### **INTERIM FINAL**

# RCRA FACILITY INVESTIGATION (RFI) GUIDANCE

### **VOLUME III OF IV**

### AIR AND SURFACE WATER RELEASES

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OFFICE OF SOLID WASTE
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#### **ABSTRACT**

On November 8, 1984, Congress enacted the Hazardous and Solid Waste Amendments (HSWA) to RCRA. Among the most significant provisions of HSWA are §3004(u), which requires corrective action for releases of hazardous waste or constituents from solid waste management units at hazardous waste treatment, storage and disposal facilities seeking final RCRA permits; and §3004(v), which compels corrective action for releases that have migrated beyond the facility propety boundary. EPA will be promulgating rules to implement the corrective action provisions of HSWA, including requirements for release investigations and corrective measures.

This document, which is presented in four volumes, provides guidance to regulatory agency personnel on overseeing owners or operators of hazardous waste management facilities in the conduct of the second phase of the RCRA Corrective Action Program, the RCRA Facility Investigation (RFI). Guidance is provided for the development and performance of an investigation by the facility owner or operator based on determinations made by the regulatory agency as expressed in the schedule of a permit or in an enforcement order issued under §3008(h), §7003, and/or 53013. The purpose of the RFI is to obtain information to fully characterize the nature, extent and rate of migration of releases of hazardous waste or constituents and to interpret this information to determine whether interim corrective measures and/or a Corrective Measures Study may be necessary.

#### **DISCLAIMER**

This document is intended to assist Regional and State personnel in exercising the discretion conferred by regulation in developing requirements for the conduct of RCRA Facility Investigations (RFIs) pursuant to 40 CFR 264. Conformance with this guidance is expected to result in the development of RFIs that meet the regulatory standard of adequately detecting and characterizing the nature and extent of releases. However, EPA will not necessarily limit acceptable RFIs to those that comport with the guidance set forth herein. This document is not a regulation (i.e., it does not establish a standard of conduct which has the force of law) and should not be used as such. Regional and State personnel must exercise their discretion in using this guidance document as well as other relevant information in determining whether an RFI meets the regulatory standard.

Mention of company or product names in this document should not be considered as an endorsement by the U.S. Environmental Protection Agency.

# RCRA FACILITY INVESTIGATION (RFI) GUIDANCE VOLUME III

#### AIR AND SURFACE WATER RELEASES

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#### LIST OF ACRONYMS

Atomic Absorption AA

Soil Adsorption Isotherm Test Αl

Agricultural Stabilization and Conservation Service ASCS

American Society for Testing and Materials ASTM

Bioconcentration Factor BCF Biological Oxygen Demand BOO

EPA Carcinogen Assessment Group CAG

CPF Carcinogen Potency Factor

Confidential Business Information CBI

Cation Exchange Capacity CEC

Comprehensive Environmental Response, Compensation, and CERCLA

Lability Act

Code of Federal Regulations CFR

Color Infrared CIR Corrective Measures CM

Corrective Measures Implementation CMI

Corrective Measures Study CMS Chemical Oxygen Demand COD

Composite Liquid Waste Sampler COLIWASA

Dinitrophenyl Hydrazine DNPH

DO Dissolved Oxygen

Department of Transportation DOT Electron Capture Detector ECD

EM EP Electromagnetic Extraction Procedure

Environmental Protection Agency EPA

Federal Emergency Management Agency Flame Ionization Detector FEMA

FID Fraction organic carbon in soil Foc **FWS** U.S. Fish and Wildlife Service

GC Gas Chromatography

GC/MS

GPR

Gas Chromatography/Mass Spectroscopy
Ground Penetrating Radar
Health and Environmental Assessment HEA Health and Environmental Effects Profile HEEP High Pressure Liquid Chromatography **HPLC** 

Hazardous and Solid Waste Amendments (to RCRA) HSWA

Hazardous Waste Management Inductively Coupled (Argon) Plasma HWM ICP

Infrared Detector ID

Kd Soil/Water Partition Coefficient

Organic Carbon Absorption Coefficient Koc Octanol/Water Partition Coefficient Kow

Lower Explosive Limit LEL

Maximum Contaminant Level MCL

Modified Method 5 MM5

Mass Spectroscopy/Mass Spectroscopy MS/MS National Flood Insurance Program NFIP

National Institute for Occupational Safety and Health NIOSH National Pollutant Discharge Elimination System **NPDES** Occupational Safety and Health Administration OSHA

#### LIST OF ACRONYMS (Continued)

OVA - Organic Vapor Analyzer
PID - Photo Ionization Detector
pKa - Acid Dissociation Constant

ppb - parts per billion
ppm - parts per million
PUF - Polyurethane Foam
Pvc - Polyvinyl Chloride

QA/QC - Quality Assurance/Quality Control

RCRA - Resource Conservation and Recovery Act

RFA - RCRA Facility Assessment

RfD - Reference Dose

RFI - RCRA Facility Investigation

RMCL - Recommended Maximum Contaminant Level

RSD - Risk Specific Dose

SASS - Source Assessment Sampling System SCBA - Self Contained Breathing Apparatus

SCS - Soil Conservation Service

SOP - Standard Operating Procedure SWMU - Solid Waste Management Unit

TCLP - Toxicity Characteristic Leaching Procedure

TEGD - Technical Enforcement Guidance Document (EPA, 1986)

TOC - Total Organic Carbon

TOT - Time of travel

TOX - Total Organic Halogen

USGS - United States Geologic Survey
USLE - Universal Soil Loss Equation

UV - Ultraviolet

VOST - Volatile Organic Sampling Train

VSP - Verticle Seismic Profiling WQC - Water Quality Criteria

#### **SECTION 12**

AIR

#### 12.1 Overview

The objective of an investigation of a release to air is to characterize the nature, extent, and rate of migration of the release of hazardous waste or constituents to that medium. This is done by characterizing long-term air concentrations (commensurate with the long-term exposures which are the basis for the health and environmental criteria presented in Section 8) associated with unit releases of hazardous wastes or constituents to air. This section provides:

- An example strategy for characterizing releases to air, which includes characterization of the source and the environmental setting of the release, and conducting a monitoring and/or modeling program which will characterize the release itself;
- Formats for data organization and presentation;
- Modeling and field methods which may be used in the investigation; and
- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all instances; it identifies possible information necessary to perform release characterizations and methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information for release characterization. This list is not a list of requirements for all releases to air. Some release investigations will involve the collection of only a subset of the items listed, while other releases may involve the collection of additional data.

Case studies 25 and 26 in Volume IV (Case Study Examples) illustrate several of the air investigation concepts discussed in this section.

#### 12.2 Approach for Characterizing Releases to Air

#### 12.2.1 General Approach

The intent of the air release investigation is to determine actual or potential effects at the facility property boundary. This differs from the other media discussed in this Guidance. During the health and environmental assessment process for the air medium (see Section 8), the decision as to whether interim corrective measures or a Corrective Measures Study will be necessary is based on actual or potential effects at the facility property boundary.

Characterization of releases from waste management units to air may be approached in a tiered or phased fashion as described in Section 3. The key elements to this approach are shown in Table 12-1. Tasks for implementing the release characterization strategy for releases to air are summarized in Table 12-2. An overview of the release characterization strategy for air is illustrated in Figures 12-1 through 12-5.

Two major elements can be derived from this strategy:

- Collection and review of data to be used for characterization of the source of the air release and the environmental setting for this source. Source characterization will include obtaining information on the unit operating conditions and configuration, and may entail a sampling and analytical effort to characterize the waste material in the unit or the incoming waste streams. This effort will lead to development of a conceptual model of the release that provides a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any), which can be used to guide the investigation.
- Development and implementation of modeling and/or monitoring procedures to be used for characterization of the release (e.g., from a

#### **TABLE 12-1**

#### **EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO AIR\***

#### INITIAL PHASE

- 1. Collect and review existing information on:
  - Waste
  - Unit

  - Environmental setting (e.g., climate, topography) Contaminant releases, including inter-media transport
  - Receptors at and beyond the facility property boundary
- 2. Identify additional information necessary to fully characterize release:
  - Waste
  - Unit

  - Environmental setting (e.g., climate, topography)
    Contaminant releases, including inter-media transport
  - Receptors at and beyond the facility property boundary
- 3. Conduct screening assessments:
  - Formulate conceptual model of release

  - Determine monitoring/modeling program objectives Obtain source characterization data needed for modeling input
  - Select release constituent surrogates
  - Calculate emission estimates based on emission rate screening
  - modeling results
    Calculate concentration estimates based on dispersion screening modeling results
  - Compare results to health based criteria
  - Conduct screening monitoring at source (as warranted)

  - Perform sensitivity analysis of modeling input/output Obtain additional waste/unit data as needed, for refined modeling
  - Consider conduct of more refined emission/dispersion modeling
- 4. Collect, evaluate and report results:
  - Account for unit/waste temporal and spatial variability and modeling input/output uncertainties
  - Determine completeness and adequacy of screening assessment
  - Evaluate potential for inter-media contaminant transfer
  - Summarize and present results in appropriate format

  - Determine if monitoring program objectives were met Compare screening results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
  - Determine whether the conduct of subsequent release characterization phases are necessary to obtain more refined concentration estimates

#### TABLE 12-1 (continued)

#### **EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO AIR\***

#### SUBSEQUENT PHASES (if necessary)

Conduct emission monitoring and dispersion modeling if necessary: 1.

> Conduct onsite meteorological monitoring if representative data are not available for dispersion modeling input

Conduct emission rate monitoring

Conduct dispersion modeling using emission rate monitoring data as

Evaluate results and determine need for confirmatory air monitoring

2. Conduct confirmatory air monitoring if necessary:

Develop monitoring procedures

Conduct initial monitoring

Conduct additional monitoring if additional information is necessary to characterize the release

3. Collect, evaluate and report results:

> Account for source and meteorological data variability during modeling and monitoring program

Evaluate long-term representativeness of air monitoring data

Apply dispersion models as appropriate to aid in data evaluation and to provide concentration estimates at the facility property boundary Compare monitoring results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency

Determine completeness and adequacy of collected data

Summarize and present data in appropriate format

Determine if modeling and monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)

Determine if monitoring/modeling program objectives were met Identify additional information needs, if necessary

Determine need to expand modeling and monitoring program

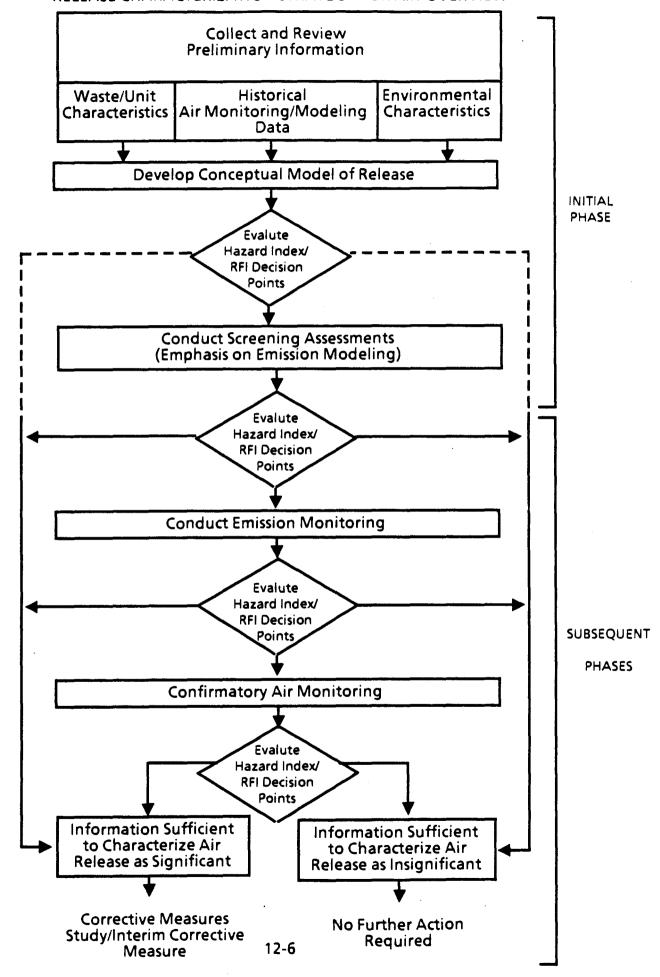
Evaluate potential role of inter-media transport

The potential for inter-media transport of contamination should be evaluated continually throughout the investigation.

