (OEPA), Ohio Department of Health (ODH), and Columbiana County Health District (CCHD) on February 10, 2023. This Plan Update was developed on behalf of NSRC by Stantec Consulting Services Inc. (Stantec) for the East Palestine Train Derailment Site East Palestine, Ohio (Site). The Plan Update builds upon and amends the February 10, 2023, Potable Water Sampling Plan developed by AECOM for NSRC.

2.0 OBJECTIVE

This Plan Update has been developed to monitor drinking water quality in the vicinity of the Site in accordance with the UAO. The sampling program was initially developed in coordination with the US EPA, OEPA, CCHD, ODH, and the Pennsylvania Department of Environmental Protection (PADEP). Currently, co-located samples are collected by NSRC consultants and CCHD in Columbiana County from private and public water system (PWS) supply wells. In Pennsylvania, samples are currently collected with PADEP, or their designee. Co-located sampling will be conducted with stakeholders, as approved by, and directed by the UE EPA. Further details on co-located sampling are provided in Section 4.3.5.7.

NSRC is reviewing the area for the presence of potable water wells and collecting samples for analysis to evaluate if groundwater in the area has been affected by the release following the derailment. The list of chemicals of concern to inform delineation of the extent of contamination for drinking water sources, as required by the UAO, represents what was on train, what subsequently is detected in surface water and sediment, and what is potentially toxic to human health. Degradation products and combustion products associated with chemicals released were also considered. Under this work plan, potable water sources are defined as private drinking water wells PWS supply wells (transient and non-transient), and springs that discharge into tanks and are used for supplying drinking water. Other well usage types, such as cisterns and/or agricultural irrigation wells, will be added to the scope of work as requested by US EPA. Sentinel wells are being installed between the derailment site and private and public drinking water wells. The sentinel well program objective is to delineate potential impacts to groundwater within the upper most aquifer downgradient of the release and is presented under a separate plan (*Sentinel Well – Monitoring Well Installation and Groundwater Sampling Work Plan*, Stantec, 2023). The locations of the sentinel wells installed as of the date of this work plan are presented on Figure 1. Implementation of this plan will be completed by NSRC, its consultants, or contractors (Responders). The study area for the potable well sampling program includes the following:

- Priority Zones 1 and 2 - established by ODH (Figure 1).
- Priority Zone 3 - drinking water sources within a 1-mile radius from the derailment, per the UAO (Figure 1)
- Priority Zone 4 - 250-foot buffer from the center line of the contaminated surface waters from unnamed ditch (at the location of the derailment, which feeds into Sulphur Run) and other downstream surface waters that lead to the Ohio River (Figure 2).

Any changes in Priority Zone designations or boundaries will be discussed with NRSC, US EPA, OEPA, ODH and CCHD, as appropriate. Additional sampling may be performed as additional data is received, if further evaluation is needed, and as directed by US EPA. Adjustments to this work plan may be made accordingly. Changes in scope, bounds of study, and/or analytical lists will require an update.

Proposed activities for Priority Zones 1, 2, 3 and 4 are summarized below:

- Obtain signed access agreements for each private well requested to be sampled and PWS supply wells prior to collecting samples,
- Collect groundwater samples from private potable and PWS supply wells.

The protocols established in this Plan Update have been prepared to assist in sampling potable water sources, by defining sampling procedures and schedules, refining the compounds of concern, and defining how results will be communicated to NSRC, responding agencies, and affected residents to meet the requirements of the UAO.

The associated OEPA Division of Environmental Response and Revitalization (DERR) Field Standard Operating Procedures (FSOPs) and US EPA Standard Operating Procedures (SOPs) are as follows (Appendix A):

Table 1 Standard Operating Procedure References

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
ASBPROC-305-R4	Potable Water Supply Sampling (June 11, 2019)	US EPA	This procedure describes general practices for collecting potable water samples from tap or spigot.
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 2.2.11	Sampling Water Supply Systems (January 5, 2021)	OEPA DERR	This procedure provides general information for collecting a representative water sample from a water supply system tap.
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
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

Reference Number	Title, Revision Date and / or Number	Originating Organization of Sampling SOP	Comments
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	U EPA 533	Method for analysis of PFAS in Water

3.0 HEALTH AND SAFETY

This work will be conducted under an approved an 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 Update. The HASP will include a job safety analysis (JSA) for each task described in this Plan Update 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 inclusive of the names of those in attendance and items discussed. NSRC-specific protocols will be followed. The JSAs will be updated when conditions change.

4.0 SCOPE OF WORK

4.1.1 Study Area

The current study area is inclusive of 4 priority zones in Ohio and Pennsylvania. The areas were defined in part based on the regional inferred groundwater flow direction, surface water flow, and the watershed basin (Figure 3). Information shown on Figure 3 is preliminary and based on a small, incomplete data set. Inferred groundwater flow directions are subject to revision as additional monitoring wells are installed and gauging events, including surface water elevations, are conducted.

4.1.2 Sampling Frequency and Duration

Currently, groundwater sampling is conducted weekly at the five PWS wells (PW-201 through PW-205), the effluent (PW-207) and one transient PWS supply well (PW-21). This sampling frequency may be increased if results from sentinel well monitoring identify impacts of chemicals of concern. The frequency may be decreased upon US EPA approval. The scope of work will not include sampling cisterns. If springs are hard plumbed to the house, the location will be sampled, if requested. Potable water sampling, as currently scheduled, will be continued until the extent of contamination at the derailment site is defined, and concurrence to stop sampling is obtained by US EPA, OEPA and CCHD. Sampling frequency may be revised once an appropriate sentinel well monitoring network is in place. Subsequent or longer-term sampling will be further discussed and worked out with appropriate State and/or local agencies.

Private potable wells will be sampled at least once, if provided access by the property/well owner. Additional samples will be collected if the resident/well owner will allow access and additional monitoring of their well, as described in the QAPP. End points and decision criteria are presented in Table 2. If a result exceeds drinking water standards for a chemical of concern, the owner will be contacted as soon as possible to be notified and schedule re-sampling.

If monitoring at sentinel wells indicates a plume of contamination is present and may potentially impact the PWS wellfield, monitoring frequency at the supply wells and treated water (PW-207) may be increased.

Evaluation of groundwater flow and contaminant fate and transport though groundwater flow modeling will be part of the scope of work under the Sentinel Well Work Plan under separate cover. The results of modeling may be used to modify sampling frequency, duration and and/or extent of the study area, if determined necessary.

Table 2: Project Objectives

Investigation Question	Action
What are the analytical results (Stantec or co-located, if provided) from potable water at private potable well or transient public water system supply well compared to selected screening	If the analytical results for the compounds of concern (Table 4) are below selected the laboratory reporting limit and selected screening

criteria for analytes that are associated with the incident in Priority Zones 1, 2 or 3 (1-mile radius from incident, excludes portion contained within Priority Zone 1)? Stantec validated data and co-located data (if provided) will be reviewed. If results between Stantec and co-located samples (if provided) have an RPD (>40) that is significant, the Stantec validated data will take precedent.	criteria, then additional sampling will be conducted every 30 to 45 days until the sentinel monitoring network is established and shows no risk to potable wells and the mainline source removal is completed. If analytical results for the compounds of concern (Table 4) exceed screening criteria for an analyte associated with the incident, then the stakeholders and owner will be immediately notified, and re-sampling will be initiated. In addition, bottled water may be provided for the resident.
What are the analytical results (Stantec or co-located, if provided) from potable water at private potable wells compared to selected screening criteria for analytes that are associated with the incident in Priority Zone 4 (250-foot buffer)? Stantec validated data and co-located data (if provided) will be reviewed. If results between Stantec and co-located samples (if provided) have an RPD (>40) that is significant, the Stantec validated data will take precedent.	If the analytical results for the compounds of concern (Table 4) are below selected the laboratory reporting limit and selected screening criteria, then no additional samples will be collected. If analytical results for the compounds of concern (Table 4) exceed screening criteria for an analyte associated with the incident, then the stakeholders and owner will be immediately notified, and re-sampling will be initiated. In addition, bottled water may be provided for the resident.
What are the analytical results (Stantec or co-located, if provided) from potable water at public water system supply wells (i.e. PW-201 through PW-205) and effluent (PW-207) exceed selected screening criteria for analytes that are associated with the incident? Stantec validated data and co-located data (if provided) will be reviewed. If results between Stantec and co-located samples (if provided) have an RPD (>40) that is significant, the Stantec validated data will take precedent.	If the analytical results for the compounds of concern (Table 4) are below laboratory reporting limits, then additional sampling will be conducted weekly until the extent of ground water contamination at the derailment site is defined and along the impacted creeks is delineated and concurrence to stop sampling is obtained by US EPA, OEPA and CCHD. If analytical results for the compounds of concern (Table 4) exceed screening criteria for an analyte associated with the incident, stakeholders and owner will be immediately notified and re-sampling will be initiated. If analytical results from the sentinel well monitoring identify impact of chemicals of concern, the sampling frequency may increase. The frequency of effluent monitoring will be increased to once per day.

4.2 SAMPLE LOCATIONS AND ACCESS

The Responders will obtain access and subsequently collect water samples from identified public and private properties located in the vicinity of the Site in coordination with US EPA, OEPA, ODH, and CCHD.

The following sections outline the identification of properties and access.

4.2.1 Property Identification

Residents with potable water supply wells that they would like to be sampled may call the Residential Re-Entry Request Hotline at (330) 849-3919. The request will be evaluated to determine if the well will be included in the sampling program using the following methodology:

- Private potable water wells located in Priority Zones 1 and 2 defined by ODH will be targeted for sampling. Priority Zones may be expanded based on the results.
- Owners of drinking water sources that have requested their well to be sampled within Priority Zone 3, a 1-mile radius from the derailment. Wells located within Zone 3 in Ohio and Pennsylvania will be included in the sampling program.
- Priority Zone 4 is a 250-foot buffer from the center line of the contaminated surface waters from unnamed ditch (leading to Sulphur Run) to the Ohio River will be targeted for sampling, per the UAO. Depending on the results of those samples, additional properties may be added to the sampling program. The buffer zone may be expanded based on the results.
- The PWS supply wells associated with the Village of East Palestine and the State Line Tavern transient PWS supply well will also be sampled. Sampling of the effluent (treated water) will also be conducted.
- Wells located outside of Priority Zones 1 through 4 that are requested to be sampled through community outreach will be discussed with the US EPA, OEPA, ODH, CCHD, and PADEP prior to sampling.
- For sampling requests at properties located outside of the study areas described above, a path forward, will be determined at a later date by the OEPA.