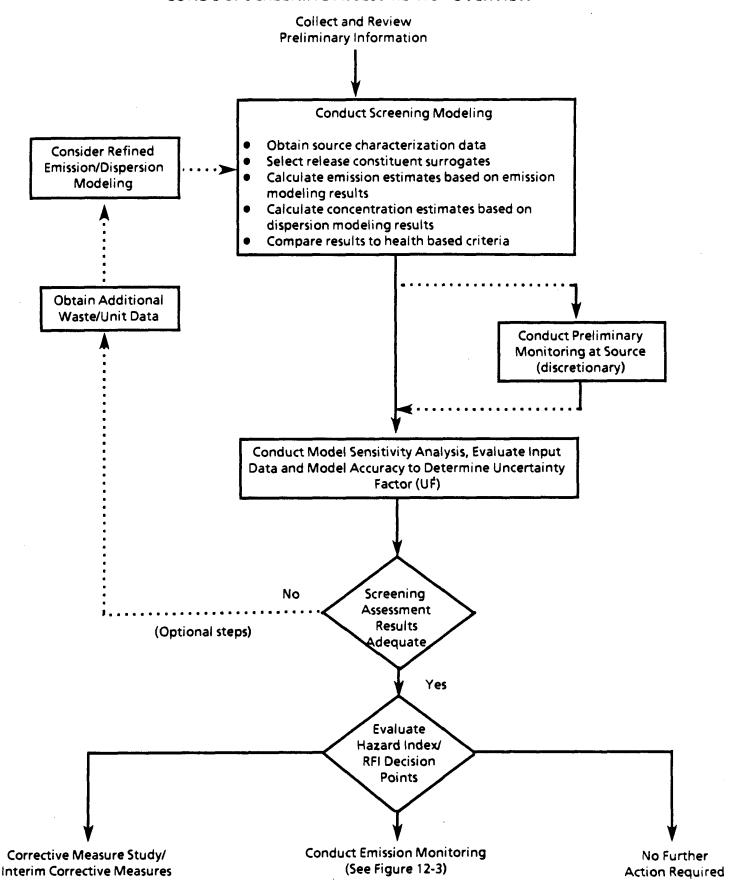
# TABLE 12-2 RELEASE CHARACTERIZATION TASKS FOR AIR

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs
1. Waste/Unit Characterization		
- Identification of waste constituents and properties	<ul> <li>See Section 3, 7 and Volume I, Appendix B List 2; Section 12.3, Section 12.4, Appendix F</li> </ul>	<ul> <li>Listing of potential release constituents</li> </ul>
<ul> <li>Prioritization of air emission constituents</li> </ul>	<ul> <li>Waste sampling and characterization</li> </ul>	<ul> <li>Listing of tar et air emission constituents for monitoring</li> </ul>
- Identification of unit characteristics which may promote an air release	- See Section 7, Section 12.3, Section 12.4, Appendix F	- Description of the unit
Environmental Setting     Characterization		
- Definition of climate	<ul> <li>Climate summaries for regional National Weather Service stations may require onsite meteorological monitoring survey)</li> </ul>	Wind roses and statistical tabulations for parameters of interest
- Definition of site-specific meteorological conditions	<ul> <li>Onsite meteorological monitoring concurrent with air monitoring</li> </ul>	<ul> <li>Wind roses and tabulations for parameters of interest</li> </ul>
Definition of soil conditions to characterize emission potential for particulate emissions and for certain units (e.g., landfills and land treatment) for gaseous emissions	- See Section 9	<ul> <li>Soil physical properties (e.g., porosity, organic matter content)</li> </ul>
- Definition of site-specific terrain	<ul> <li>See Section 7, 9 and Appendix A (Volume 1) of RFI and recent aerial photographs and U.S. Geologoical Survey maps</li> </ul>	· Topographic map of site area
- Identification of potential air-pathway receptors	<ul> <li>Census data, area surveys, recent aerial photographs and U.S. Geological Survey topographic maps</li> </ul>	<ul> <li>Map with identification of nearby populations and buildings</li> </ul>
3. Release Characterization		
- Emission rate modeling	- Air emission models as discussed in Section 12.4	<ul> <li>Unit-specific and constituent- specific emission rates</li> </ul>
- Dispersion modeling	Atmospheric dispersion models as discussed in Section 12.5	<ul> <li>Air concentration estimates at facility property boundary (tabular summaries or graphical presentations which may include release concentration isopleths)</li> </ul>
- Emission rate monitoring	Direct emission source tests for point sources, isolation flux chamber for area sources or onsite air monitoring (Section 12.8)	<ul> <li>Listing of emission rate monitoring results</li> </ul>
- Air monitoring	<ul> <li>Upwind/downwind air monitoring for release mapping</li> </ul>	- Air, concentration estimates at facility property boundary (tabular summaries or graphical presentations which may include release concentration isopleths)

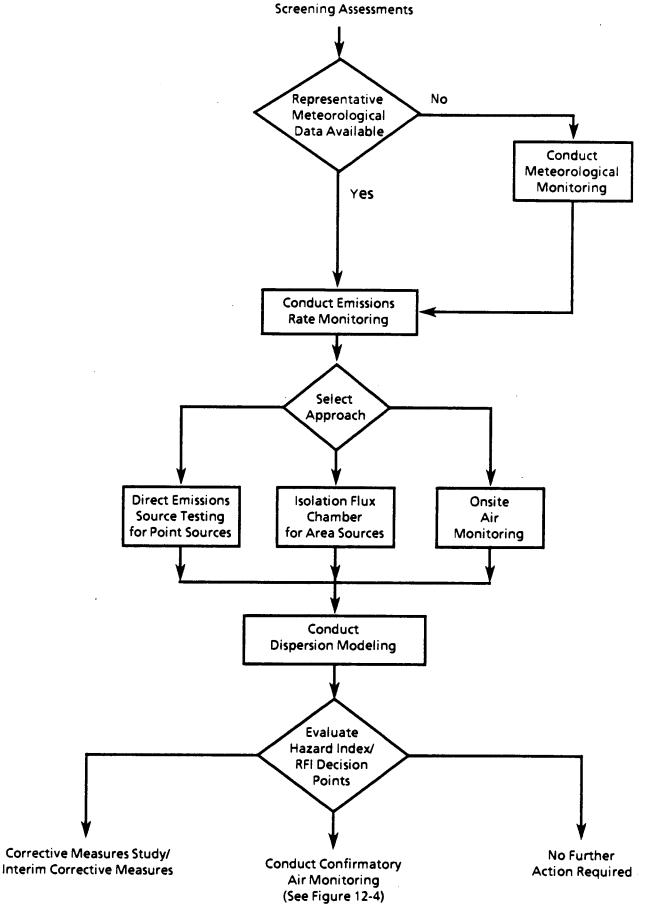
FIGURE 12-1
RELEASE CHARACTERIZATION STRATEGY FOR AIR-OVERVIEW



# FIGURE 12-2 CONDUCT SCREENING ASSESSMENTS - OVERVIEW



# FIGURE 12-3 CONDUCT EMISSION MONITORING - OVERVIEW



# FIGURE 12-4 CONDUCT CONFIRMATORY AIR MONITORING

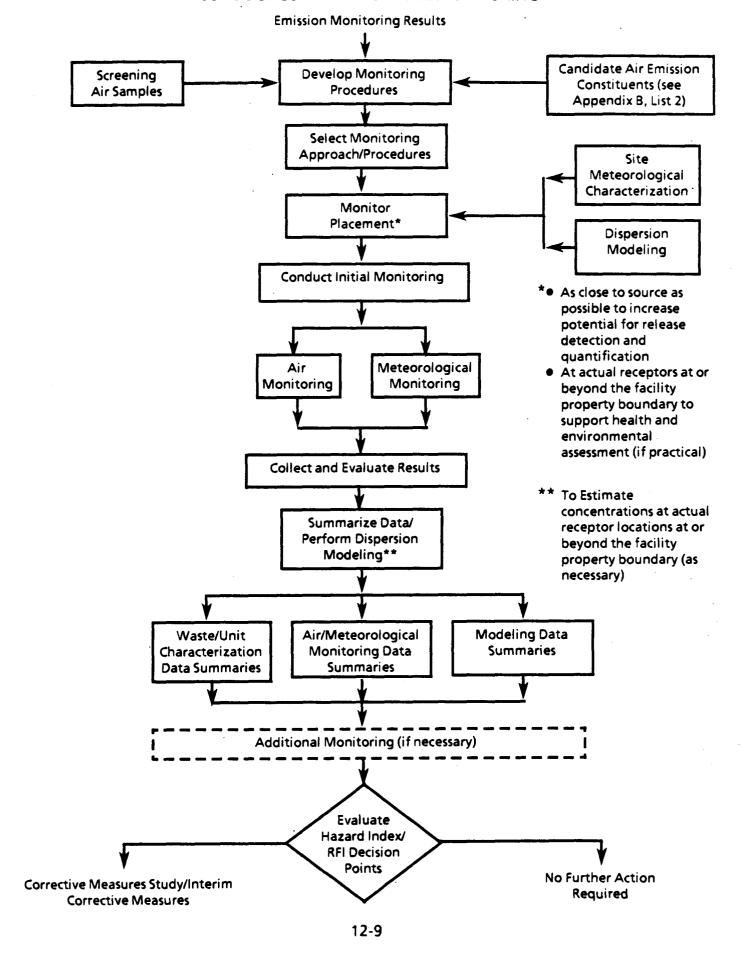
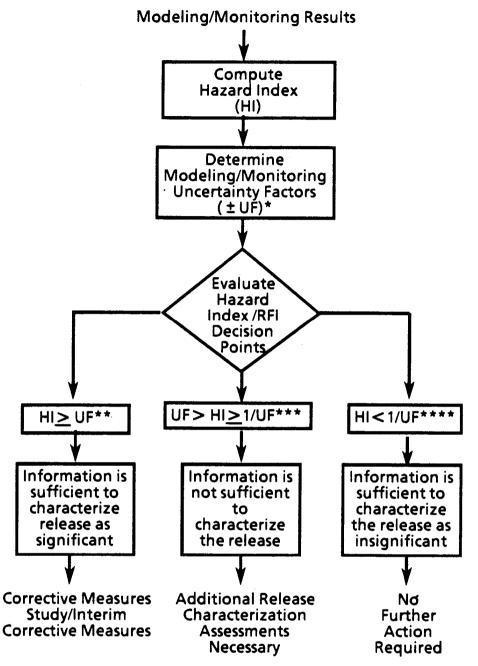


FIGURE 12-5
EVALUATION OF MODELING/MONITORING RESULTS



Uncertainty Factor assumed to be ≥1.0

 $HI \ge 1$  Generally used for evaulation of confirmatory air monitoring results.

This alternative is generally not used to evaluate confirmatory air monitoring results. However, additional air monitoring may be warranted if monitoring objectives were not acheived. Confirmatory air monitoring will generally be conducted during worst-case long-term emission/dispersion conditions. Therefore, this facilitates the use of more rigorous evaluation criteria for this final air release characterization step prior to RFI decision making.

HI< 1 Criterion generally used for evaluation of confirmatory air monitoring results.

12-10

unit or contaminated soil). Utilizing a phased approach, the air release is characterized in terms of the types and amounts of hazardous constituents being emitted, leading to a determination of actual or potential exposure at the facility property boundary. This may involve emission modeling (to estimate unit-specific emission rates), air monitoring (to determine concentrations at the facility property boundary), emission monitoring (monitoring at the source to determine emission rates), and dispersion modeling (to estimate concentrations at the facility property boundary). A phased approach utilizing both modeling and monitoring may not always be necessary to achieve adequate release charterization.

As indicated in Section 1 of this Guidance (See Volume I), standards for the control and monitoring of air emissions at hazardous waste treatment, storage and disposal (TSD) facilities are being developed by the Agency pursuant to HSWA Section 3004(n). These standards will address specific methodologies and regulatory requirements for the identification and control of air releases at TSD facilities. The Guidance provided herein is intended to provide interim methodologies and procedures for the identification and delineation of significant air releases. In particular, the Guidance addresses those releases which may pose an existing and significant hazard to human health and the environment, and thus, should be addressed without delay, i.e., prior to the issuance of the Section 3004(n) regulations.

The RFI release characterization strategy for air includes several decision points during the characterization process to evaluate the adequacy of available information and to determine an appropriate course of action from the following alternatives (as illustrated in Figures 12-1 through 12-5).

- Information is sufficient to characterize the air release as significant and a Corrective Measures Study/Interim Corrective Measures is warranted.
- Information is sufficient to characterize the air release as insignificant, therefore, no further air assessments are required.

• Information is not sufficient to characterize the air release, therefore further release characterization is warranted.

Criteria for decisionmaking involves consideration of the uncertainty associated with release characterization results (modeling/monitoring), which is facilitated by use of a Hazard Index as illustrated in Figure 12-5. The Hazard Index is defined as the ratio of exposure concentration levels or estimates, to specific health criteria for an individual constituent or a mixture of constituents with similar potential health impacts. Further guidance on the computation and application of the Hazard Index is provided in Section 8.

The uncertainty associated with concentration estimates based on air pathway modeling and monitoring results is factored into the decision making effort through use of uncertainty analyses. A primary component of the uncertainty analysis is the accuracy of the modeling and/or monitoring approach utilized for the release characterization. Model-specific and monitoring method-specific accuracies should be used as available for the uncertainty analysis. The quality of the input data to models is another important component of the uncertainty analysis that should be accounted for. Generally, conduct of a model sensitivity analysis (i.e., varying the values of input parameters based on their uncertainty range to evaluate the effect on model output), will provide a quantitative basis to characterize input data quality. This step is particularly important for some unit-specific models. For example, the spatial variability of wastes at a landfill and the uncertainty of other input parameters (e.g., soil porosity) can significantly affect the overall uncertainty associated with emission modeling results.

As concentration measurements or estimates at the facility property boundary become available, both within and at the conclusion of discrete investigation phases, they should be reported to the regulatory agency as directed. The regulatory agency will compare the concentrations with applicable health and environmental criteria to determine the need for (1) interim corrective measures; and/or (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the data with respect to adequacy and completeness to determine the need for any additional characterization efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are

provided in Section 8. A flow diagram illustrating RFI Decision Points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is advised to follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

The strategy for characterizing releases to air consists of an initial phase and, if necessary, subsequent phases, as illustrated in Table 12-1 and Figure 12-1. Additional phases may not be needed depending on the site-specific modeling/monitoring data available, and the nature and magnitude of the release. A summary discussion of the initial phase is presented in Section 12.2.1.1 and the subsequent phases in Section 12.2.1.2.

#### 12.2.1.1 Initial Phase

The initial phase of the release characterization strategy for air involves the collection and review of preliminary information and the conduct of a screening assessment.

#### 12.2.1 .1.1 Collect and Review Preliminary Information

The first step is to collect, review and evaluate available waste, unit, environmental setting and release (monitoring and modeling) data. The air pathway data collection effort should be coordinated, as appropriate, with similar efforts for other media investigations.

Evaluation of these data may, at this point, clearly indicate that a Corrective Measures Study and/or interim corrective measures are necessary or that no further action is required. For example, the source may involve a large, active storage surface impoundment containing volatile constituents located adjacent to residential housing. Therefore, action instead of further studies may be appropriate. Another case may involve a unit in an isolated location, where an acceptable modeling/monitoring data base may be available which definitively

indicates that the air release can be considered insignificant and therefore' further studies are not warranted. In most cases, however, further release characterization will be necessary.

A conceptual model (as discussed in Volume I - Summary Section and Section 3.2) of the release should then be developed based on available information. This model (not a computer or numerical simulation model) should provide a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any). The model should be testable/verifiable and flexible enough to be modified as new data become available. For example, transport pathway and exposure modes for a contaminated surface area may involve air emissions due to volatilization, wind erosion and mechanical disturbances. These air emissions are expected to result in inhalation exposure for offsite receptors. In addition, the deposition of air emissions on soil, water bodies and crops, and infiltration and runoff from the onsite source, may contribute to overall exposures.

#### 12.2.1 .1.2 Conduct Screening Assessment

Following review of existing information and development of the conceptual model, a screening assessment should be conducted to characterize the air release (see Figure 12-2). The initial screening should be based on conservative (i.e., worst-case assumptions). A screening assessment based on more realistic assumptions should be conducted if initial air concentration predictions exceed health criteria.

The <u>Draft Final Air Release Screening Assessment Methodology</u>, presented in Appendix G, describes the screening assessment in detail. It consists of emission rate and dispersion models and involves the following steps:

- Obtain source characterization input data
- Select release (target) constituents which may be present in the waste and have health criteria for the air pathway (see Section 8.0)
- Calculate emission estimates
- Calculate concentration estimates at facility property boundary
- Compare results to health based criteria

In order to assure adequate source characterization input data, it may be necessary to collect additional waste/unit data. This may involve field sampling of the waste to identify waste constituents and determine concentration levels. At this early RFI stage, it may be more effective and conclusive to sample the wastes (with relatively higher concentration levels) instead of the release. In general, if obtaining source-specific data is not practical, conservative source assumptions should be used.

Preliminary monitoring at the source may also be conducted to aid in the evaluation of the screening/modeling results. Preliminary monitoring may involve the use of screening or quantitative methods, and is discussed in Section 12.6. The preliminary monitoring period will generally be limited to a few days. Although preliminary monitoring results may identify release constituents that were not expected based on modeling, or vice versa, the limitations of modeling and monitoring should be considered when comparing these data and determining appropriate followup activities.

A sensitivity analysis should also be conducted to evaluate model input data quality. The results of the sensitivity analysis as well as consideration of model accuracy should be used to compute the UF for the screening assessment. The results of the screening assessment should then be compared to the health and environmental assessment criteria (as previously discussed) to determine appropriate followup actions. Collection of additional waste/unit data and/or considering the application of more refined emission/dispersion models are also possible options if initial results from the screening assessment are inconclusive.

#### 12.2.1.2 Subsequent Phases

Subsequent phases of the release characterization strategy for air may be necessary if screening assessment results are not conclusive to characterize the air release, and should involve the conduct of emission monitoring and confirmatory air monitoring as indicated in Figure 12-1. These are discussed below.

#### 12.2.1.2.1 Conduct Emission Monitoring

Source monitoring should be used in conjunction with dispersion modeling to further characterize the release, as indicated in Figure 12.3. Direct emission sampling should be used for point sources such as vents and stacks. An isolation flux chamber may be used for area source emission measurements. Onsite air monitoring (particularly near the emission source) is an alternative approach for characterizing area source emissions if direct emission monitoring is not practical (e.g., considering equipment availability). Guidance for the conduct of these field programs is presented in Section 12.6 and 12.8.

The development of emission monitoring procedures should address selection of target air emission constituents. One acceptable approach is to monitor for all potential Appendix VIII air emission constituents (see Appendix B, List 3) applicable to the unit or release of concern. An alternative approach is to use unit and waste-specific information to identify constituents that are expected to be present, thus reducing the number of target constituents (see Section 3.6). The target constituents selected should be limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8).

Representative meteorological data as well as emission monitoring results should be available as input data for dispersion modeling. Therefore, it may be necessary to conduct an onsite meteorological monitoring survey. The meteorological monitoring survey should be conducted, at a minimum, for a period sufficient to identify and define wind and stability patterns for the season associated with worst-case, long-term source emission/dispersion conditions. However, it may also be desirable to obtain sufficient data to characterize annual dispersion conditions at the site. The season associated with the highest long-term air concentration is determined by evaluating seasonal emission/dispersion modeling results based on available meteorological data (e.g., National Weather Service data). This modeling application accounts for the complex relationships between meteorological conditions and emissions potential and dispersion potential. For example, high average wind speeds may increase the long-term emission potential of organics at a surface impoundment, but worst case long-term dispersion conditions would be associated with low average wind speed conditions. Seasonal temperature conditions would also affect the emission potential.

Therefore, it would be necessary to compare seasonal air concentration results to identify the season with worst case long term exposure conditions. This season would be the candidate period to collect several months of onsite meteorological data to support more refined modeling analyses (e.g., dispersion modeling using emission rate monitoring data as input). Guidance on selection of the emission monitoring period within this worst case season is presented in Section 12.6.4.2. Guidance on the conduct of a meteorological monitoring program is provided in Sections 12.6.3 and 12.8.1.

Dispersion models are used to estimate constituent concentrations based on source and meteorological monitoring input data. Guidance on the selection and application of dispersion models is presented in Section 12.5 and in <u>Guidance on Air Quality Models</u> (U.S. EPA, July 1986) and <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications</u> (U.S. EPA, December 1988). The results of the dispersion modeling assessment should then be compared to the health and environmental assessment criteria (as previously discussed) to determine appropriate followup actions.

#### 12,2.1 .2.2 Confirmatory Air Monitoring

Confirmatory air monitoring (as outlined in Figure 12-4), may also be appropriate to provide additional release characterization information for RFI decision making. Air monitoring data will provide a basis for release mapping and for evaluation and confirmation of modeling estimates. The conduct of an air monitoring program should include the following components:

- Develop monitoring procedures
- Conduct initial monitoring
- Collect and evaluate results
- Conduct additional air monitoring (if necessary)

The development of monitoring procedures should address selection of target air emission constituents. One acceptable approach is to monitor for all potential Appendix VIII air emission constituents (See Appendix B, List 3) applicable to the unit or release of concern. An alternative approach is to use unit and waste-specific information to identify constituents that are expected to be present, thus reducing

the number of target monitoring constituents (See Section 3.6). The target constituents selected should be limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8.0).

The development of monitoring procedures should also include selection of appropriate field and analytical methods for conducting the air monitoring program. Candidate methods and criteria for monitoring program design (e.g., relevant to sampling schedule and monitor placement) should be limited to standard published protocols (such as those available from EPA, NIOSH, and ASTM). The selection of appropriate methods will be dependent on site and unit-specific conditions, and is discussed further in Section 12.8.

A limited screening-type sampling program may be appropriate for determining the design of the air monitoring program. The objective of this screening sampling will be to verify a suspected release, if appropriate, and to further assist in identifying and quantifying release constituents of concern. Screening sampling at each unit for a multiple-unit facility, for example, can be used to prioritize release sources. The emphasis during this screening will generally be on obtaining air samples near the source, or collecting a limited number of source emission samples. The availability of air monitoring data on units with a limited set of air emission constituents may preclude the need for screening sampling during the investigation.

An initial air monitoring program should be conducted, as necessary, to characterize the magnitude and distribution of air concentration levels for the target constituents selected. Initial monitoring should be conducted for a period sufficient to characterize air concentrations at the facility property boundary, as input to the health and environmental assessment (e.g., a 90-day period may be appropriate for a flat terrain site with minimal variability of dispersion and source conditions).

The basic approach for the initial air monitoring will consist of collection of ambient air samples for four target zones: the first zone located upwind of the source to define background concentration levels; the second zone located downwind at the unit boundary; the third zone located downwind at the facility property boundary for input into the health and environmental assessment; and a

#### 12.3 Characterization of the Contaminant Source andthe Environmental Setting

Release investigations can be conducted in an efficient, effective and representative manner if certain information is obtained prior to implementation of the effort. This information consists of both waste/unit characterization and characterization of the environmental setting. Review of information from existing sources can be used to identify data gaps and to initiate data collection activities to fill these data gaps. Waste/unit characterization and characterization of the environmental setting are discussed below:

Waste and unit specific information: Data on the specific constituents present in the unit that are likely to be released to the air can be used to design sampling efforts and identify candidate constituents to be monitored. This information can be obtained from either review of the existing information on the waste or from new sampling and analysis. The manner in which the wastes are treated, stored or disposed may have a bearing on the magnitude of air emissions from a unit. In many cases, this information may be obtained from facility records, contact with the manufacturer of any control devices, or, in some cases, from the facility's RCRA permit application.

Environmental setting information: Environmental setting information, particularly climatological data, is essential in characterizing an air release. Climatologica parameters such as wind speed and temperature will have a significant impact on the distribution of a release and in determining whether a particular constituent will be released. Climatological and meteorological information for the area in which the facility is located can be obtained either through an onsite monitoring effort or from the National Climatic Data Center (Asheville, NC). The climatological data should be evaluated considering site topography and other local influences that can affect the data representatives.

Information pertaining to the waste, unit, and environmental setting can be found in many readily available sources. General information concerning waste/unit characterization is discussed in Section 7. Air specific information is provided in the following discussions.