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Authorized access to each private property will be obtained, in accordance with the Communication Plan for Potable Water Sampling (under separate cover).

4.3 SAMPLE COLLECTION AND FIELD ACTIVITY PROCEDURES

4.3.1 Scheduling

For wells selected for inclusion in the sampling program, Stantec contacts the owner directly to schedule sampling with the resident.

4.3.2 Field Activities

The following process will be followed to collect potable water samples:

- Property surveys will be conducted to the extent practicable to collect information regarding well design and usage.
    - Water usage – potable and/or agricultural, etc.
    - Well logs
    - Location on property using Global Positioning System (GPS) technology, if possible. If the exact location of the well is beneath a structure or is otherwise obscured, then the nearest structure will be used as the location.
    - Historical testing of water
- Sampling will be scheduled with property owners once access has been granted and specific sampling procedures have been approved by NSRC and regulatory agencies.
- Potable water samples will be collected.

4.3.3 Preparation for Field activities

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

- Develop sampling list for the day in coordination with NSRC and regulatory agencies, as necessary
- Designate a Safety Officer
- Complete required health and safety paperwork and confirm field team members have completed required training
- Gather appropriate PPE, including but not limited to nitrile gloves.
- Confirm sample bottles with appropriate preservatives, coolers and analyte-free deionized water are obtained, and sampling and sample arrival dates are communicated to the laboratories
- Obtain required functional and calibrated field instruments, including health and safety equipment
- Complete sample paperwork, including chain-of-custody forms and sample labels
- Obtain ice daily prior to beginning work for sample preservation.

4.3.4 Well-Owner Questionnaire

The property survey will be conducted prior to the date of first sample collection or on the same date of sample collection. The property survey will be reviewed with the well owner prior to subsequent sampling events to document any changes or additional information that may be available during those events.

The survey process will include filling out a well-owner questionnaire with the property owner to obtain available information about the potable water source including:

- Presence of wells, springs, or cisterns
- Well construction details as applicable (i.e., depth, construction material, installation date, etc.)
- Uses of water (irrigation, agricultural, residential, etc.) or if the well is not in use
- Is the water treated onsite (i.e. for hardness or filtered), and which taps receive treated or untreated water
- Septic system type and location (if present, known or identifiable) relative to well location
- Determine if the well source has ever gone dry or if water supply is a concern
- Water quality concerns or complaints if any
- Is there a water storage tank on the property and if so, tank capacity.

During the initial survey, the field technician will collect photos of the water supply system including plumbing, filtration systems that may be present, and storage tanks connected to the system. Photos will be collected of the heater and fuel storage units that may be present (i.e., heating oil tank, propane tank).

As part of the initial survey, photo documentation will be collected of the water supply (i.e., well, spring box, cistern). Details will be collected of the condition of the water supply as applicable (i.e., material, integrity, condition of the cap seal). Photos will be collected during the initial survey of the water supply and the surrounding area. During subsequent sampling events, photos will only be taken of the point of sample collection, and changes in water supply system, heater and fuel storage units, and surrounding areas.

Once the survey is complete, a potable water sample will be collected from the property. If sampling is refused or the sampling team is unable to sample the location, the reason will be documented on the field forms.

4.3.5 Sampling Methods and Procedures

Sampling water supply systems will be completed in general accordance with the OEPA DERR FSOP 2.2.11 in Appendix A. Potable water sampling will be completed in general accordance with the EPA analytical methods and the US EPA Potable Water Sampling SOP (ASBPROC-305-R4) in Appendix B. The wells will be sampled using a method to collect valid and representative samples from a potable water supply, as described in the SOPs.

If Per- and Polyfluorinated Substances (PFAS) sampling is requested by US EPA, private potable water samples will be collected in accordance with the *OEPA SOP For Per- and Polyfluorinated Alkyl Substances Sampling at Public Water Systems (March 3, 2020)* in Appendix C and the *PFAS Field Sampling Protocol Checklist* in Appendix D. PFAS analysis has been included in PWS supply wells and

the PWS transient supply well and additional monitoring for PFAS may be conducted if determined necessary based on laboratory analytical results and if requested by US EPA.

4.3.5.1 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 and, if necessary, repairs will be made prior to equipment use. If equipment is not in the proper working condition, that piece of equipment will be repaired prior to use or taken out of service and replaced. Additional information regarding field equipment inspection and testing is included in the QAPP.

4.3.5.2 Field Documentation

Field documentation associated with investigation activities will be recorded on either digital or paper field forms (Figure 4 – Example of Potable Well Questionnaire and Sample Form) and using geographic information system (GIS)/ GPS documentation, when appropriate. Additional information regarding field documentation is provided below and included in the QAPP.

4.3.5.3 Field Logs

Field observations and measurements will be recorded and maintained on days that samples are collected to document field activities, including sample collection and management. Field observations and measurements will be recorded on the Potable Well Questionnaire and Sampling Form, and/or a similar paper or digital form (Figure 4). Deviations from applicable work plans will be documented in the field forms during sampling and data collection operations.

4.3.5.4 Chain-of-Custody Forms

Samples will have chain-of-custody (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 and a QC check of samples in each cooler compared to sample identifications (IDs) on the COC form.

4.3.5.5 Photographs

Photographs of field activities will also be used to document the field investigation. A photo log will be developed, and each photo in the log will include the location, date taken, and a brief description of the photo content.

4.3.5.6 Water Sampling Forms

A water sample collection form will be used to document sampling activities including but not limited to description of the sampling location, location of water treatment (before or after sample location), water purging duration, water quality parameter measurements, color or odor, and other observations on the Potable Well Questionnaire and Sampling Form or similar. An example form is provided as Figure 4.

4.3.5.7 Co-located Sampling

Co-located sampling may be conducted when sampling is concurrent with CCHD 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. The samples will be submitted to separate laboratories.

4.3.6 General Sampling Procedures

Prior to sampling, a 15-minute purge will be conducted in general accordance with the EPA test methods and US EPA Potable *Water Supply Sampling* (ASBPROC-305-R4, 2019) protocols (Appendix B). a multi-parameter meter will be used to record conventional water parameters at the sampling point. Water quality measurement instruments will be calibrated and used in accordance with the QAPP. Conventional field parameters to be measured include:

Dissolved Oxygen (milligrams per Liter, mg/L)

Oxidation Reduction Potential (millivolts, mV)

pH (Standard Units)

Specific Conductance (microSiemens per centimeter [µS/cm].

Temperature (degrees Celsius, ºC)

Turbidity (Nephelometric Turbidity Units, NTUs)

The sampling point will be selected from within the water piping system as close to the wellhead as possible but prior to the addition of water softeners, filters, treatment systems and holding tanks when possible. If a sample cannot be collected prior to a water treatment device, the type of treatment device will be documented in the sampling form. Aerators and screens/fixtures attached to the faucet will be removed prior to sampling. The system will be purged by allowing cold water to run for at least 15 minutes. During purging, three sets of field parameters will be collected within the 15-minutes. If field measured water quality parameters have not stabilized after 15 minutes of purging, the sampler will document the condition, record the final field parameter values, and collect a sample.

The appropriate bottles for each analysis will be filled, labeled, documented, packaged, and shipped in accordance with this Work Plan and the QAPP.

4.3.6.1 Water Sampling from a Tap

Water samples will be collected directly from a faucet or pipe valve, with screens/fixtures removed or from the screenless/fixtureless faucet directly into laboratory-supplied bottle ware utilizing new, clean High-density polyethylene (HDPE) tubing connected to the tap/faucet. The tubing will be connected to the tap/faucet via a properly decontaminated adapter with a ribbed nipple that will be screwed on the faucet outlet, if needed. The sample will be collected at the indoor or outdoor tap closest to the wellhead, prior to

water treatment devices. If a sample cannot be collected prior to a water treatment device, then the type of treatment device will be documented in the sampling form.

4.3.7 Sample Preservation and Handling

Samples intended for analysis at a Eurofins laboratory location or other approved laboratory will follow the procedures in this section and the associated QAPP, for sample preservation and handling. Once each sample container is filled, the lid will be secured, and each sample container will be checked to ensure that it is sealed, labelled legibly, 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.

The original COC form will be placed in a re-sealable plastic bag taped to the inside lid of the cooler. A copy of the COC form will be retained with the sampling form 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 with copies (marked as such) 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 (if present) 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.

4.3.8 Equipment Decontamination Procedures

Equipment decontamination will be performed for non-dedicated sampling equipment and instruments that come in contact with groundwater to prevent cross-contamination.

Decontamination activities will be performed away from sampling areas. Decontamination of non-disposable sampling equipment or instruments can be performed using water and Liquinox® or other

appropriate non-phosphatic detergent in 5-gallon buckets. Following decontamination, fluids will be disposed in accordance with Section 4.3.9.

Decontamination of sampling equipment and instruments (i.e., water quality cups/probes etc.) will be performed in accordance with OEPA FSOP 2.2.4 (Appendix A) prior to use and between sampling locations. Decontamination activities will be documented in the field notes.

Additional information regarding equipment decontamination procedures is in the QAPP.

4.3.9 Waste Management

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

- Personal Protective Equipment
- Decontamination fluids
- General trash.

IDW will be handled in accordance with the waste management plan, and local, state, and federal regulations. Transportation and disposal of IDW will be coordinated with NSRC and Incident Command Center personnel.

4.4 SAMPLE ANALYSES

Samples have been analyzed for all or part of the analytes listed on Tables 3 by the indicated analytical methods presented in the QAPP. Table 3 represents a combined list of initial round residential potable water samples and subsequent private residential potable water samples and PWS well samples. The samples have been analyzed for all or part of the following: volatile organic compounds (VOCs) via USEPA Method 524.2 and semi-volatile organic compounds (SVOCs)/pesticides via USEPA 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 (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. Through the data validation process/chemical evaluation, compounds including, but not limited to bis(2-ethylhexyl) phthalate, acetone, methylcyclohexane may be attributed to laboratory contamination/interferants. This information has been utilized in the refinement of the analyte list. Bis(2-ethylhexyl) phthalate, acetone, and methylcyclohexane

will continue to be monitored and reviewed by the laboratory in accordance with their SOP to discern if the chemicals are interferants.

Upon further evaluation, the analyte list presented in Table 4 has been refined for subsequent sampling events. This list has been further refined during the development of this Plan Update in coordination with stakeholders to eliminate compounds that are not associated with the incident and/or do not have established screening criteria for comparison (for example, ethanol). The analyte list presented in Table 4 will be utilized going forward for all analyses associated with this work plan, both private potable and PWS supply wells. Table 4 may be refined 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.