#### 12.3.1 Waste Characterization

Several waste characteristics contribute to the potential for a waste constituent to be released via the air pathway. These characteristics, in conjunction with the type of unit and its operation, will determine whether a release will be via volatilization of the constituent or as particulate entrainment. Major factors include the types and number of hazardous constituents present, the concentrations of these constituents in the waste(s), and the chemical and physical characteristics of the waste and its constituents. All of these factors should be considered in the context of the specific unit operation involved. It is important to recognize that the constituents of concern in a particulate release may involve constituents that are either sorbed onto the particulate, or constituents which actually comprise the particulate.

#### 12.3.1.1 Presence of Constituents

The composition of the wastes managed in the unit of concern will influence the nature of a release to air. Previous studies may indicate that the constituents are present in the unit or that there is a potential for the presence of these constituents. In determining the nature of a release, it may be necessary to determine the specific waste constituents in the unit if this has not already been done. Guidance on selecting monitoring constituents is presented in Section 3 (and Appendix B); waste characterization guidance is presented in Section 7.

#### 12.3.1.2 Physical/Chemical Properties

The physical and chemical properties of the waste constituents will affect whether they will be released, and if released, what form the release will take (i.e., vapor, particulate, or particulate-associated). These parameters are identified in Table 12-3 as a function of emission and waste type. Important parameters to consider when assessing the volatilization of a constituent include the following:

 Water solubility. The solubility in water indicates the maximum concentration at which a constituent can dissolve in water at a given temperature. This value can help the investigator estimate the

# TABLE 12-3 PARAMETERS AND MEASURES FOR USE IN EVALUATING POTENTIAL RELEASES OF HAZARDOUS WASTE CONSTITUENTS TO AIR

Emission and Waste Type	Units of Concern <sup>11</sup>	Useful Parameters and Measures	
A. Vapor Phase Emissions			
<ul> <li>Dilute Aqueous Solution<sup>21</sup></li> </ul>	Surface Impoundments, Tanks, Containers	Solubility, Vapor Pressure, Partial Pressure	
- Conc. Aqueous Solution <sup>21</sup>	Tanks, Containers, Surface impoundments	Solubility, Vapor Pressure, Partial Pressure, Raoults Law	
Immiscible Liquid	Containers, Tanks	Vapor Pressure, Partial Pressure	
- Solid	Landfills, Waste Piles, Land Treatment	Vapor Pressure, Partial Pressure, Octanol/Water Partition Coefficient, Porosity	
B. Particulate Emissions			
- Solid	Landfills, Waste Piles, Land Treatment	Particle Size Distribution, Unit Operations, Management Methods	

- Incinerators are not specifically listed on this table because of the unique issues concerning air emissions from these units. Although incinerators can burn many forms of waste, the potential for release from these units is primarily a function of incinerator operating conditions and emission controls, rather than waste characteristics.
- 2/ Although the octanol/water partition coefficient of a constituent is usually not an important characteristic in these waste streams, there are conditions where it can be critical. Specifically, in waste containing high concentrations of organic particulates, constituents with high octanol/water partition coefficients will adsorb to the particulates. They will become part of the sludge or sediment matrix, rather than volatilizing from the unit.
- 3/ Applicable to mixtures of volatile components.

distribution of a constituent between the dissolved aqueous phase in the unit and the undissolved solid or immiscible liquid phase. Considered in combination with the constituent's vapor pressure, volubility can provide a relative assessment of the potential for volatilization of a constituent from an aqueous environment.

- Vapor pressure. This property is a measure of the pressure of vapor in equilibrium with a pure liquid. It is best used in a relative sense; constituents with high vapor pressures are more likely to be released than those with low vapor pressures, depending on other factors such as relative volubility and concentration (e. g., at high concentrations releases can occur even though a constituent's vapor pressure is relatively low).
- Octanol/water partition coefficient The octanol/water partition coefficient indicates the tendency of an organic constituent to sorb to organic components of soil or waste matrices. Constituents with high octanol/water partition coefficients tend to adsorb readily to organic carbon, rather than volatilizing to the atmosphere. This is particularly important in landfills and land treatment units, where high organic carbon content in soils or cover material can significantly reduce the release potential of volatile constituents.
- Partial pressure. For constituents in a mixture, particularly in a solid matrix, the partial pressure of a constituent will be more significant than pure vapor pressure. A partial pressure measures the pressure which each component of a mixture of liquid or solid substances will exert in order to enter the gaseous phase. The rate of volatilization of an organic chemical when either dissolved in water or present in a solid mixture is characterized by the partial pressure of that chemical. In general, the greater the partial pressure, the greater the potential for release. partial pressure values are unique for any given chemical in any given mixture and may be difficult to obtain. However when waste characterization data are available, partial pressure can be estimated using methods commonly found in engineering and environmental science handbooks.

# TABLE 12-4 PHYSICAL PARAMETERS OF VOLATILE HAZARDOUS CONSTITUENTS

Hazardous constituent	Molecular weight	Vapor pressure at 25°C (mm Hg)	Volubility at 25°C (mg/1)	Henry's Law constant (atm <sup>-3</sup> /mol)
Acetaldehyde	44	915	1.00E +06	9.50E-05
Acrolein	56	244	4.00E +05	4.07E-05
Acrylonitrile	53	114	7.90E +04	8.80E-05
Allylchioride	76.5	340		340E-01
Benzene	78	95	1.78E +03	5.50E-03
Benzyl chloride	126.6	1.21	1.00	
Carbon tetrachloride	154	109	8.00E +02	2.00E-02
Chlorobenzene	112	12	5.00E +02	2.00E-03
Chloroform	119	192	8.00E +03	3.00E-03
Chloroprene	88.5	215		
Cresols	108	0.4	2.00E +04	4.60E-07
Cumene (isopropyl benzene)	120	4.6	50.0	2.00E-04
1,4-dichlorobenzene	147	1.4	49.00	
1,2-dichloroethane	99	62	8.69E +03	1.00E-04
Dichloromethane	85	360	2.00E +04	2.00E-03
Dioxin	178	7.6E-7	3.17E-04	1.20E-03
Epichlorohydrin	92.5	13	6.00E +04	3.08E-05
Ethyl benzene	106	10	152	7.00E-03
Ethylene oxide	44	1,095	1.35E +05	
Formaldehyde	30	3,500	3.00E +05	
Hexachlorobutadiene	261	0.15		
Hydrogen cyanide	27	726		
Hydrogen flouride	20	900		
Hydrogen sulfide	34	15,200		
Hexachlorocyclopentadiene	273	0.03		
Maleic anhydride	98	0.3	1.63E +05	
Methyl acetate	74	170	3.19E +05	1.00E-04
N-Dimethylnitrosamine	81	3.4		
Naphthlene	123	0.23		
Nitrobenzene		0.3	1.90E +03	1.30E-05
Nitrosomorpholine		5.3		
Phenol	94	0.34	9.30E +04	1.02E-05
Phosgene	98	1,300		
Phthalic anhydride	148	0.03	6.17E +03	9.00E-07
Propylene oxide		400		
1,1,2,2-tetrachloroethane	168	9	2.90E +03	2.00E-04
Tetrachloroethylene	166	15	200	
Toluene	92	30	534	5.00E-03
1,1,1-trichloroethane	133	123	720	2.15E-02
Trichloroethylene	131	90	1.10E +03	8.92E-03
Vinylchloride	62.5	2,600	6.00E +03	1.90E-01
Vinylidenechloride	97	500		
Xylenes	106	8.5	1.00	4.04E-04

TABLE 12-5
PHYSICAL PARAMETERS OF PCB MIXTURES\*

Arochlor (PCB)	Vapor pressure at 25°C (atm)	Volubility at 25°C (mg/1)	Henry's Law constant (atm-m³/mol)
1242	2.19E-07	2400	238E-08
1248	1.02E-07	520	1.02E-08
1254	1.85E-08	120	1.40E-08
1260	5.17E-09	30	6.46E-08

<sup>\*</sup> All values estimated based on calculations.

formation. For example, the presence of ash materials and similar wastes would be a case in which particulate emissions would be of concern.

#### 12.3.2 Unit Characterization

Different types of units may have differing release potentials. The particular type of unit, its configuration, and its operating conditions will have a great effect on the nature, extent, and rate of the release. These practices or parameters should be determined and reasonable worst-case operating practices or conditions should also be identified prior to initial sampling.

# 12.3.2.1 Type of Unit

The type of unit will affect its release potential and the types of releases expected. For the purpose of this guidance, units have been divided into three general types with regard to investigating releases to air. These are:

- Area sources having solid surfaces, including land treatment facilities, surfaces of landfills, and waste piles;
- Point sources, including vents, (e.g., breathing vents from tanks) and ventilation outlets from enclosed units (e.g., container handling facilities or stacks); and
- Area sources having liquid surfaces, including surface impound merits and open-top tanks.

The following discussion provides examples for each of these unit types and illustrates the kind of data that should be collected prior to establishing a sampling plan. Table 12-6 indicates types of releases most likely to be observed from each of these example unit types. It should also be recognized that releases to air can be continuous or intermittent in nature.

<u>Waste piles</u> -- Waste piles are primary sources of particulate releases due to entrainment into the air of solid particles from the pile. Waste piles are generally comprised of dry materials which may be released into the air by wind or

# TABLE 12-6 SUMMARY OF TYPICAL UNIT SOURCE TYPE AND AIR RELEASE TYPE

	Source Type			Potential Phase of Release	
Typical Unit Type	Area Sources with Liquid Surface	Area Sources with Solid Surface	Point Sources	Vapor	Particulate
Waste Piles		Х		Х	Х
Land Treatment Units		х		х	х
Landfills		х	х	х	х
Drum Handling Facilities			х	х	х
Tanks	х		х	х	
Surface Impoundments	х			Х	
Incinerators*			х	х	х

<sup>\*</sup> Includes units (e.g., garbage incinerators) not covered by 40 CFR Part 264, Subpart O which pertains to hazardous waste incinerators.

operational activities. The major air contaminants of concern from waste piles will be those compounds that are part of or have been adsorbed onto the particulates. Additionally, volatilization of some constituents may occur. Important unit factors include the waste pile dimensions (e.g., length, width, height, diameter and shape), and the waste management practices (e.g., the frequency and manner in which the wastes are applied to the pile and whether any dust suppression procedures are employed). The pile dimensions determine the surface area available for wind erosion. Disturbances to the pile can break down the surface crust and thus increase the potential for particulate emissions. Dust suppression activities, however, can help to reduce particulate emissions.

Land treatment units -- Liquid or sludge wastes may be applied to tracts of soil in various ways such as surface spreading of sludges, liquid spraying on the surface, and subsurface liquid injection. These methods may also involve cultivation or tilling of the soil. Vapor phase and particulate contaminant releases are influenced by the various application techniques. Particulate or volatile emission releases are most likely to occur during initial application or during tilling, because tilling keeps the soil unconsolidated and loose, and increases the air to waste surface area.

Important unit factors in assessing an air release from a land treatment unit include:

- Waste application method Liquid spraying applications tend to minimize particulate releases while increasing potential volatile releases.
   Subsurface applications generally reduce the potential for particulate and volatile releases.
- Moisture content of the waste Wastes with high moisture content will be less likely to be released as particulates; however, a potential vapor phase release may become more likely.
- Soil characteristics Certain constituents, such as hydrophobic organics, will be more likely to be bound to highly organic soils than non-organic soils. Therefore, releases of these types of constituents are most likely to be associated with particulate emissions.

<u>Landfills</u> -- Landfills can result in particulate and vapor phase releases. This process generally involves placement of waste in subsurface disposal cells and subsequent covering of the waste with uncontaminated soil. Landfill characteristics that can affect contaminant release include:

- Porosity and moisture content of the soil or clay covering can influence the rate at which vapor phase releases move through the soil towards the surface. Finer soils with lower porosities will generally slow movement of vapors through the unit. The frequency of applying soil cover to the open working face of a landfill will also affect the time of waste exposure to the air.
- Co-disposal of hazardous and municipal wastes will often increase the
  potential for vapor phase releases, because biodegradation of municipal
  wastes results in the formation of methane gas as well as other volatile
  organics. Methane gas may act as a driving force for release of other
  volatile hazardous components that may be in the unit (See Section 11 Subsurface Gas.)
- Landfill gas vents, if present, can act as sources of vapor phase emissions of contaminated landfill gases.
- Leachate collection systems can be sites of increased vapor phase emissions due to the concentrated nature of the leachate collected.
   Open trenches are more likely to be emission sources than underground collection sumps due to the increased exposure to the atmosphere.
- Waste mixing or consolidation areas where bulk wastes are mixed with soil or other materials (e.g., fly ash) prior to landfilling can be contributors to both particulate and vapor phase air releases. Practices such as spreading materials on the ground to release moisture prior to landfilling will also increase exposure to the atmosphere.

<u>Drum handling facilities--</u>Emissions from drum or container handling areas can result from several types of basic operations. Frequently, emissions from these operations are vented to the air through ducts or ventilation systems. Air sampling

to assess emissions from these operations may include sampling of the control device outlets, the workplace atmosphere at each operation, or the ambient air downwind of the unit. Factors which effect emissions include:

- Filling operations can be a major source of either vapor or particulate emissions due to agitation of the materials during the filling process. Spillage which occurs during loading may also contribute to emissions. Organic waste components with high volatility will readily vaporize into the air. Similarly, particulate matter can be atmospherically entrained by agitation and wind action. The emission potential of filling operations will be affected by exposure to ambient air. Generally, fugitive emissions from an enclosed building will be less than emissions created during loading in an open structure.
- Cleaning operations can have a high potential for emissions. These
  emissions may be enhanced by the use of solvents or steam cleaning
  equipment. The waste collection systems at these operations usually
  provide for surface runoff to open or below ground sumps, which can
  also contribute to air emissions.
- Volatilization of waste components can also occur at storage units. Since it is common practice to segregate incompatible wastes during storage, the potential for air releases may differ within a storage unit depending on the nature of the wastes stored in any particular area. The most common source of air emission releases from drum storage areas is spills from drums ruptured during shipping and handling.
- For offsite facilities, storage areas frequently are located where drums are sampled during the waste testing/acceptance process. This process involves drum opening for sampling and could also include spillage of waste materials on the ground or floor.

Important release information includes emission rates, and data to estimate release rise (e.g., vent height and diameter as well as vent exit temperature and velocity). Information pertaining to building dimension/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the

stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

<u>Tanks</u>--Tanks can emit volatile waste components under various circumstances. A major determinant of any air emission will be the type of tank being studied. Closed or fixed roof storage tanks will most likely exhibit less potential for air emissions than open topped tanks. Some tanks are equipped with vapor recovery systems that are designed to reduce emissions. Important process variables for understanding air emissions from tanks can be classified as descriptive and operational variables:

- Descriptive variables include type, age, location, and configuration of the tank.
- Operational variables include aeration, agitation, filling techniques, surface area, throughput, operating pressure and temperature, sludge removal technique and frequency, cleaning technique and frequency, waste retention and vent pipe dimensions and flow rate.

Important release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity). Information pertaining to building dimensions/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

<u>Surface impoundments-</u>-Surface impoundments are similar in many ways to tanks in the manner in which air emissions may be created. Surface impoundments are generally larger, at least in terms of exposed surface areas, and are generally open to the atmosphere. The process variables important for the evaluation of releases to air from surface impoundments can also be classified as descriptive and operational.

 Descriptive parameters include dimensions, including length, width, and depth, berm design, construction and liner materials used, and the location of the unit on the site. • Operational parameters include freeboard, filling techniques (in particular, splash versus submerged inlet), depth of liquid and sludge layers, presence of multiple liquid layers, operating temperature, sludge removal techniques and frequency, cleaning technique and frequency, presence of aerators or mixers, biological activity factors for biotreatment, and the presence of baffles, oil layers, or other control measures on the liquid surface. (These factors are relevant to some tanks aswell.)

Some surface impoundments are equipped with leak collection systems that collect leaking liquids, usually into a sump. Air emissions can also occur from these sumps. Sump operational characteristics and dimensions should be documented and, if leaks occur, the volume of material entering the sump should be documented. (These factors are relevant to some tanks as well.)

Incinerators - Stack emissions from incinerators (i.e., incinerator units not addressed by RCRA in Part 264, Subpart O, e.g., municipal refuse incinerators) can contain both particulate and volatile constituents. The high temperatures of the incineration process can also cause volatilization of low vapor pressure organics and metals. Additional volatile releases can occur from malfunctioning valves during incinerator charging. The potential for air emissions from these units is primarily a function of incinerator operating conditions and emission controls. Important unit release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity), as well as building dimensions/orientation of the unit and nearby structures. This information is needed to assess the aerodynamic behavior of the stack/vent release and for input to atmospheric dispersion models.

#### 12.3.2.2 Size of Unit

The size of the unit(s) of concern will have an important impact on the potential magnitude of a release to air. The release of hazardous constituents to the air from an area source is often directly proportional to the surface area of the unit, whether this surface area is a liquid (e.g., in a tank) or a solid surface (e.g., a land treatment unit). The scope of the air investigation may be a function of the

size of the unit. Generally, more sampling locations will be required as the unit increases in size, due primarily to increased surface area. Also, as the total amount of waste material present in a particular unit increases, it will represent a larger potential reservoir or source of constituents which may be released.

Scaling factors, such as surface area to volume ratios should also be evaluated. One large waste pile, for instance, can exhibit a lower ratio of surface area to total volume than the sum of two smaller piles in which the total volume equals that of the larger pile. Other units such as tanks may exhibit a similar economy of surface area, based on the compact geometry of the unit.

Because releases to air generally occur at the waste/atmosphere interface, surface area is generally a more important factor than total waste volume. Consequently, operations that increase the atmosphere/waste interface, such as agitation or aeration, splash filling, dumping or filling operations, and spreading operations will tend to increase the emission rate. Total emissions, however, will be a function of the total mass of the waste constituent(s) and the duration of the release.

For point sources, the process or waste throughput rate will be the most important unit information needed to evaluate the potential for air emissions (i. e., stack/vent releases).

#### 12.3.2.3 Control Devices

The presence of air pollution control devices on units can have a major influence on the nature and extent of releases. Control devices can include wet or dry scrubbers, electrostatic precipitators, baghouses, filter systems, wetting practices for solid materials, oil layers on surface impoundments, charcoal or resin absorption systems, vapor flares, and vapor recovery systems. Many of these controls systems can be installed on many of the unit types discussed in this section. Due to the variety of types of devices and the range of operational differences, an in depth discussion of individual control devices is not presented here. Additional information on control technologies for hazardous air pollutants is available in the following references:

U.S. EPA. 1986. <u>Handbook - Control Technologies for Hazardous Air Pollutants.</u> EPA/625/6-86/014. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. 1986. <u>Evaluation of Control Technologies for Hazardous Air Pollutants:</u> Volume 1 - Technical Report. EPA/600/7-86/009a. NTIS PB 86-167020. Volume 2 - Appendices. EPA/600/7-86/009b. NTIS PB 86-167038. Office of Research and Development. Research Triangle Park, N.C. 27711.

If a control device is present on the unit of concern, descriptive and operational characteristics of the unit/control device combination should be reviewed and documented. In many cases, performance testing of these devices has been conducted after their installation on the unit(s). Information from this testing may help to quantify releases to air from the unit(s); however, this testing may not have been performed under a "reasonable worst-case" situation. The conditions under which the testing was performed should be documented.

# 12.3.2.4 Operational Schedules

Another characteristic which can affect the magnitude of a release to air from a unit is the unit's operational schedule. if the unit is operational on a part time or batch basis, the emission or release rate should be measured during both operational and non-operational periods. In contrast to batch operations, emission or release rates from continuous waste management operations may be measured at any time.

#### 12.3.2.5 Temperature of Operation

Phase changes of liquids and solids to gases is directly related to temperature. Therefore, vapor phase releases to air are directly proportional to process temperature. Thus, it is important to document operational temperature (i.e., waste temperature) and fluctuations to enhance the understanding of releases to air from units. Particular attention should be paid to this parameter in the review of existing data or information regarding the operation of the unit.

The release rate of volatile components also generally increases with temperature. Frequently, the same effect is observed. for particulate, because entrainment is enhanced as materials are dried. Thus, the evaporation of any water from solids, which generally increases as temperature increases, will likely increase the emissions of many particulate in the waste streams. Evaporation of water may also serve to concentrate wastes, leading to conditions more conducive to vapor phase releases to air. It should also be noted that the destruction efficiency of incinerators is also a function of temperature (i. e., higher temperatures are generally associated with greater destruction efficiency).

# 12.3.3 Characterization of the Environmental Setting

Environmental factors can influence not only the rate of a release to air but also the potential for exposure. Significant environmental factors include climate, soil conditions, terrain and location of receptors. These factors are discussed below.

#### 12.3.3.1 Climate

Wind, atmospheric stability and temperature conditions affect emission rates from area sources as well as atmospheric dispersion conditions for both area and point sources. Historical summaries of climatic factors can provide a basis to assess the long-term potential for air emissions and to characterize long-term ambient concentration patterns for the area. Short-term measurements of these conditions during air monitoring will provide the meteorological data needed to interpret the concurrent air quality data. Meteorological monitoring procedures are discussed in Section 12.8. Available climatic information, on an annual and monthly or seasonal basis, should be collected for the following parameters:

- Wind direction and roses (which affects atmospheric transport, and can be used to determine the direction and dispersion of release migration);
- Mean wind speeds (which affects the potential for dilution of releases to air);
- Atmospheric stability distributions (which affects dispersion conditions);

- Temperature means and extremes (which affects the potential for volatilization, release rise and wind erosion);
- Precipitation means (which affects the potential for wind erosion of particulate);
- Atmospheric pressure means (which affects the potential for air emissions from landfills); and
- Humidity means (which can affect the air collection efficiencies of some absorbents - see Section 12.8).

The primary source of climate information for the United States is the National Climatic Data Center (Asheville, NC). The National Climatic Data Center can provide climate summaries for the National Weather Service station nearest to the site of interest. Standard references for climatic information include the following:

National Climatic Data Center. Local Climatological Data - Annual Summaries with Comparative Data, published annually. Asheville, NC 28801.

National Climatic Data Center. <u>Climates of the States</u>. 1973. Asheville, NC 28801.

National Climatic Data Center. <u>Weather Atlas of the United States</u>. 1968. Asheville, NC 28801.

The climatological data should be evaluated considering the effects of topography and other local influences that can affect data representativeness.

A meteorological monitoring survey may be conducted prior to ambient air monitoring to establish the local wind flow patterns and for determining the number and locations of sampling stations. The survey results will be used to characterize local prevailing winds and diurnal wind flow patterns (e. g., daytime upslope winds, nighttime downslope winds, sea breeze conditions) at the site. The survey should be conducted for a one-month period and possibly longer to adequately characterize anticipated wind patterns during the air monitoring

reprogram. Inland, flat terrain conditions may not necessitate an onsite meteorological monitoring survey if representative data are available from previous onsite studies or from National Weather Service stations.

The meteorological monitoring data collected during the initial monitoring phase can serve as a basis for the placement of air sampling stations during any subsequent monitoring phases.

#### 12.3.3.2 Soil Conditions

Soil conditions (e.g., soil porosity) can affect air emissions from landfills and the particulate wind erosion potential for contaminated surface soils. Soil conditions pertinent to characterizing the potential for air emissions include the following:

- Soil porosity (which affects the rate of potential gaseous emissions);
- Particle size distribution (which affects the potential for particulate emissions from contaminated soils); and
- Contaminant concentrations in soil (i. e., potential to act as air emission sources).

Soil characterization information is presented in Section 9.

#### 12.3.3.3 Terrain

Terrain features can significantly influence the atmospheric transport of air emissions. Terrain heights relative to release heights will affect groundlevel concentration. Terrain obstacles such as hills and mountains can divert regional winds. Likewise, valleys can channel wind flows and also limit horizontal dispersion. In addition, complex terrain can result in the development of local diurnal wind circulations and affect wind speed, atmospheric turbulence and stability conditions. Topographic maps of the facility and adjacent areas are needed to assess local and regional terrain. Guidance on the appropriate format and sources of topographic and other maps is presented in Section 7 and Appendix A.