EPA has requested further evaluation of the behavior and potential presence of degradation products (acrylic acid CAS 79-10-7, butanol CAS 71-36-3, butyraldehyde CAS 123-72-8, butanoic acid CAS 107-92-6) associated with chemicals released at the site. The referenced analytes are not included on the approved analyte list for the methods in use and other analytical methods have not been identified for these compounds. In addition, screening levels are not established for these compounds. An evaluation of these compounds as degradation products will be performed and a review of potential methods for analysis will be discussed with the laboratory. If an analytical method is identified, analysis will be conducted. Findings of the evaluation will be summarized in a technical memorandum. At this time decisions will not be made based on presence of these compounds.

If deemed necessary by US EPA, in consultation with OEPA, 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 analytes is presented in Table 5, along with applicable standards.

4.5 QUALITY ASSURANCE/QUALITY CONTROL

The QAPP describes quality assurance/quality control (QA/QC) requirements for the overall Investigation, including, but not limited to SOPs (preparation and analysis), quality manual, accreditations by analyte. The following sections provide details regarding QA/QC requirements specific to the potable water sampling.

4.6 OBJECTIVES

The Data Quality Objectives (DQOs) process is a tool employed during the project planning stage to make sure that data generated from an investigation are appropriate and of sufficient quality to address the investigation objectives. The investigation Project Manager considered key components of the DQO process in developing investigation-specific work plans to guide the data collection efforts for the investigation.

4.7 QUALITY CONTROL CHECKS

QA/QC samples will be collected during sampling activities: equipment rinsate blanks, field duplicate samples, matrix spike/matrix spike duplicate (MS/MSD) samples, and field blanks. 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 (ie: OH private potable wells, PWS supply wells, transient PWS supply wells, and PA private potable wells). 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 Table 6. 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 sampling form. 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, with the exception of 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, when non-dedicated equipment is used. The equipment blank will be collected by pouring organic-free deionized water into or over the decontaminated sampling equipment (e.g., groundwater pump), then into the appropriate sample containers. The time and location of collecting the equipment 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 for each sampling activity/event (OH private potable wells, PWS supply wells, transient PWS supply wells, and PA private potable wells) 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 6 summarizes the field quality control sample minimum frequencies.

Table 6 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 and prior to deploying/redeploying dedicated sample pumps

Notes: VOC - Volatile Organic Compounds; MS/MSD - Matrix Spike/Matrix Spike Duplicate

4.7.1 Sample Labels and Identification System

Sample 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.

Groundwater samples collected for laboratory chemical analysis will be labelled as follows (As of the date of this Plan Update):

- Two-letter prefix describing the sampling program
    - PW for Potable/Private Residential Wells sampling
        - Three-digit sample location ID (001-999)
        - One-letter designation if multiple wells exist on a property (A-C)
    - PWS wells: PW-201, PW-202, PW-203, PW-204, PW-205 and
    - PWS effluent: PW-207
    - SP for Spring sampling
- Date as YYYYMMDD

QA/QC sample nomenclature will utilize the acronyms in Table 6.

Examples:

PW-006-20230301 – this is a private well sampled on March 1, 2023

PW-007A-20230301 – More than one well exists on the property. This is one private well on the property sampled on March 1, 2023

PW-007B-20230301 – More than one well exists on the property. This is a second private well on the property sampled on March 1, 2023

SP -001-20230301 – this is a sample collected from the spring on March 1, 2023

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

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

5.0 DATA EVALUATION AND REPORTING

The results of the analysis will be reviewed following data validation and compared to selected screening Drinking Water Standards (DWSs) in units of micrograms per liter (ug/L). DWSs for comparison to site data for drinking water sources sampled as part of this Plan Update have been established based on the following criteria, which will be applied in a stepwise fashion in the order identified below:

1. Analytes with criteria presented in Ohio Administrative Code (OAC) Chapter 3745-81 (OAC 3745-81) and US EPA Maximum Contaminant Levels (MCLs).

2. Analytes not listed in (OAC 3745-81) and 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.

3. 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).

For example, if an analyte has a standard in OAC 3745-81, then that will be the standard selected regardless of if other criteria, such as RSLs or MCLs exist.

A summary of the selected DWSs for the chemicals that will be analyzed for (chemicals of concern) are presented in Table 4. A report of all sampling events will be provided to NSRC, US EPA, OEPA, ODH and CCHD. De-identified results may be posted on CCHD website or other applicable location, if directed by US EPA.

For PWS supply wells (such as, PW-201, PW-202, PW-203, PW-204, PW-205 and PW-207 (effluent)) and transient PWSs (PW-21), preliminary results (non-validated) will be reviewed upon receipt from the analytical laboratory and if detections of chemicals of concern are found at level above criteria, stakeholders will be notified as soon as possible and additional sampling efforts will be initiated, as specified in the QAPP.

For private potable water wells, letters, supplemented by verbal communications will be used to provide owners with the results of the sampling in accordance with the Communication Plan to support the potable water sampling Plan Update.

The need for subsequent sampling event(s) will be determined in accordance with the QAPP.

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

TABLES

Table 3
Combined Analyte List with Selected Screening Criteria - Potable Well Sampling
Potable Water Sampling Work Plan Update
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	19	4
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

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Potable Water Sampling Work Plan Update
East Palestine Train Derailment, East Palestine, Ohio

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
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	
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	--	

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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 4
Analysis List with Selected Screening Criteria - Potable Water Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Analyte	CAS#	MDL	RL	Analytical Method[5]	Units	Selected Screening Drinking Water Standard
1,1-Dichloropropene	563-58-6	0.2	0.5	524.2	µg/L	0.47 [4]
1,2,4-Trimethylbenzene	95-63-6	0.2	0.5	524.2	µg/L	56 [2]
1-Methylnaphthalene	90-12-0	0.02	0.1	525.2	µg/L	1.1 [2]
2-Methylnaphthalene	91-57-6	0.01	0.1	525.2	µg/L	36 [2]
Acenaphthene	83-32-9	0.01	0.1	525.2	µg/L	530 [2]
Acenaphthylene	208-96-8	0.01	0.1	525.2	µg/L	12 [4]
Anthracene	120-12-7	0.01	0.1	525.2	µg/L	1800 [2]
Benzene	71-43-2	0.2	0.5	524.2	µg/L	5 [1,3]
Benzo[a]anthracene	56-55-3	0.01	0.1	525.2	µg/L	0.03 [2]
Benzo[a]pyrene	50-32-8	0.012	0.02	525.2	µg/L	0.2 [1,3]
Benzo[b]fluoranthene	205-99-2	0.01	0.1	525.2	µg/L	0.25 [2]
Benzo[g,h,i]perylene	191-24-2	0.02	0.1	525.2	µg/L	0.12 [4]
Benzo[k]fluoranthene	207-08-9	0.01	0.1	525.2	µg/L	2.5 [2]
Chrysene	218-01-9	0.01	0.1	525.2	µg/L	25 [2]
2-Butyloxyethanol (Ethylene Glycol Monobutyl Ether)*	111-76-2	1.1	4	8270C	µg/L	2000 [2]
2-Ethylhexyl acrylate*	103-11-7	0.5	0.5	524.2	µg/L	500 [4]
Dibenz(a,h)anthracene	53-70-3	0.01	0.1	525.2	µg/L	0.025 [2]
Ethylbenzene	100-41-4	0.2	0.5	524.2	ug/L	700 [1,3]
Fluoranthene	206-44-0	0.01	0.1	525.2	µg/L	800 [2]
Fluorene	86-73-7	0.0099	0.099	525.2	ug/L	290 [2]
Indeno[1,2,3-cd]pyrene	193-39-5	0.01	0.1	525.2	µg/L	0.25 [2]
m-Xylene & p-Xylene	179601-23-1	0.5	0.5	524.2	µg/L	19 [4]
Naphthalene	91-20-3	0.01	0.1	525.2	µg/L	0.12 [2]
n-Butyl acrylate	141-32-2	0.5	1	524.2	µg/L	560 [4]
o-Xylene	95-47-6	0.2	0.5	524.2	µg/L	190 [2]
Phenanthrene	85-01-8	0.01	0.1	525.2	µg/L	50 [4]
Pyrene	129-00-0	0.01	0.1	525.2	µg/L	120 [2]
Toluene	108-88-3	0.2	0.5	524.2	µg/L	1000 [1,3]
Vinyl chloride	75-01-4	0.2	0.2	524.2	µg/L	2 [1,3]

Notes:

CAS - Chemical abstract service

MDL - Method Detection Limit

RL - Reporting Limit

USEPA - United States Environmental Protection Agency

RSL - Regional screening level

-- - 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

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

*Analyzed by laboratory-modified method shown.

Table 5
Analyte Summary with Applicable Residential Standards for PFAS
Potable Water Sampling Work Plan
East Palestine Train Derailment, East Palestine, Ohio

Analyte	Abbreviation	CAS #	Units	Ohio Drinking Water Standards[a]	Pennsylvania MCLs[c]	USEPA Proposed MCL[d]
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	21		
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	ppt	--		--
Perfluorobutanoic acid	PFBA	375-22-4	ppt	--		--
Perfluorobutanesulfonic acid	PFBS	375-73-5	ppt	2100[b]		--
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	140[b]		--
Perfluorohexanoic acid	PFHXa	307-24-4	ppt	--		--
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	21[b]		--
1H, 1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	ppt	--		--
Perfluorooctanesulfonic acid	PFOS	1763-23-1	ppt	70	18	4
Perfluorooctanoic acid	PFOA	335-67-1	ppt	70	14	4
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

[a]Ohio Per- and Polyfluoroalkyl Substances (PFAS) Actoin Plan for Drinking Water (December 2019)

[b]Ohio PFAS - Technical Information and Supporting Documentation (January 2022)

[c] Pennsylvania Safe Drinking Water PFAS MCL Rule [53 Pa.B. 333] [Saturday, January 14, 2023]

[d]USEPA Proposed PFAS National Primary Drinking Water Regulation (March 2023)

FIGURES

1. Site Map – Priority Zones 1, 2, and 3
2. Site Map – Priority Zone 4
3. Watershed Basin Map
4. Example of Potable Well Questionnaire and Sample Form