#### 12.3.3.4 Receptors

Information concerning the locations of nearby buildings and the population distribution in the vicinity of the site are needed to identify potential air-pathway receptors. This receptor information provides a basis for determining the need for interim corrective measures. Both environmental and human receptor information is needed to assess potential air-pathway exposures. Such information may include:

- A site boundary map;
- Location of nearest buildings and residences for each of the sixteen 22.5 degree sectors which corresponds to major compass points (e.g., north, north-northwest);
- Location of buildings and residences that correspond to the area of maximum offsite ground level concentrations based on preliminary modeling estimates (these locations may not necessarily be near the site boundary for elevated releases); and
- Identification of nearby sensitive receptors (e.g., nursing homes, hospitals, schools, critical habitat of endangered or threatened species).

The above information should be considered in the planning of an air monitoring program. Additional guidance on receptor information is provided in Section 2.

# 12.3.4 Review of Existing Information

The review of existing air modeling/monitoring data entails both summarizing the reported air contaminant concentrations as well as evaluating the quality of these data. Air data can be of many varieties and of varying utility to the RFI process. Modeling data should be evaluated based on the applicability of the model used, model accuracy, as well as the quality and representativeness of the input data.

One of the most basic parameters to review in any type of air monitoring data should be the validity of the sampling locations used during the collection of the monitoring data. The results of previous investigations should be assessed with respect to the upwind-downwind pattern around the unit to determine the likelihood that the sampling devices would have measured releases from the unit of concern. For relatively simple sites (e.g., flat terrain, constant wind speed and direction), this determination should be fairly straight-forward; however, for complex sites (e.g., complex terrain, variable winds, multiple sources, etc.), assessing the appropriateness of past sampling locations should consider such factors as potential interferences that may not have been addressed by the sampling scheme.

The most useful monitoring data are compound-specific results which can be associated with the unit being investigated, or, for point sources (such as vent stacks or ventilation system outlets), direct measurements of the exhaust prior to its release into the atmosphere. Because the hazardous properties and health and environmental criteria are compound-specific, general compound category or class data (e.g., hydrocarbon results) are less meaningful. Any existing air data should also be described and documented as to the sampling and analysis methods utilized, the associated detection limits, precision and accuracy, and the results of QA/QC analyses conducted. Results reported as non-detected (i. e., not providing numerical detection limits) are likely to be of no value.

In addition, available upwind and downwind air data should be evaluated to determine if the contamination is due to releases from the unit. If background data are available for the unit of concern, the data will be of much greater use in the planning of additional air monitoring tasks. Upwind data (to characterize ambient air background levels) are important for evaluating if downwind contamination can be attributed to the unit of concern. If background data are not available, the existing downwind air concentration data will be of less value in characterizing a release; however, the lack of background data does not negate the utility of the available monitoring data.

Data may also be available from air monitoring studies that did not focus directly on releases from a unit of concern. Many facilities conduct onsite health and safety programs, including routine monitoring of air quality for purposes of evaluating worker exposure. This type of data may include personnel hygiene

monitoring results from personal sampling systems worn by employees as they perform their jobs, general area monitoring of zones at which hazardous operations are conducted, or actual unit-emission monitoring. The detection limits of these methods (generally in parts per million) are frequently higher than are needed for RFI purposes. However, this type of industrial hygiene monitoring is frequently compound-specific, and can be useful in qualitatively evaluating the air emissions from particular sources.

Indoor air monitoring, generally only applicable to units that are enclosed in a building (e.g., drum handling areas or tanks), often includes flow monitoring of the ventilation system. Monitoring of hoods and ductwork systems may have been conducted to determine exchange time and air circulation rates. These flow determinations could prove to be useful in the evaluation of air emission measurements during the RFI.

Another important aspect of the existing data review is to document any changes in composition of the waste managed in the unit of concern since the air data were collected. Also, changes in operating conditions or system configuration for waste generation and/or unit functions could have major effects on the nature or extent of releases to air. If such operational or waste changes have occurred, they should be summarized and reviewed to determine their role in the evaluation of existing data. This summary and review will not negate the need to take new samples to characterize releases from the unit. However, such information can be useful in the planning of the new air monitoring activities.

#### 12.3.5 Determination of "Reasonable Worst-Case" Exposure Period

A "reasonable worst-case" exposure period over a 90 day period should be identified if an air monitoring program is to be conducted. Determination of reasonable worst-case exposure conditions will aid in planning the air monitoring program and is dependent on seasonal variations in emission rates and dispersion conditions.

The selection of the "reasonable worst-case" 90-day exposure period for the conduct of air monitoring should account for the following factors:.

- For vapor phase releases, wind speed and temperature are the key factors affecting releases from the unit. In general, the higher the temperature and windspeed, the greater the rate of volatilization of constituents of concern from the waste. This process is tempered, however, by the fact that at higher windspeeds, dispersion of the release is generally greater, resulting in lower downwind concentrations at potential exposure points.
- For particulate releases, wind speed is the key meteorological factor. The amount of local precipitation contributing to the degree of moisture of the waste may also be important. In general, the higher the windspeed, and the drier the waste, the greater will be the potential for particulate release. As with vapor phase releases, higher wind speeds may also lead to greater dispersion of the release, resulting in lower downwind concentrations.
- For point source releases, increased wind speeds and unstable atmospheric conditions (e. g., during cloudless days) enhance dispersion but also tend to reduce plume height and can lead to relatively high groundlevel concentrations.
- Constituent concentrations at any downwind sector will also be directly affected by the wind direction and frequency.

Air emission release rate models and atmospheric dispersion models can be used to identify reasonable worst-case exposure conditions (i.e., to quantitatively account for the above factors). For this application, it is recommended that the modeling effort be limited to a screening/sensitivity exercise with the objective of obtaining "relative" results for a variety of source and meteorological scenarios. By comparing results in a relative fashion, only those input meteorological parameters of greatest significance (e.g., temperature, wind speed and stability) need to be considered.

In general, the summer season will be the "reasonable worst-case" exposure period at most sites because of relatively high temperatures and low windspeeds. Spring and fail are also candidate monitoring seasons that should be evaluated on a

site-specific basis. Winter is generally not a prime season for air monitoring due to lower temperatures and higher wind speeds.

# 12.4 Air Emission Modeling

# 12.4.1 Modeling Applications

Air emission models can be used to estimate constituent-specific emission rates based on waste/unit input data for many types of waste management units. (An emission rate is defined as the source release rate for the air pathway in terms of mass per unit of time.)

An important application of emission models in the RFI release characterization strategy for air is the conduct of screening assessments. For this application, available waste/unit input data for emission models, in conjunction with dispersion modeling results, are used to estimate concentrations at locations of interest. These results can then be evaluated to determine if adequate information is available for RFI decision making or if monitoring is needed to further reduce the uncertainty associated with characterizing the release. Depending on the degree of uncertainty in the estimated concentrations relative to the differences between the estimated concentrations and the health based levels, modeling results may be sufficient to characterize the release as significant (i.e., implementation of corrective action would be appropriate) or as insignificant (i. e., no further action is warranted).

Emission rate models can also be used to identify potential major air emission sources at a facility (especially multiple-unit facilities). For this type of application, modeling results are used to compare routine long-term emissions from various units to prioritize the need for release characterization at each unit. For example, modeling results may indicate that 90 percent of the volatile organic compound emissions at a facility are attributable to surface impoundment units and only 10 percent to other sources. Therefore, emphasis should be on characterizing releases from the surface impoundments.

Emission modeling is not available for all air-related phenomenon associated with waste management. For example, anaerobic biological activity in surface

impoundments may, in certain instances, contribute to air pollution by emitting constituents not contained in the waste placed in the impoundment and which available models do not adequately address. in such instances, source testing or monitoring may be necessary; based on such monitoring, emission rates can be developed.

#### 12.4.2 Model Selection

The information gathered during the initial stage of the air investigation should be used to select appropriate models and to estimate unit-specific and constituent-specific emission rates. A thorough understanding of the available models is needed before selecting a model for an atypical emission source. When gathering information on any emission source, it would be useful to obtain a perspective of the potential variability of the waste and unit input data. A sensitivity analysis of this variability relevant to emission rate estimates would help determine the level of confidence associated with the emission modeling results.

Air emission models can be classified into two categories; models which can be used to estimate volatile organic releases, and models which can be used to estimate particulate emissions. These are discussed below.

#### 12.4.2.1 Organic Emissions

Comprehensive guidance on the application of air emission models for volatile organic releases from various units is presented in the following references:

- U.S. EPA. December 1987. <u>Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Air Emission Model</u>s. EPA-450/3-87-026. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.
- U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

These references provide modeling guidance for the following units:

# Surface impoundments

Storage impoundments
Disposal impoundments
Mechanically aerated impoundments
Diffused air systems
Oil film surfaces

# I Land treatment

Waste application
Oil film surfaces
Tilling

#### I Landfills

Closed landfills Fixation pits Open landfills

# I Waste piles

I Transfer, storage and handling operations

Container loading
Container storage
Container cleaning
Stationary tank loading
Stationary tank storage

· Spills

Fugitive emissions
Vacuum truck loading

Emission factors for various evaporation loss sources (e.g., storage and handling of organic liquids) are provided in the following reference:

U.S. EPA. 1985. (Fourth edition and subsequent supplements) <u>Compilation of Air Pollutant Emission Factors</u>. EPA AP-42. NTIS PB 86-124906. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

An emission factor is generally defined as an average value which relates the quantity of a pollutant released to the atmosphere with the activity associated with the release of the pollutant. However, for estimation of organic releases from storage tanks, the emission factors are presented in terms of empirical formulae which can relate emissions to such variables as tank diameter, liquid temperature, etc.

Selection of an appropriate air emission model will be based primarily on selection of a model which is appropriate for the unit of concern, has technical credibility and is practical to use. Some of the models presented in <a href="Hazardous Waste Treatment">Hazardous Waste Treatment</a>, Storage and Disposal Facilities (TSDF) - Air Emission Models (U.S. EPA, December 1987), are available on a diskette for use on a microcomputer. Computer-compatible air emission models (referred to as CHEMDAT6 models) are available for the following sources.

- Nonaerated impoundments
- Open tanks
- Aerated impoundments
- Land treatment
- Landfills

These models are prime candidates for RFI air release characterization applications.

#### 12.4.2.2 Particulate Emissions

Guidance on the selection and application of air emission models for particulate releases is presented in the following references:

U.S. EPA. February 1985. Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites. EPA/600-18-85/002. Office of Health and Environmental Research. Washington, D.C. 20460.

U.S. EPA. 1985. (Fourth edition and subsequent supplements) <u>Compilation of Air Pollutant Emission Factors</u>. EPA, AP-42. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. 1978. <u>Fugitive Emissions from Integrated Iron and Steel Plants</u>. EPA 600/2-78-050. Washington, D.C. 20460.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analysis for Superfund Applications</u>. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

These references provide modeling guidance for the following particulate sources and associated operations and activities (e.g., vehicular traffic):

- Wastepiles
- Flat, open surfaces

The air emission models for both types of sources should account for both wind erosion potential as well as releases due to mechanical disturbances.

The U.S. EPA-Office of Air Quality Planning and Standards is currently developing guidance regarding particulate emissions from hazardous waste transfer, storage and disposal facilities.

# 12.4.3 General Modeling Considerations

Organics in surface impoundments, land treatment facilities, landfills, and wastepiles, can depart through a variety of pathways, including volatilization, biological decomposition, adsorption, photochemical reaction, and hydrolysis. To allow reasonable estimates of organic disappearance, it is necessary to determine which pathways predominate for a given chemical, type of unit, and set of meteorological conditions.

Source variability will significantly influence the relative importance of the pathways. For highly variable sources it may be possible to exclude insignificantly small pathways from consideration. The relative magnitude of these pathways then

can be computed by applying the methodology to a model facility to determine relative differences among various compounds. A summary of typical pathways for air emission sources is presented in Table 12-7.

It is also necessary to consider the variation of waste composition as a function of time as well as other potential variations in source conditions. These variable conditions may necessitate multiple modeling scenarios to adequately characterize representative waste/unit conditions.

# 12.5 Dispersion Modeling

# 12.5.1 Modeling Applications

Atmospheric dispersion models can be used to estimate constituent-specific concentrations at locations of interest based on input emission rate and meteorological input data. The major RFI dispersion modeling applications for characterizing releases to air can be summarized as follows:

- Screening assessments: Dispersion models can be used to estimate concentrations at locations of interest using input emission rate data based on air emission modeling.
- Emission monitoring: Dispersion models can be used to estimate concentrations at locations of interest using input emission rate data based on emission rate monitoring.
- Confirmatory air monitoring: Dispersion modeling can be used to assist in designing an air monitoring program (i. e., to determine appropriate monitoring locations and monitoring period) as well as for interpretation and extrapolation of monitoring results.