Figure No.
1

DRAFT

Title
Site Map - Priority Zones 1, 2 and 3

Client/Project
Norfolk Southern

Project Location
East Palestine, Columbiana Co., OH

Prepared by BS on 2023-04-19

N

0 3,000 6,000 Feet

(At original document size of 11x17)
1:2,098,286

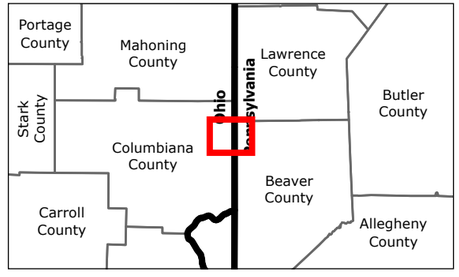
- Incident Area

Priority Sampling Zones

- Priority Zone 1
- Priority Zone 2
- Priority Zone 3
- Priority Zone 4
- Regional Inferred Groundwater Flow Direction
- Sentinel Wells
- Transient PWS Supply Well
- Private Potable Well (Sampling Requested)

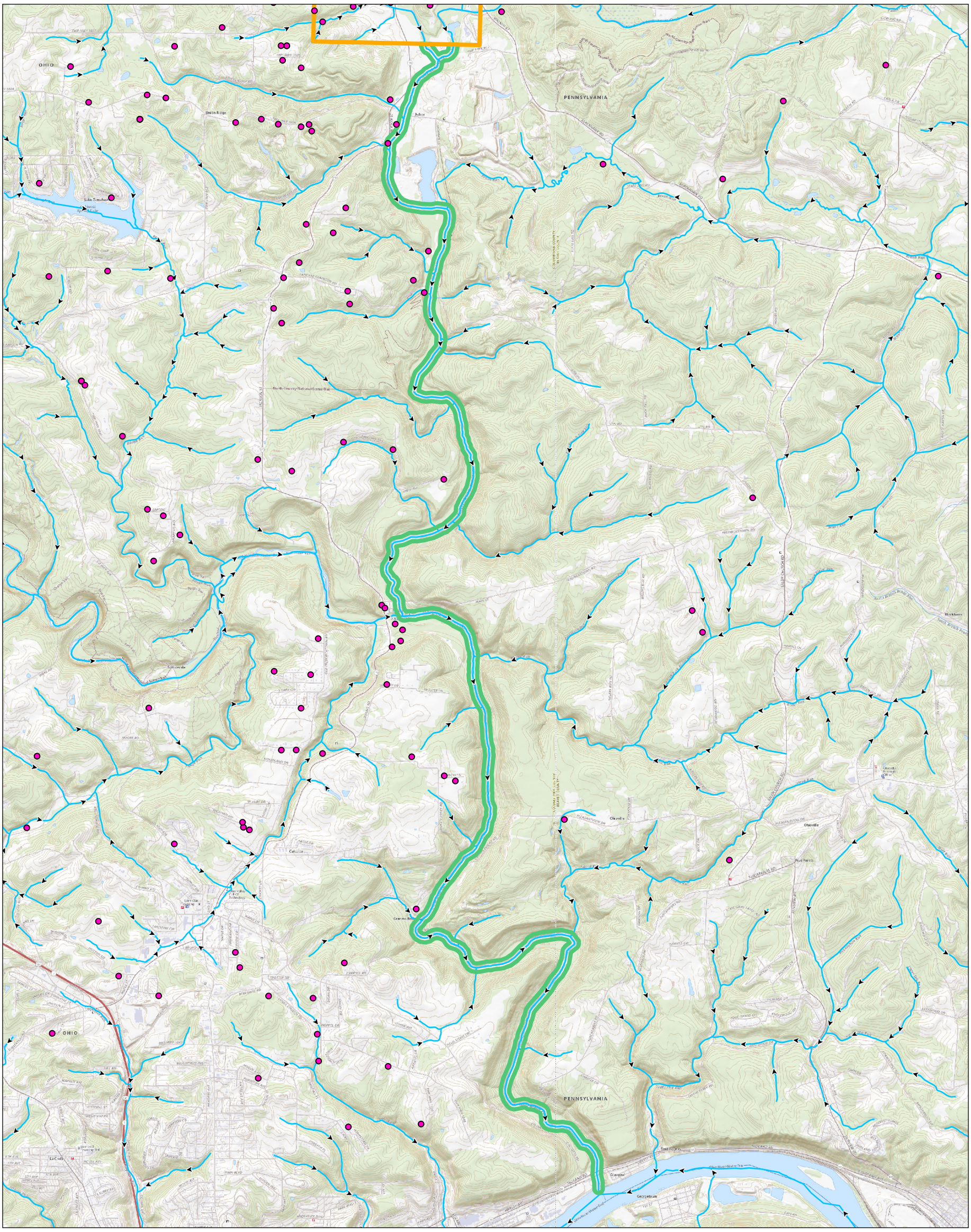
OHDNR Wells

- PWS Supply Well
- Watershed Boundary
- Streams



Notes
1. Coordinate System: WGS 1984 Web Mercator Auxiliary Sphere
2. Data Sources: USGS, ODNR
ODNR wells were obtained from Ohio DNR Water Wells Database - 03/21/2023
3. Background: USGS 7.5 Minute Quadrangle

Stantec



Priority Sampling Zones

- Priority Zone 2
- Priority Zone 4
- Streams
- Private Potable Well (Sampling Requested)

0 6,000 12,000 Feet

(At original document size of 11x17)
1:72,000

N

Stantec

Notes

1. Coordinate System: WGS 1984 Web Mercator Auxiliary Sphere
2. Data Sources: USGS, ODNR
ODNR wells were obtained from Ohio DNR Water Wells Database - 03/21/2023
3. Background: USGS 7.5 Minute Quadrangle

Project Location
East Palestine, Columbiana Co., OH

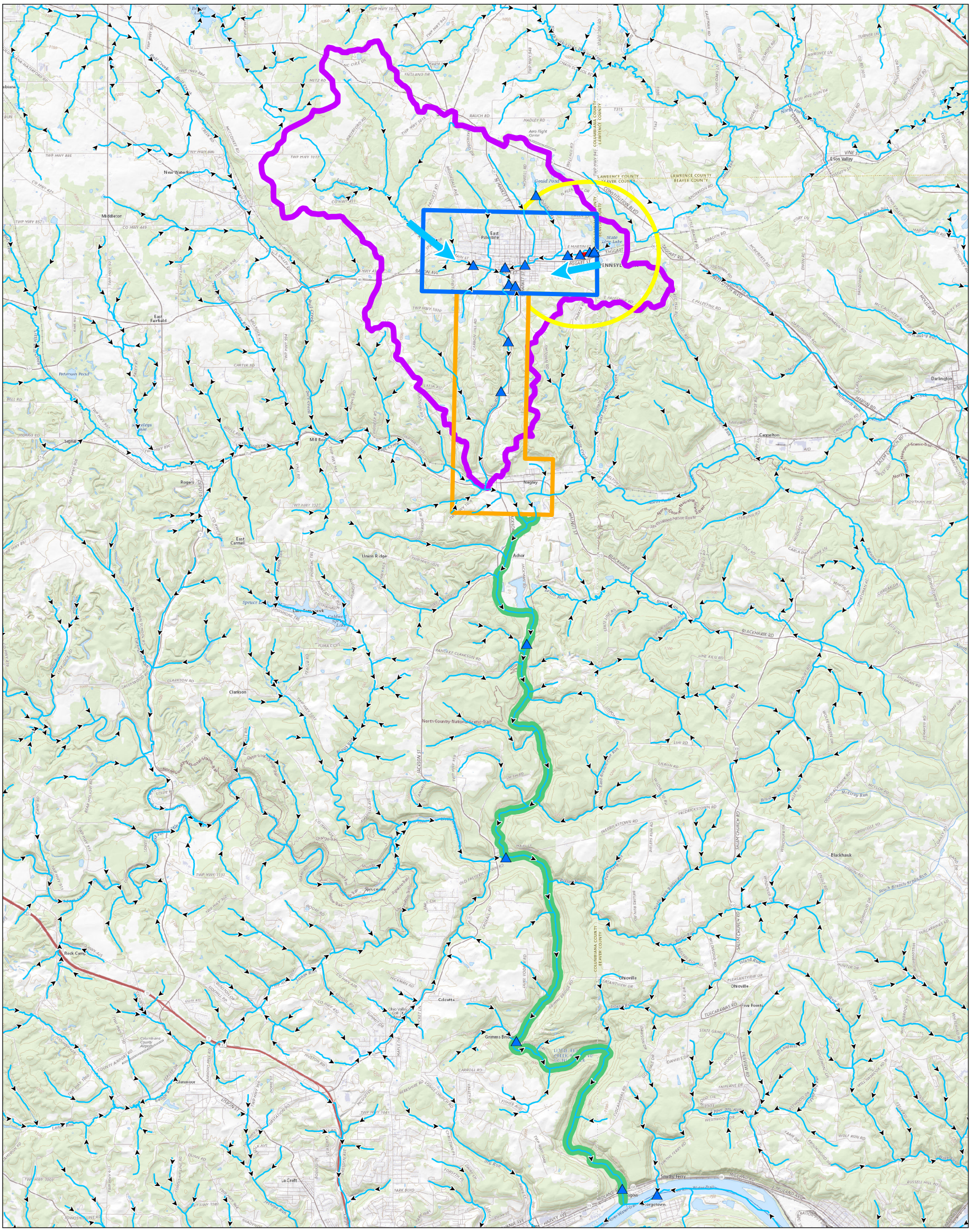
Prepared by BS on 2023-04-19

Client/Project
Norfolk Southern

Figure No.
2

DRAFT

Title
Site Map - Priority Zone 4



Mahoning County | Lawrence County | Columbiana County | Beaver County | Ohio | Pennsylvania

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

0 5,000 10,000 Feet

(At original document size of 11x17)
1:120,000

N

Stantec

Project Location
East Palestine, Columbiana Co., OH

Prepared by KAB on 2023-04-19

Client/Project
Norfolk Southern

Figure No.
3

Title
Watershed Basin Map

U:\Spill_Response\172607922\gis_cad\gis\pro\Norfolk_03212023\Norfolk_03212023.aprx Revised: 2023-04-19 By: ishuck

FIGURE 4 - EXAMPLE OF POTABLE WELL QUESTIONNAIRE AND SAMPLE FORM

Potable Water Sampling Questionnaire and Sample Form

Well ID: _____ Date: _____ Time: _____

Weather: _____ Staff: _____

Well Survey

Name of person(s) interviewed: _____

Contact info of person(s) interviewed (phone, email, etc.): _____

Location/Address: _____

_____

Well use (drinking water, watering lawn/agriculture, nothing, etc.): _____

Well construction information (if known)

Location (part of property, etc.) _____

_____

Date installed: _____ Driller: _____ Depth: _____

Surface Casing materials/construction (circle): PVC Steel Other

If other, describe: _____

Is a well liner present (circle) Yes No

Pump Intake Depth: _____ Type of pump: Submersible Jet Other

If other describe: _____

Are copies of well records available from the homeowner? Yes No

Is a holding tank present? Yes No Tank Capacity (gal): _____

Is the water treated? Yes No

If yes, where is the treatment system: _____
Describe system: _____
Which taps affected: _____

Sketch of water distribution system from entry point, filter, etc. Indicate sample collection point.

Signature: _____ Date: _____

FIGURE 4 - EXAMPLE OF POTABLE WELL QUESTIONNAIRE AND SAMPLE FORM

Potable Water Sampling Questionnaire and Sample Form

Location ID: _____

Other observations and notations:

Sample Collection

Field Testing Equipment: Make Model Serial Number

Time	pH (s.u)	Temp. `(C)	Spec. Cond (uS/cm)	D.O. (mg/L)	ORP (millivolts)	Turbidity (NTU)	Color	Other

Sample Location: _____

Estimated flow rate: _____ Duration of purging: _____

Sample ID	Container Type	No. of Containers	Preservation	Analysis	Date	Time

Signature: _____ Date: _____

APPENDIX A

Ohio EPA Field Standard Operating Procedures (FSOP)

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) = $\mathbf{D}^2/4 \times 3.14 \times (\mathbf{Hd} - \mathbf{Hw}) \times 7.48$ 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 (<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)

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

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 (<u>cold water only</u>) 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

APPENDIX B

Potable Water Supply Sampling SOP

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
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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 =

$$\frac{\sum \text{TIC area of DDT degradation peaks (DDE+DDD)}}{\sum \text{TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% endrin breakdown =

$$\frac{\sum \text{TIC area of endrin degradation peaks (EA+EK)}}{\sum \text{TIC area of total endrin peaks (endrin+EA+EK)}} \times 100$$

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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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

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS 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) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
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-Heptachloro-biphenyl	0.50	0.45	11	90	0.15
Hexachlorobenzene	0.50	0.41	6.0	82	0.074
2,2',4,4',5,6'-Hexachloro-biphenyl	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'-Octachloro-biphenyl	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-Heptachloro-biphenyl	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

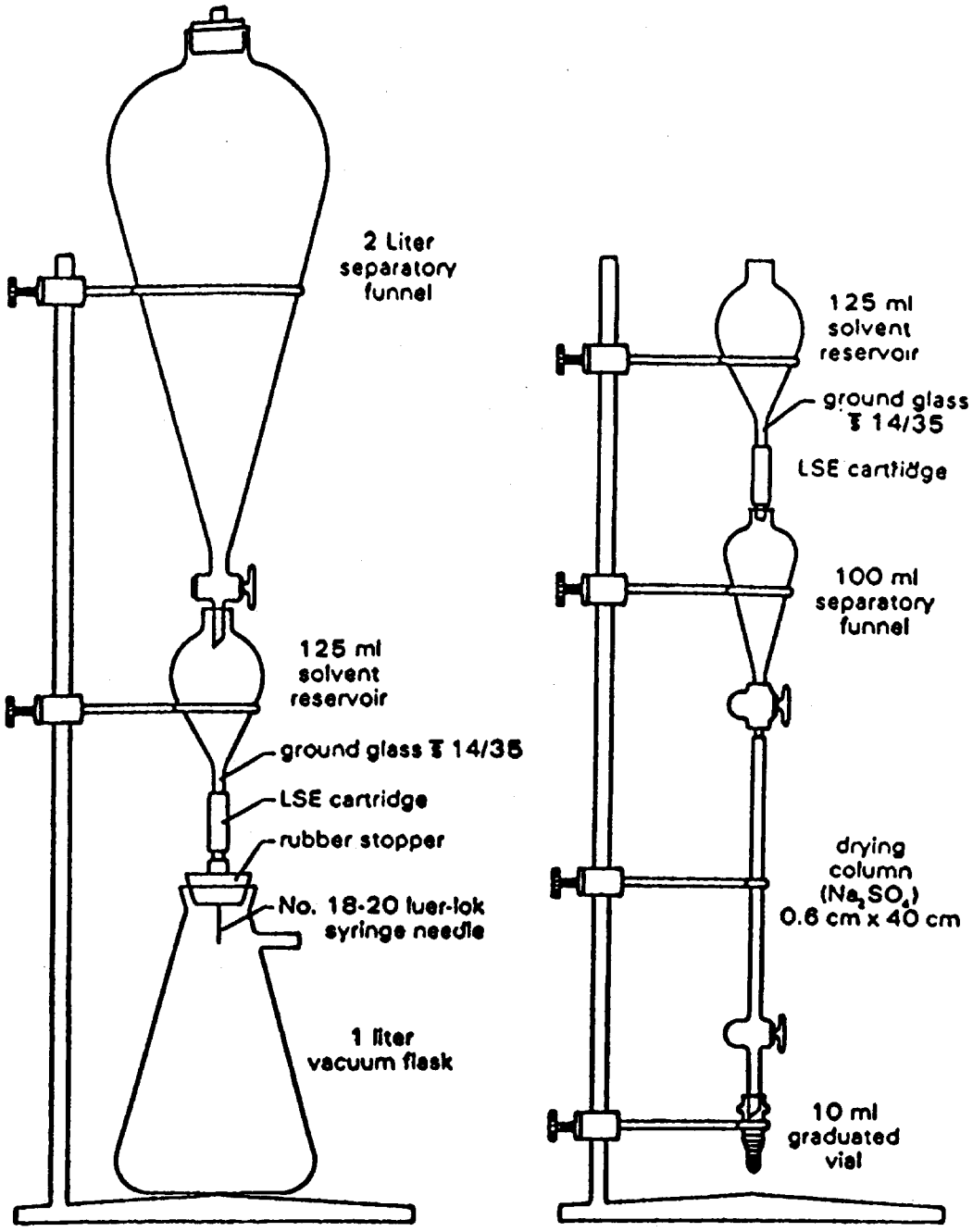
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

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

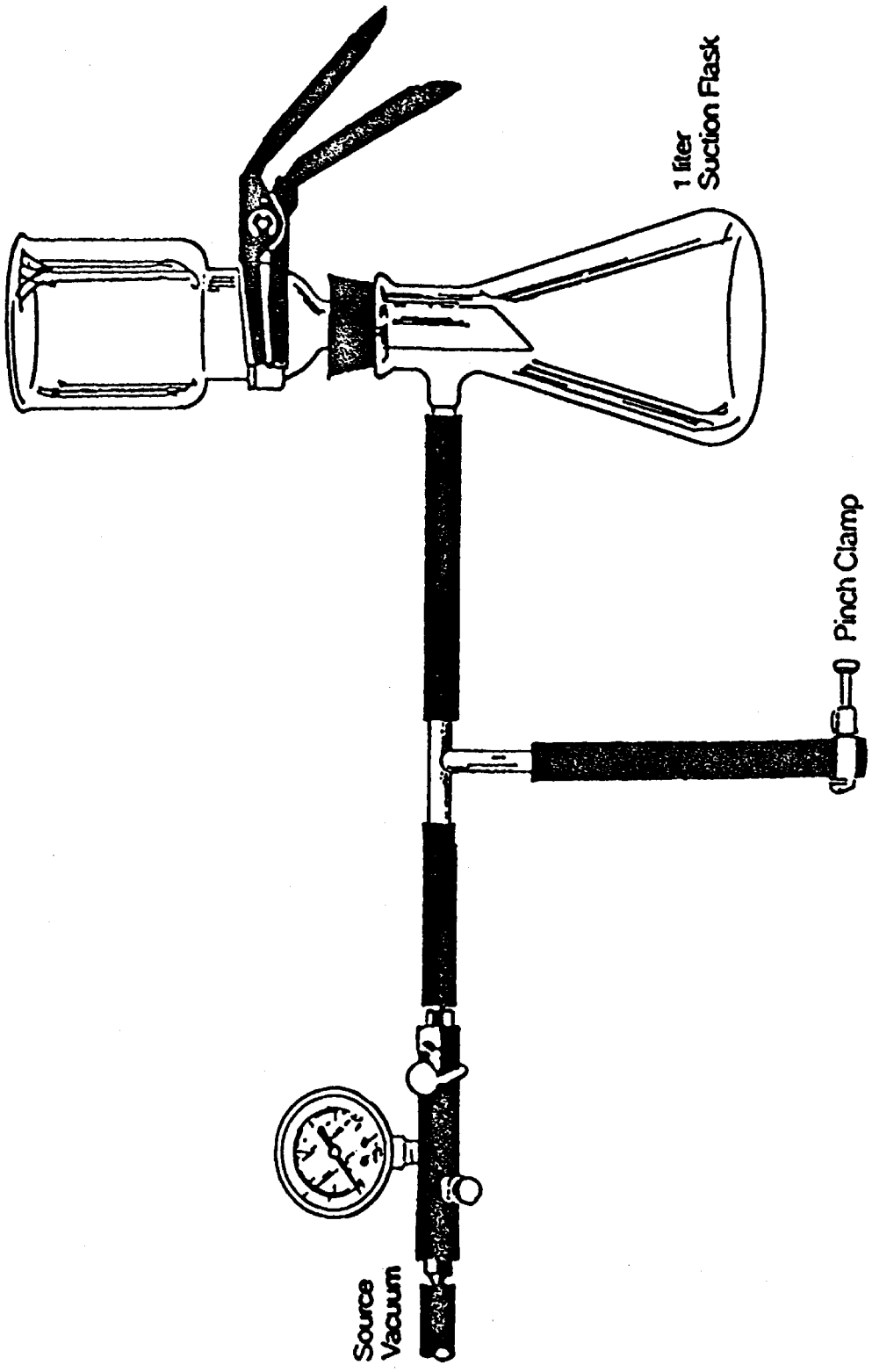
Compound	True Conc.	Mean	% RSD	% REC
2,4,5-Trichlorobiphenyl	5.0	5.2	5.1	103
Tricyclazole	5.0	4.8	5.2	96
Trifluralin	5.0	5.9	7.8	119
Vernolate	5.0	5.4	3.3	108

[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
Source
Vacuum

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
OFFICE OF RESEARCH AND DEVELOPMENT
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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 =

$$\frac{\sum \text{TIC area of DDT degradation peaks (DDE+DDD)}}{\sum \text{TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% endrin breakdown =

$$\frac{\sum \text{TIC area of endrin degradation peaks (EA+EK)}}{\sum \text{TIC area of total endrin peaks (endrin+EA+EK)}} \times 100$$

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

1. Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave, and W. L. Budde. "Trace Analyses for Wastewaters", Environ. Sci. Technol. 1981 15, 1426-1435. or 40 CFR, Part 136, Appendix B.