Atmospheric dispersion models can be used for monitoring program design applications to identify areas of high concentration relative to the facility property boundary or actual receptor locations. High concentration areas which correspond to actual receptors are priority Locations for air monitoring stations.

TABLE 12-7

TYPICAL PATHWAYS FOR AREA EMISSION SOURCESa

Pathway	Surface Impoundments	Land Treatment	Landfill
Volatilization			
Biodegradation	1	1	S
Photodecomposition	S	N	N
Hydrolysis	S	N	N
Oxidation/reduction	N	N	N
Adsorption	N	N	N
Hydroxyl radical reaction	N	N	N
Migration	N	N	N
Runoffb	N	N	N

I = Important

S = Secondary

N = Negligible or not applicable

- a Individual chemicals in a given site type may have dominant pathways different from the ones shown here.
- b Water migration and runoff are considered to have negligible effects on ground and surface water in a properly sited, operated, and maintained RCRA-permitted hazardous waste treatment, storage, and disposal facility.

Dispersion models (with input emission rates based on emission models) can also be used to provide seasonal air concentration "patterns" based on available representative historical meteorological data (either onsite or offsite). Comparison of seasonal air concentration patterns can be used to identify the "reasonable worst case" period for monitoring. Air concentration patterns based on modeling results can similarly be used to evaluate the representativeness of the actual data collection period. Representativeness is determined by comparing the air concentration patterns for the actual air monitoring period with historic seasonal air concentration patterns.

The objective of the modeling applications discussed above involves the estimation of long-term (i.e., several months to years) concentration patterns. These long-term patterns do not have the variability associated with short-term (i.e., hours to days, such as a 24-hour event) emission rate and dispersion conditions, and are more conducive to data extrapolation applications. For example, near source and fenceline air monitoring results can be used to back calculate an emission rate for the source. This estimated emission rate can be used as dispersion modeling input to estimate offsite air concentrations for the same downwind sector and exposure period as for the air monitoring period.

#### 12.5.2 Model Selection

Guidance on the selection and application of dispersion models is provided in the following references:

U.S. EPA. July 1986. <u>Guidelines on Air Quality Models (Revised)</u>. EPA-450/12-78-027R. NTIS PB86-245248. Office of Air Quality Planning and Standards. Research Triangle Part, NC 27711.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

The following information is based primarily on guidance provided in these references.

#### 12.5.2.1 Suitability of Models

The extent to which a specific air quality model is suitable for the evaluation of source impact depends upon several factors. These include: (1) the meteorological and topographic complexities of the area; (2) the level of detail and accuracy needed for the analysis; (3) the technical competence of those undertaking such simulation modeling; (4) the resources available; and (5) the detail and accuracy of the data base, i.e., emissions inventory, meteorological data, and air quality data, Appropriate data should be available before any attempt is made to apply a model. A model that requires detailed, precise, input data should not be used when such data are unavailable. However, assuming the data are adequate, the greater the detail with which a model considers the spatial and temporal variations in emissions and meteorological conditions, the greater the ability to evaluate the source impact and to distinguish the effects of various control strategies.

Air quality models have been applied with the most accuracy or the least degree of uncertainty to simulations of long term averages in areas with relatively simple topography. Areas subject to major topographic influences experience meteorological complexities that are extremely difficult to simulate. Although models are available for such circumstances, they are frequently site-specific and resource intensive. In the absence of a model capable of simulating such complexities, only a preliminary approximation may be feasible until such time as better models and data bases become available.

Models are highly specialized tools. Competent and experienced personnel are an essential prerequisite to the successful application of simulation models. The need for specialists is critical when the more sophisticated models are used or the area being investigated has complicated meteorological or topographic features. A model applied improperly, or with inappropriately chosen data, can lead to serious misjudgments regarding the source impact or the effectiveness of a control strategy.

The resource demands generated by use of air quality models vary widely depending on the specific application. The resources required depend on the nature of the model and its complexity, the detail of the data base, the difficulty of

the application, and the amount and level of expertise required. The costs of manpower and computational facilities may also be important factors in the selection and use of a model for a specific analysis. However, it should be recognized that under some sets of physical circumstances and accuracy requirements, no present model may be appropriate. Thus, consideration of these factors should not lead to selection of an inappropriate model.

#### 12.5.2.2 Classes of Models

Dispersion models can be categorized into four generic classes: Gaussian, numerical, statistical or empirical, and physical. Within these classes, especially Gaussian and numerical models, a large number of individual "computational algorithms" may exist, each with its own specific applications. While each of the algorithms may have the same generic basis, e.g., Gaussian, it is accepted practice to refer to them individually as models. In many cases the only real difference between models within the different classes is the degree of detail considered in the input or output data.

Gaussian models are the most widely used techniques for estimating the impact of nonreactive pollutants. Numerical models may be more appropriate than Gaussian models for area source urban applications that involve reactive pollutants, but they require much more extensive input data bases and resources and therefore are not as widely applied. Statistical or empirical techniques are frequently employed in situations where incomplete scientific understanding of the physical and chemical processes or lack of the required data bases make the use of a Gaussian or numerical model impractical.

Physical modeling, the fourth generic type, involves the use of wind tunnel or other fluid modeling facilities. This class of modeling is a complex process requiring a high level of technical expertise, as well as access to the necessary facilities. Nevertheless, physical modeling may be useful for complex flow situations, such as building, terrain or stack down-wash conditions, plume impact on elevated terrain, diffusion in an urban environment, or diffusion in complex terrain. It is particularly applicable to such situations for a source or group of sources in a geographic area limited to a few square kilometers. The publication "Guideline for Fluid Modeling

of Atmospheric Diffusion" provides information on fluid modeling applications and the limitations of that method (U.S. EPA, 1981).

# 12.5.2.3 Levels of Sophistication of Models

In addition to the various classes of models, there are two levels of sophistication. The first level consists of general, relatively simple estimation techniques that provide conservative estimates of the air quality impact of a specific source, or source category. These are screening techniques or screening models. The purpose of such techniques is to eliminate the need for further more detailed modeling for those sources that clearly can be characterized and evaluated based on simple screening assessments.

The second level consists of those analytical techniques that provide more detailed treatment of physical and chemical atmospheric processes, require more detailed and precise input data, and provide more specialized concentration estimates. As a result they provide a more refined and, at least theoretically, a more accurate estimate of source impact and the effectiveness of control strategies. These are referred to as refined models.

The use of screening techniques followed by a more refined analysis is always desirable, however, there are situations where the screening techniques are practically and technically the only viable option for estimating source impact. In such cases, an attempt should be made to acquire or improve the necessary data bases and to develop appropriate analytical techniques.

#### 12.5.2.4 Preferred Models

Guidance on EPA preferred models for screening and refined applications is provided in the following references:

U.S. EPA. July 1986. <u>Guidelines on Air Quality Models (Revised)</u>. EPA-450/2-78-027R. NTIS P886-245248. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. October 1977. <u>Guidelines for Air Quality Maintenance Planning and Analysis</u>. Vol. 10 (Revised): Procedures for Evaluating Air Quality Impact of <u>New Stationary Sources</u>. EPA-450/4-77-001. NTIS PB274-087. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Appropriate dispersion models commensurate with the above guidance and suitable for mainframe computer use are included in the UNAMAP series available from NTIS. Versions of the UNAMAP models suitable for use on a microcomputer are also available from commercial sources.

Alternative screening approaches based on hand calculations are available for point sources located in flat terrain based on the following guidance:

Turner, D.B. 1969. <u>Workbook of Atmospheric Dispersion Estimates</u>. Public Health Service. Cincinnati, OH.

U.S. EPA. March 1988 Draft. <u>A Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants</u>. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Preferred models for selected applications in simple terrain are identified in Table 12-8. Appropriate dispersion models for complex terrain applications generally need to be determined on a case-by-case basis. Acceptable models may not be available for many complex terrain applications.

The use of the Industrial Source Complex (ISC) Model is recommended as a prime candidate for RFI atmospheric dispersion modeling applications. Applicable ISC source types include stack area and volume sources. Concentration estimates can be based on times of as shot-t as one hour and as long as one year. The model can be used for both flat and rolling terrain. The ISC model can also account for atmospheric deposition (i.e., inter-media transport to soil). The ISC Model (See EPA

TABLE 12-8
PREFERRED MODELS FOR SELECTED APPLICATIONS IN SIMPLE TERRAIN

Short Term (1-24 hours)	Land Use	Model*
Single Source	Rural Urban	CRSTER RAM
Multiple Source	Rural Urban	MPTER RAM
Complicated Sources**	Rural/Urban	ISC*
Buoyant Industrial Line Sources	Rural	B LP
Long Term (monthly, seasonal or annual)		
Single Source	Rural Urban	CRSTER RAM
Multiple Source	Rural Urban	MPTER CDM 2.0 or RAM***
Complicated Sources**	Rural/Urban	ISC*
Buoyant Industrial Line Sources	Rural	BLP

<sup>•</sup> The long-term version of ISC (i.e., ISCLT) is recommended as the preferred dispersion model for RFI applications.

<sup>\*\*</sup> Complicated sources are sources with special problems such as aerodynamic downwash, particle deposition, volume and area sources, etc.

<sup>\*\*\*</sup>If only a few sources in an urban area are to be modeled, RAM should be used.

450/4-86-005a and b) is included in the UNAMAP series available through the NTIS (U.S. EPA, June 1986).

Additional guidance on dispersion model selection and application is available from EPA Regional Office and State modeling representatives as well as from the EPA Model Clearinghouse.

If other than preferred models are selected for use, early discussions with the regulatory agency is encouraged. Agreement on the data base to be used, modeling techniques to be applied and the overall technical approach, prior to the actual analyses, helps avoid misunderstandings concerning the final results and may reduce the later need for additional analyses. The preparation (and submittal to the appropriate regulatory agency) of a written modeling protocol is recommended for all RFI atmospheric dispersion modeling applications.

#### 12.5.3 General Modeling Considerations

Dispersion modeling results are limited by the amount, quality and representativeness of the input data. In addition to meteorological and source data modeling input, the following are also important modeling factors:

- Location of facility property boundary
- Dispersion coefficients
- Stability categories
- Plume rise
- Chemical transformation
- Gravitational settling and deposition
- Urban/rural classification

In designing a computational network for modeling, the emphasis should be placed on location with respect to the facility property boundary. The selection of sites should be a case-by-case determination taking into consideration the topography, the climatology, monitor sites, and should be based on the results of the initial screening procedure, Additional locations may be needed in the high concentration location if greater resolution is indicated by terrain or source factors.

Gaussian models used in most applications should employ dispersion coefficients consistent with those contained in the preferred models available in UNAMAP. Factors such as averaging time, urban/rural surroundings, and type of source (point vs. line) may dictate the selection of specific coefficients.

The Pasquill approach to classifying stability is generally required in all preferred models. The Pasquill method, as modified by Turner, was developed for use with commonly observed meteorological data from the National Weather Service (NWS) and is based on cloud cover, insolation and wind speed.

Procedures to determine Pasquill stability categories from other than NWS data are presented in <u>Guidelines on Air Quality Models (Revised)</u> (U.S. EPA, July 1986). Any other method to determine Pasquill stability categories should be justified on a case-by-case basis.

The plume rise methods incorporated in the EPA preferred models are recommended for use in all modeling applications. No provisions in these models are made for fumigation or multi-stack plume rise enhancement or the handling of such special plumes as flares; these problems should be considered on a case-by-case basis.

Where aerodynamic downwash occurs due to the adverse influence of nearby structures, the algorithms included in the ISC model should be used.

Use of models incorporating complex chemical mechanisms should be considered only on a case-by-case basis with proper demonstration of applicability. These are generally regional models not designed for the evaluation of individual sources but used primarily for region-wide evaluations.

An "infinite half-life" should be used for estimates of total suspended particulate concentrations when Gaussian models containing only exponential decay terms for treating settling and deposition are used. Gravitational settling and deposition may be directly included in a model if either is a significant factor. At least one preferred model (ISC) contains settling and deposition algorithms and is recommended for use when particulate matter sources can be quantified and settling and deposition are problems.