2. "Carcinogens - Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

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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

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS 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) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
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-Heptachloro-biphenyl	0.50	0.45	11	90	0.15
Hexachlorobenzene	0.50	0.41	6.0	82	0.074
2,2',4,4',5,6'-Hexachloro-biphenyl	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'-Octachloro-biphenyl	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-Heptachloro-biphenyl	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

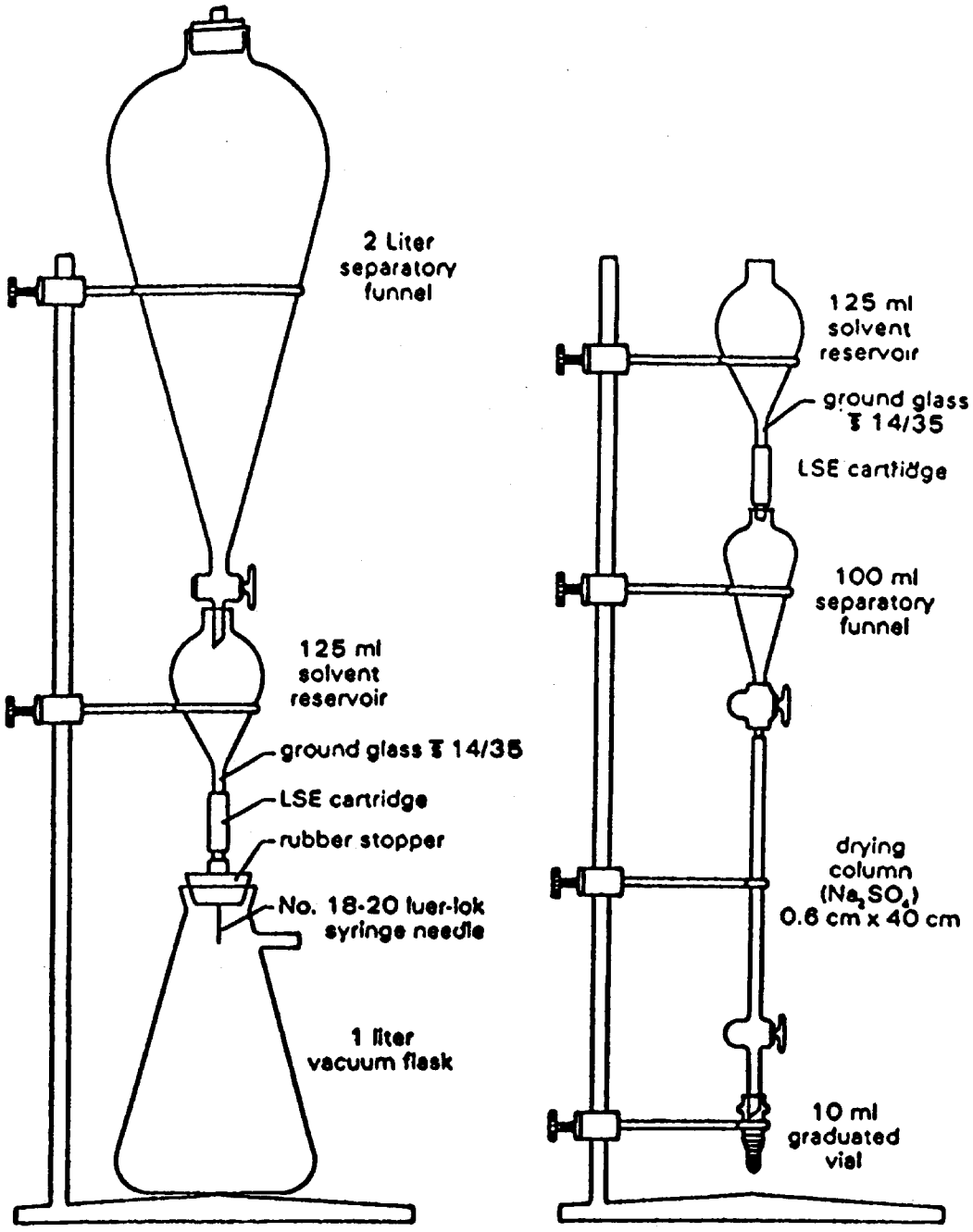
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

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

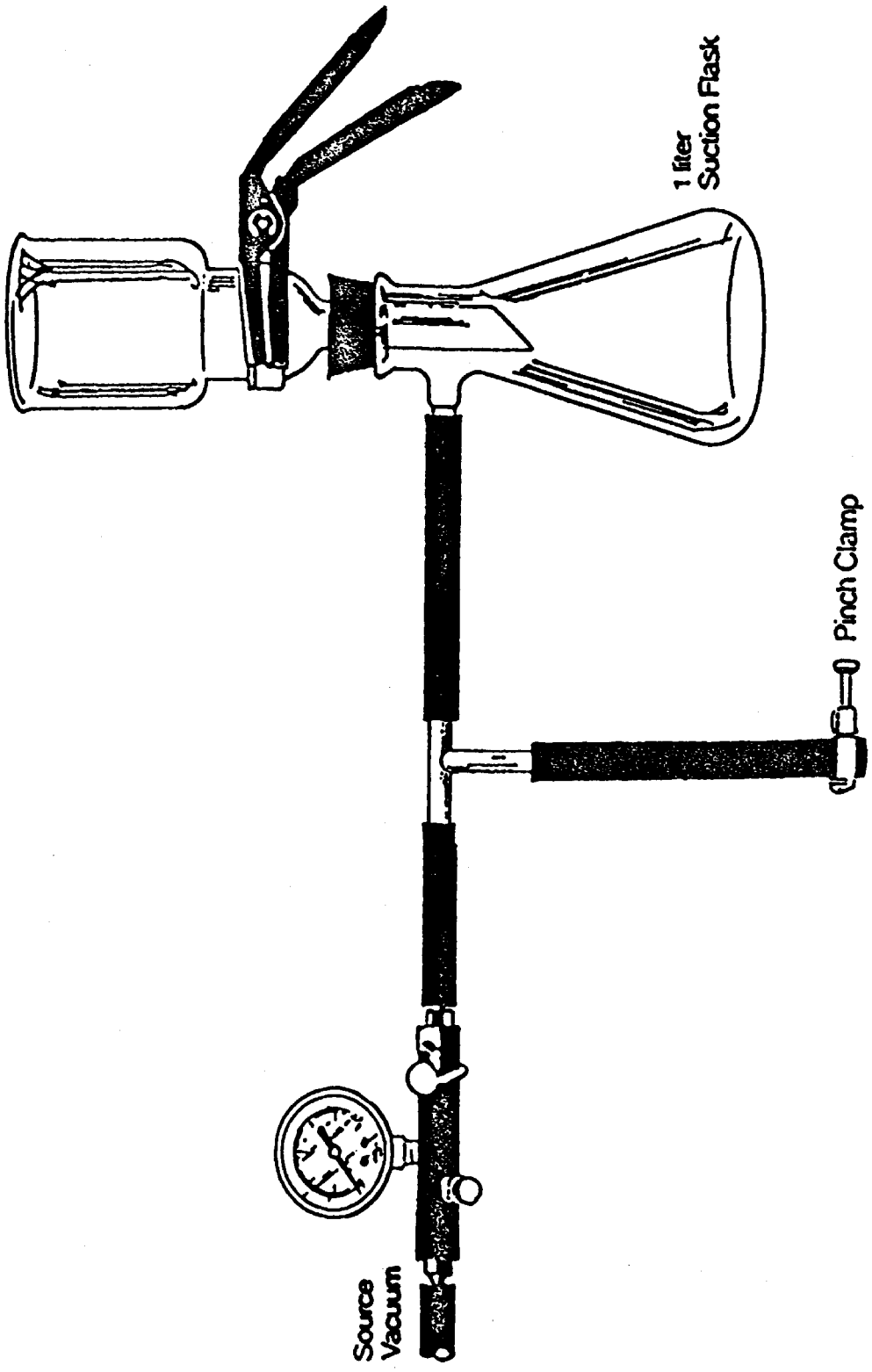
Compound	True Conc.	Mean	% RSD	% REC
2,4,5-Trichlorobiphenyl	5.0	5.2	5.1	103
Tricyclazole	5.0	4.8	5.2	96
Trifluralin	5.0	5.9	7.8	119
Vernolate	5.0	5.4	3.3	108

[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
Source
Vacuum

Region 4 U.S. Environmental Protection Agency Laboratory Services and Applied Science Division Athens, Georgia	
Operating Procedure	
Title: **Potable Water Supply Sampling**	ID: **ASBPROC-305-R4** (Formerly SESDPROC-305)
Issuing Authority: Chief, Applied Science Branch	
Effective Date: June 11, 2019	

Purpose

This document describes general and specific procedures, methods and considerations to be used and observed when collecting samples from public and private potable water supplies.

Scope / Application

When collecting water samples from a "Potable Water Supply," the primary objective is to characterize the quality of the drinking water system. Sampling may be done for a variety reasons including assessing the safety and potability of the supply for both regulated and unregulated contaminants, or to assist in determining the source of any contamination that might have reached the system. Whenever health-based levels of contaminants are exceeded in potable water supply samples, the operators and/or users of the drinking water system need to be notified as soon as the finalized data is available.

An investigation often targets a specific analyte or group of analytes. Sampling protocols designed to meet the needs of the investigation's data quality objectives need to be used and detailed in the site-specific Sampling and Analysis Plan. For example, an investigation's objective might be to simulate worst-case conditions, so the sample design would include sampling the initial flush of water from the pipes.

EPA's National Primary Drinking Water Regulations (NPDWRs) are legally enforceable primary standards and treatment techniques that apply to public water systems by limiting the levels of contaminants in drinking water. When a public drinking water supply is being monitored for compliance with the NPDWRs, approved "drinking water" analytical methods are required. However, there are cases when using alternative analytical methods, such as EPA SW-846 methods, may be more appropriate. An example of using a non-drinking water method is when monitoring residential wells near a Superfund site where the homes have been provided an alternate drinking water source.

The procedures contained in this document are to be used by field personnel when collecting and handling potable water supply samples in the field. On the occasion that LSASD field personnel determine that any of the procedures described in this procedure are inappropriate, inadequate or impractical, and that another procedure must be used to obtain a potable water supply sample, the variant procedure will be documented in the field logbook, along with a description of the circumstances requiring its use.

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1.0 General Potable Water Sampling Guidance

1.1 Site Access / Owner Information

Before collecting samples from potable water supplies, permission from the property owner or resident is required. The Program Office requesting LSASD's assistance is responsible for obtaining site access prior to the field sampling investigation.

Applied Science Branch (ASB) staff are required to obtain the following information when collecting samples of potable drinking water:

- the name(s) of the resident(s), property owner or water supply operator
- the exact physical address of the sampling location
- the exact mailing address (if different from the physical address)
- the resident's / operator's home, work and mobile telephone numbers (when available)

The above information is required so the residents or water supply owner / operators can be informed of the analytical results of the sampling. Immediately upon receipt of potable water analytical data, Branch personnel shall carefully examine the results for the presence of contaminants that exceed NPDWR standards or other health advisory levels. If there are exceedances of health advisories, or of primary or secondary drinking water standards, the ASB Chief and the requesting program's Branch Chief should be immediately notified.

1.2 Laboratory Coordination

Collecting samples from residential potable wells or public drinking water supplies require close coordination with the laboratories conducting the analyses to ensure that data quality objectives are met. If a contract laboratory is used, the Project Leader should determine if a National Environmental Laboratory Accreditation Program (NELAP) certified Drinking Water laboratory is required along with the appropriate documentation for data verification and validation.

NPDWR standards and treatment techniques protect public health by limiting the levels of contaminants in drinking water. The types of regulated contaminants include microorganisms, disinfectants, disinfectant by-products, inorganic and organic chemicals, and radionuclides. Because of the types and numbers of contaminants of interest, there are many different tests and analytical methods used to quantify them. Due to the number of laboratories and instruments conducting various drinking water analyses, it is critical to closely coordinate with the laboratory conducting the analyses for all details of the potable water supply sampling. These details include sample containers, container filling, sample

volume, preservatives, dechlorination agents, holding times, sample handling procedures, and quality control samples.

Table 1 provides some of the common drinking water methods along with LSASD's capabilities and sample collection details. Since analytical methods and standard operating procedures are continuously revised, the Project Leader should verify that the version of the standard(s) is current prior to sampling.

1.3 Potable Water Sample Site Selection Considerations

- Taps selected for sample collection should be supplied with water from a service pipe connected directly to a water main in the segment of interest.
- Whenever possible, choose the tap closest to the water source, and prior to the water lines entering the residence, office, building, etc., and prior to any holding or pressurization tanks.
- The sampling tap must be protected from exterior contamination associated with being too close to a sink bottom or to the ground where contaminants may splash into the sample containers. Additionally, there must be adequate clearance so that the sample container does not touch the faucet, which is a potential source of contamination. If the tap is too close to the ground for direct collection into the appropriate container, it is acceptable to use a smaller container to transfer sample to a larger container. The smaller container should be made of similar material as the large container and should be pre-cleaned to the same standards.
- Leaking taps that allow water to discharge from around the valve stem handle and down the outside of the faucet are a potential source of contamination and should be avoided.
- Disconnect any hoses, filters, or aerators attached to the tap before sampling. In addition to these devices ability to alter the water chemistry, they can harbor a bacterial population if they are not routinely cleaned or replaced.
- 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 both hot-water and cold-water taps are present at a proposed location, sample the cold-water tap.
- When the investigation's objective allows it, outside taps are more practical and efficient to sample than interior residential kitchen or bathroom faucets.
- Sampling outside taps during heavy precipitation or dusty conditions should be avoided.

Table 1. EPA's Region 4 Laboratory Services and Applied Science Division (LSASD) Capabilities for Drinking Water Methods

Analysis	Drinking Water Method	LSASD can analyze	Container	Preservative	Dechlorination	Holding Time	Filling	Ice
Total Residual Chlorine	SM4500-CL G-2011	In-situ	Glass vial	None	None	In-situ	Neck of container	N/A
Total / free chlorine test strips	various manufactures	In-situ	Plastic	None	None	In-situ	Neck of container	N/A
Nitrate (as N)	353.2	Yes	Plastic (2)	Sulfuric acid	None	28 days	Neck of container	<4° C
Nitrite (as N)	353.2	Yes	Plastic (2)	None	None	48 hours	Neck of container	<4° C
Total Oragnic Carbon	SM 5310	Yes	Glass / plastic	Sulfuric acid	None	28 days	Neck of container	<4° C
Metals	200.7 rev 4.4/ 200.8	Yes	Plastic - wide mouth	Nitric acid	None	6 mos	Neck of container	<4° C
Mercury	200.8 / 245.1	Yes	Plastic - wide mouth	None	None	28 days	Neck of container	<4° C
Fluoride	300.0	Yes	Plastic - wide mouth	None	None	28 days	Neck of container	<4° C
Bromide	300.0	Yes	Plastic - wide mouth	None	None	28 days	Neck of container	<4° C
Semi-Volatile Organic Compounds / Pesticides	525.2	Yes	Amber glass	Hydrochloric Acid	Sodium sulfite	14 days to extract, followed by 30 days	Neck of container	<4° C
Volatile Organic Compounds	524.4	Yes	40 ml glass vials	Maleic acid	Abscorbic acid	14 days	Zero headspace	<4° C
Total Trihalomethanes	524.4	Yes	40 ml glass vials	Maleic acid	Abscorbic acid	14 days	Zero headspace	<4° C
Haloacetic Acids (HAAs)	552.3	No	Amber glass	Ammonium chloride	None	14-28 days	Neck of container	<4° C
per&polyfluoroalkyl substances (PFAS)	537	No	250 ml polyproylene	None	Trizma	14-28 days	Neck of container	<10° C
Total coliform / E. coli	SM 9223 B-2004	No	Sterile plastic	None	Sodium thiosulfate	8 - 30 hours	100 ml line or neck	<10° C

Analyzing water samples using Drinking Water methods are non-routine analyses for the LSASD laboratory. Therefore, Drinking Water methods shall be specified when the project is scheduled with the lab and on the chain-of-custody when the samples arrive at the custody room.

1.4 Special Sampling and Handling Precautions

- A clean pair of new, non-powdered, disposable gloves shall be worn each time a different location is sampled, and the gloves should be donned immediately prior to sampling. The gloves should not come in contact with the media being sampled and should be changed any time during sample collection when their cleanliness is compromised.
- Samplers should be careful when handling acids and other preservatives and take necessary precautions by wearing gloves and eye protection.
- Do not rinse the bottle containing the preservatives or dechlorination agents before it is filled and avoid overfilling the container during the sampling process.
- During sample collection, make sure that the tap or spigot does not contact the sample container.
- Samples collected in zero-headspace vials (i.e. volatile organic analysis (VOA), or total trihalomethanes (TTHMs)) must not have any headspace (see Section 1.5). All other sample containers must be filled with an allowance for ullage. Some sample containers may have designated fill lines that indicate how much sample should be placed in them.
- All samples requiring preservation must be preserved as soon as practically possible, immediately after sample collection is ideal. Adequate mixing should be conducted to thoroughly mix the preservative with the sample.
- Samples requiring reduced temperature storage should be placed on ice immediately.

1.5 Specific Analyte Requirements

- VOAs and TTHMs: Samples should be collected with as little agitation or disturbance as possible. The vial should be filled so that there is a meniscus at the top of the vial and absolutely no bubbles or headspace should be present in the vial after it is capped. After the cap is securely tightened, the vial should be inverted and tapped on the palm of one hand to see if any undetected bubbles are dislodged. If a bubble or bubbles are present, the vial should be topped off using a minimal amount of sample to re-establish the meniscus. Care should be taken not to flush any preservative out of the vial during topping off. If, after topping off and capping the vial, bubbles are still present, a new vial should be obtained, and the sample re-collected.
- Biological Contaminants: Sample containers are sterile, so care must be taken not to contaminate the bottle or cap. Once the distribution line is flushed and the flow reduced, quickly open the container. DO NOT set the cap down and hold the cap by its outside edges only. Fill the sample bottle to just above the 100 mL line (leaving headspace) before promptly capping.
- Lead and Copper Rule Compliance Samples: Select a cold-water faucet for sampling which is free from devices that are designed to change the water

composition, such as water softeners or point of use filters. DO NOT remove any screens or aeration devices. If you are collecting a first-flush sample for lead/copper, allow the water to sit undisturbed in the water line for at least six hours. DO NOT intentionally flush the water line before the start of the six-hour period. Place a wide-mouth 1 L container under the faucet. Open the faucet and collect the first water out of the tap (initial flush). For more detailed sampling instructions, refer to the EPA's "Clarification of Recommended Tap Sampling Procedures for Purposes of the Lead and Copper Rule" at: https://www.epa.gov/sites/production/files/2016-02/documents/epa_lcr_sampling_memorandum_dated_february_29_2016_508.pdf.

1.6 Dechlorination Agents

Potable water samples that have been treated with chlorine require the addition of dechlorination agents for certain parameters to remove free chlorine and prevent analytical interference. ASB staff can check for the presence of chlorine in the potable water while they are in the field. Maleic acid is used to dechlorinate the samples being analyzed for Volatile Organic Compounds (VOCs) and THHMs. Sodium sulfite is used to dechlorinate the samples being analyzed for Semi-Volatile Organic Compounds. Sodium thiosulfate is used to dechlorinate samples being analyzed for bacteriological contaminants, and Trizma® is used to dechlorinate samples being analyzed for per & polyfluoroalkyl substances (PFAS). The laboratory conducting the analyses will be able to provide the correct dechlorination agent for the specific analysis of concern.

2.0 Flushing / Purging of Potable Water Supplies

2.1 Initial Flush, Flushing and Purging Goals

The objective of a study will determine how long to flush or purge a potable water supply, or if a stagnation period, where the potable water in the system is not used for a specific time, is required. Public health is paramount when sampling drinking water supplies and should always dictate the sample design. In general, flushing and purging are conducted to obtain representative samples of the potable water supply while a stagnant period followed by sampling the initial flush is used to collect samples representative of the potable water supply with contributions from the distribution system. It is important to note that longer flush / purge times may yield more representative samples of the water supply, but it may not be protective of the public consuming the potable water. People do not usually pour a glass of water after flushing their faucet for 15 minutes.

The sampling investigation objective(s) should be detailed in a site-specific Sampling and Analysis Plan along with the sampling and flushing / purging protocols; sample initial flush, sample after a designated flush period (i.e. 5 minutes), or sample after water quality parameters of the water supply stabilize.

2.2 Flushing and Purging Adequacy

Flushing is a term associated with municipal drinking water, whereas purging is more associated with residential and monitoring well sampling. Both are done to remove stagnant water in lines immediately prior to sampling. To determine when an adequate flush or purge has occurred, field investigators should monitor the water quality parameters such as temperature, pH, specific conductance and turbidity of the water removed during purging. For potable water supply sampling, it is recommended to purge the system until field quality parmeters are stabilized with the turbidity below five Nephelometric Turbidity Units (NTUs). Stabilization criteria for temperature, pH and specific conductance are for at least three consecutive measurements with the temperature constant (± 0.1° C), the pH remains constant (± 0.1 Standard Units) and the specific conductance varies no more than approximately five percent. If the parameters have not stabilized after 15 minutes, it is at the discretion of the project leader whether to collect a sample or to continue purging.

3.0 Potable Residential Well Sampling

3.1 Potable Well Sample Tap or Spigot

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 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.

3.2 Stabilization for Potable Wells

During the purge period, obtain at least three sets of readings as follows: after purging for several minutes, measure the temperature, pH, specific conductivity and turbidity of the water. Continue to measure these parameters to assess for stabilization. After three sets of stabilized readings have been obtained, samples may be collected. If stabilization has not occurred after the 15-minute purge period, it is at the discretion of the project leader to collect the sample or continue purging and monitoring the parameters. This would depend on the condition of the system and the specific objectives of the investigation.

3.3 Potable Well Sample Collection

Samples should be collected following purging from a valve or cold water tap as near to the well as possible, preferably prior to any storage / pressure tanks or physical / chemical treatment system that might be present. Remove any hose that may be present before sample collection and reduce the flow to a low level to minimize sample disturbance, particularly with respect to volatile organic compounds. Samples should be collected directly into the appropriate containers. It may be necessary to use a secondary container, such as a clean 8 oz. (or similar size) sample jar or a stainless-steel scoop, to obtain and transfer samples from spigots with low ground clearance. All measurements for temperature, pH, specific conductance and turbidity should be recorded at the time of sample collection.

4.0 Public Water Supply Sampling

Samples should be collected directly into the appropriate containers. It may be necessary to use a secondary container, such as a clean 8 oz. (or similar size) sample jar or a stainless-steel scoop, to obtain and transfer samples from spigots with low ground clearance. All measurements for temperature, pH, specific conductance and turbidity should be recorded at the time of sample collection.

4.1 Potable Treatment Plant Sampling

Municipal water supply plants and wells that continuously operate require NO PURGE other than opening a valve and allowing it to flush for a few minutes. Remove any hoses on the sample taps. If a storage tank is present, a spigot, valve or other sampling point should be located between the pump and the storage tank. If not, sample from the valve closest to the tank. Measurements of temperature, pH, specific conductance and turbidity are recorded at the time of sampling when water quality parameters are required.

When sampling at a water treatment plant, samples are often collected from the raw water supply and from the treated or finished water after chlorination.

4.2 Potable Water Distribution Sampling

Occasionally, samples are collected to determine the contribution of system-related variables (e.g., transmission pipes, water coolers, water heaters, holding tanks, pressurization tanks, etc.) to the quality of potable water supplies. In these cases, it may be necessary to ensure that the water source has not been used for a specific time interval (e.g., six-hours or over a weekend). Sample collection may consist of collecting a sample of the initial flush, collecting a sample after flushing for several minutes, and collecting another sample after the system being investigated has been flushed until one or more of the water quality parameters stabilize.

When sampling drinking water from the interior of residential homes, it useful to record in the logbook both the interior plumbing and service line material (i.e. PVC, galvanized iron, copper and / or lead), and any filters which are in use. Also, photographs of the sample tap, and the underlying fixtures are recommended.

Additionally, federal and state regulations require monitoring water within the distribution system under three specific rules: Total Coliform Rule, Lead and Copper Rule, and Trihalomethane Rule. Consequently, when samples are being analyzed for one of these parameters, prescriptive sampling will need to be followed and approved drinking water methods will be required for the analyses.

4.2.1 Total Coliform Rule – controls the microbial water quality aspects by testing for coliform bacteria and chlorine residuals.

4.2.2 Lead and Copper Rule – deals with the corrosivity of water distributed to homes with lead and copper plumbing. Water is tested for lead and copper in the ends of water mains and from the drinking water taps of homes after a stagnant period. Other useful water quality measurements include pH, alkalinity and the residual of any corrosion inhibitor applied to the water.

4.2.3 Trihalomethane Rule – monitors for disinfection by-products such as Trihalomethanes and chlorine residuals.

5.0 References

SESD Operating Procedure for Potable Water Supply Sampling, SESDPROC-305-R3, May 30, 2013

US EPA. Laboratory Services Branch Laboratory Operations and Quality Assurance Manual. Region 4 SESD, Athens, GA, May 2019.

US EPA. 2001. Environmental Investigations Standard Operating Procedures and Quality Assurance Manual. Region 4 Science and Ecosystem Support Division (SESD), Athens, GA

US EPA. Region 8. Quick Guide to Drinking Water Sample Collection (2nd Edition). Region 8 Laboratory, 16194 W. 45th Dr., Golden, CO 80403, September 2016

US EPA. Office of Ground Water & Drinking Water. "Clarification of Recommended Tap Sampling Procedures for Purposes of the Lead and Copper Rule" memorandum, February 29, 2016

Water Distribution System Operation and Maintenance (6th Edition), California State University, Sacramento, California, College of Engineering and Computer Science, Office of Water Programs, 2012

6.0 Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions of the document are maintained by the LSASD Document Control Coordinator.

History	Effective Date
ASBPROC-305-R4, Potable Water Supply Sampling, replaces SESDPROC-305-R3	June 11, 2019
SESDPROC-305-R3, *Potable Water Supply Sampling*, replaces SESDPROC-305-R2	May 30, 2013
SESDPROC-305-R2, *Potable Water Supply Sampling*, replaces SESDPROC-305-R1	January 29, 2013
SESDPROC-305-R1, *Potable Water Supply Sampling*, replaces SESDPROC-305-R0	November 1, 2007
SESDPROC-305-R0, *Potable Water Supply Sampling*, Original Issue	February 05, 2007

APPENDIX C

OEPA SOP For Per- and Polyfluorinated Alkyl Substances Sampling at Public Water Systems Ohio EPA LOE Contractors Revision 1.1 March 3, 2020, and EPA 533 Analytical Method for PFAS and PFOS

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.**

[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:

[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)

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

Technical questions concerning this analytical method should be addressed to:

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Questions concerning this document or policy should be addressed to: safewater@epa.gov

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Shimadzu Scientific Instruments (Columbia, MD)
Thermo Fisher Scientific (Sunnyvale, CA)
Weck Laboratories, Inc. (City of Industry, CA)
Vogon Laboratory Services Ltd. (Cochrane, Alberta, Canada)

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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Tables

Figures

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* ± 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.
2. US EPA. *Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator*; EPA 815-R-11-001; Office of Water: Cincinnati, OH, December 2010.

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

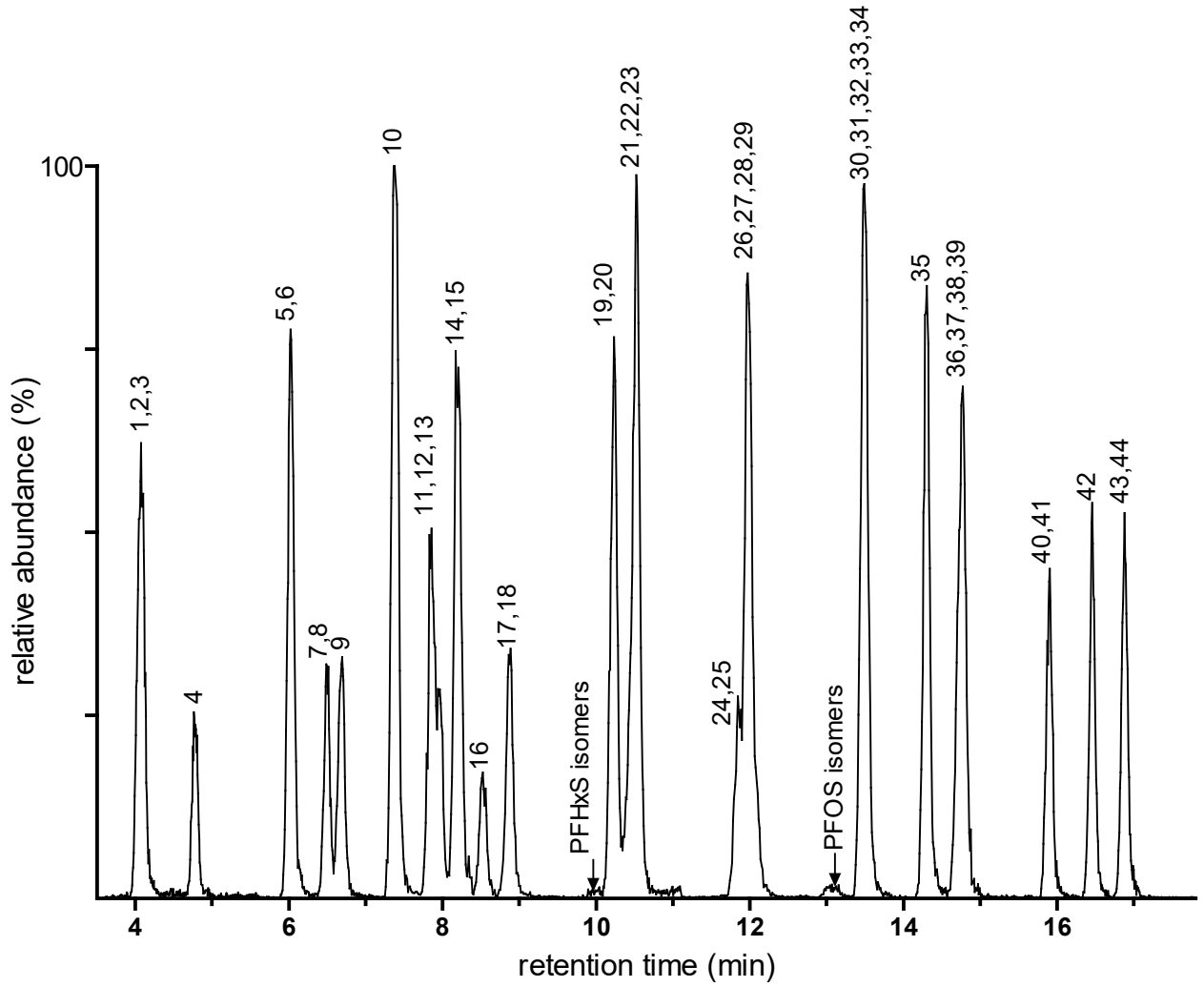
Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 10.2.2	Establish retention times for branched isomers	Each time chromatographic conditions change	All isomers of each analyte must elute within the same MRM window.
Section 9.1.1	Demonstration of low system background	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 D

Field Sampling Protocol Checklist

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 _____