The selection of either rural or urban dispersion coefficients in a specific application should follow one of the procedures presented in <u>Guidelines on Air Quality Models (Revised)</u> (U.S. EPA, July 1986). These include a land use classification procedure or a population based procedure to determine whether the character of an area is primarily urban or rural.

#### 12.6 Design of a Monitoring Program to Characterize Releases

Monitoring procedures should be developed based on the information previously described, including determination of reasonable worst-case scenarios as discussed above. This section discusses the recommended monitoring approaches.

Primary elements in designing a monitoring system include:

- Establishing monitoring objectives;
- Determining monitoring constituents of concern;
- Monitoring schedule;
- Monitoring approach; and
- Monitoring locations.

Each of these elements should be addressed to meet the objectives of the initial monitoring phase, and any subsequent monitoring that may be necessary. These elements are described in detail below.

# 12.6.1 Objectives of the Monitoring Program

The primary goal of the air investigation is to determine concentrations at the facility property boundary as input to the health and environmental assessment process. As discussed previously, the monitoring program may be conducted in a phased approach, using the results of initial monitoring and/or modeling to determine the need for and scope of subsequent monitoring.

Principal components of both the initial and subsequent monitoring phases are:

- Identification or verification of constituents;
- Characterization of long-term air constituent concentrations (based on a "reasonable worst case" exposure period) at:
  - the unit boundary to maximize the potential for release detection the facility property boundary
  - actual offsite receptor locations (for determining the need for interim corrective measures)
  - areas upwind of the release source (to characterize background concentrations); and
- Collection of meteorological data during the monitoring period to aid in evaluating the air monitoring data.

Atmospheric dispersion modeling may also be used to estimate concentrations, if monitoring is not practical, as discussed previously.

Subsequent monitoring may be necessary if initial monitoring and modeling data were not sufficient to characterize long-term ambient constituent concentrations.

## 12.6.2 Monitoring Constituents and Sampling Considerations

Sampling and analysis may be conducted for all appropriate Appendix VIII constituents that have an air pathway potential (See Section 3 and Appendix B). An alternative approach is to use unit and waste-specific information to identify constituents that are not expected to be present and thus, reduce the list of target monitoring constituents. For example, the industry specific monitoring constituent lists presented in Appendix B, List 4 can be used to identify appropriate air monitoring constituents for many applications (especially for units that serve only a limited number of industrial categories). The target constituents selected should be

limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8).

Results from screening assessment, emission monitoring, and/or screening sampling phase (as defined later in Section 12.6.4.1) may also be used as a basis for selection of monitoring constituents. These results may confirm/identify appropriate monitoring constituents for the unit of concern.

#### 12.6.3 Meteorological Monitoring

Monitoring of onsite meteorological conditions should be performed in concert with other emission rate and air monitoring activities. Meteorological monitoring results can serve as input for dispersion models, can be used to assure that the air monitoring effort is conducted during the appropriate meteorological conditions (e.g., "reasonable worst case" period for initial monitoring), and to aid in the interpretation of air monitoring data.

# 12.6.3.1 Meteorological Monitoring Parameters

The following meteorological parameters should be routinely monitored while collecting ambient air samples:

- Horizontal wind speed and direction;
- Ambient temperature;
- Atmospheric stability (e.g., based on the standard deviation of horizontal wind direction or alternative standard methodologies);
- Precipitation measurements if representative National Weather Service data are not available; and
- Atmospheric pressure (e.g., for landfill sites or contaminated soils) if representative National Weather Service data are not available.

It is recommended that horizontal wind speed and direction, and air temperature be determined onsite with continuous recording equipment. Estimates from offsite monitors are not likely to be representative for all of the conditions at the site. Input parameters for dispersion models, if appropriate, should be reviewed prior to conducting the meteorological data collection phase to ensure that all necessary parameters are included.

Field equipment used to collect meteorological data can range in sophistication from small, portable, battery-operated units with wind speed and direction sensors, to large, permanently mounted, multiple sensor units at varying heights. Individual sensors can collect data on horizontal wind speed and direction, three-dimensional wind speed, air temperature, humidity, dew point, and mixing height. From such data, variables for dispersion models such as wind variability and atmospheric stability can be determined. Additional guidance on meteorological measurements can be obtained from:

- U.S. EPA. June 1987. <u>On-Site Meteorological Program Guidance for Regulatory Modeling Applications.</u> EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.
- U.S. EPA. February 1983. Quality Assurance handbook for Air Pollution Measurements Systems: Volume IV. Meteorological Measurements. EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, N.C. 27711.
- U.S. EPA. July 1986. <u>Guidelines on Air Quality Models (Revised)</u>. EPA-405/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

Appropriate performance specifications for monitoring equipment are given in the following document:

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80/012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

#### 12.6.3.2 Meteorological Monitor Siting

Careful placement of meteorological monitoring equipment (e.g., sensors) is important in gathering relevant data. The objective of monitoring tower placement is to position sensors to obtain measurements representative of the conditions that determine atmospheric dispersion in the area of interest. The convention for placement of meteorological monitoring equipment is:

- At or above a height of 10 meters above ground; and
- At a horizontal distance of 10 times the obstruction height from any upwind obstructions.

In addition, the recommendations given in Table 12-9 should be followed to avoid effects of terrain on meteorological monitors.

Depending on the complexity of the terrain in the area of interest and the parameters being measured, more than one tower location may be necessary. Complex terrain can greatly influence the transport and diffusion of a contaminant release to air so that one tower may not able to account for these influences. The monitoring station height may also vary depending on source characteristics and logistics. Heights should be selected to minimize near-ground effects that are not representative of conditions in the atmospheric layer into which a constituent of concern is being released.

A tower designed specifically to mount meteorological instruments should be used. Instruments should be mounted on booms projecting horizontally out from the tower at a minimum distance of twice the tower diameter. Sound engineering practice should be used to assure tower integrity during all meteorologic conditions.

Further guidance on siting meteorological instruments and stations is available in the following publications:

TABLE 12-9
RECOMMENDED SITING CRITERIA TO AVOID TERRAIN EFFECTS

Distance from Tower (meters)	Maximum Acceptable Construction or Vegetation Height (meters)
0 - 1 5	0.3
15-30	0.5- 1.0
30-100	3
100-300	10

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. June 1987. <u>On-Site Meteorological Program Guidance for Regulatory Modeling Applications</u>. EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. February 1983. <u>Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV. Meteorological Measurements.</u> EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, N.C. 27711.

## 12.6.4 Monitoring Schedule

Establishment of a monitoring schedule is an important consideration in developing a monitoring plan. When appropriate, air monitoring should coincide with monitoring of other media (e.g., subsurface gas, soils, and surface water) that have the potential for air emissions. As with all other aspects of the monitoring program, the objectives of monitoring should be considered in establishing a schedule. As indicated previously, monitoring generally consists of screening sampling, emission monitoring, and air monitoring. The monitoring schedule during each of these phases is discussed below.

## 12.6.4.1 Screening Sampling

A limited screening sampling effort may be necessary to focus the design of additional monitoring phases. Therefore, screening samples may be warranted during the screening assessment or prior to initiating emission monitoring or air monitoring studies. This screening phase can also be used to supplement modeling and emission monitoring results as available, to verify the existence of a release to air, and to prioritize the major release sources at the facility.

Screening sampling should be used to characterize air emissions (e.g., by using total hydrocarbon measurements as an indicator), and to confirm/identify the presence of candidate constituents. Screening samples should generally consist of

source emissions measurements or ambient air samples collected at or in close proximity to the source. This approach will provide the best opportunity for detection of air emission constituents. (A discussion of available screening methods is presented in Section 12.8.) An alternative screening approach involves collection of a limited number of air samples to facilitate the analysis of a wide range of constituents (e.g., collection via Tenax adsorption tubes or whole air sampling with analysis by GC/MS -see Section 12.8).

The screening study should generally involve collection of a limited number of grab or time-integrated samples (several minutes to 24 hours) for a limited time period (e.g., one to five days). Sampling should be conducted during emission/dispersion conditions that are expected to result in relatively high concentrations, as discussed previously. Screening results should be interpreted considering the representativeness of the waste and unit operations during the sampling, and the detection capabilities of the screening methodology used.

## 12.6.4.2 Emission Monitoring

Emission rate monitoring may be necessary to characterize a release if screening assessment results are not conclusive. This approach involves stack or vent emission monitoring for point sources. Point source monitoring is not dependent on meteorological conditions. However, emission rate monitoring for both point and area sources should be conducted during typical or "reasonable worst case" emission rate conditions. Therefore, emission monitoring should be conducted when source conditions (e.g., unit operations and waste concentrations) as well as meteorological conditions are conducive to "reasonable worst case" emission rate conditions. Emission rate monitoring for area sources should not be conducted during or immediately following precipitation or if hourly average wind speeds are greater than 15 miles per hour. It should also be noted that soil or cover material (if present) should be allowed to dry prior to continuing monitoring operations, as volatilization decreases under saturated soil conditions. In these cases, the monitoring should be interrupted and resumed as soon as possible after the unfavorable conditions pass. Similarly, operational interruptions such as unit shutdown should also be factored into the source sampling schedule.

Point source emission sampling generally requires only a few hours of sampling and occurs during a more limited time (e.g., one to three days). Guidance on point-source sampling schedules is presented in the following:

- U.S. EPA. November 1985. <u>Practical Guide Trial Burns for Hazardous Waste incinerators.</u> NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.
- U.S. EPA. <u>Code of Federal Regulations. 40 CFR Part 60: Appendix A: Reference Methods.</u> Office of the Federal Register. Washington, D.C.
- U.S. EPA. 1978. <u>Stack Sampling Technical Information</u>, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042a,b,c. NTIS PB 80-161672, 80-161680, 80-161698. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.
- U.S. EPA. February 1985. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, NC 27711.
- U.S. EPA. March 1984. Protocol for the Collection and Analysis of Volatile POHCs Using VOST. EPA-600/8-84-007. NTIS PB 84-170042. Office of Research and Development. Research Triangle Park, NC 27711.
- U.S. EPA. February 1984. <u>Sampling and Analysis Methods for Hazardous Waste Combustion.</u> EPA-600/8-84-002. NTIS PB 84-155845. Washington, D.C. 20460.
- U.S. EPA. 1981. <u>Source Sampling and Analysis of Gaseous Pollutants</u>. EPA-APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, NC 27711.
- U.S. EPA. 1979. <u>Source Sampling for Particulate Pollutants.</u> EPA-APTI Course Manual 450. NTIS PB 80-188840, 80-182439, 80-174360, Air Pollution Control Institute. Research Triangle Park, NC 27711,

U.S. EPA. 1986. <u>Test Methods for Evaluating Solid Waste</u>. 3rd Edition. Office of Solid Waste. EPA/SW-846. GPO No. 955-001 -00000-1.- Washington, D.C. 20460.

Emission rate monitoring should be conducted during a 1 to 3 day period representative of "reasonable worst case" source emission conditions. The worst case short-term emission rate conditions should be determined by parametric analyses (i.e., by modeling a wide range of source operational conditions and associated waste concentrations as well as meteorological conditions for parameters such as wind speed and temperature). Historical meteorological data representative of the site should be reviewed to determine the season and time of day associated with worst case emission conditions. These results should be used to select and schedule (along with meteorological forecasts for local conditions and expected source operational and waste concentration) the emission monitoring period.

Emission rate monitoring results based on measurements during worst-case conditions should be initially used as dispersion modeling input. If these initial results exceed health criteria then the emission monitoring results should be scaled to represent long term (i.e., annual) conditions. The scaling factor should be based on the ratio of emission rate modeling results (using meteorological conditions during the monitoring period as input) compared to modeling results based on typical (annual) meteorological conditions.

Guidance on area source emission rate monitoring is provided in the following:

- U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces

  Using an Emission Isolation Flux Chamber: User's Guide. EPA/600/8-86/008.

  NTIS PB86-223161. Environmental Monitoring Systems Laboratory. Las Vegas,

  NV 89114.
- U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

#### 12.6.4.3 Air Monitoring

The primary objective of confirmatory monitoring is to characterize long-term exposures that may be associated with air emissions from the unit under reasonable worst-case conditions. A schedule should be proposed that will provide an adequate degree of confidence that those compounds that may be released will be detected (i.e., by sampling during the season associated with the highest air concentrations as determined based on modeling). Laboratory analytical costs typically range from \$200 to over \$1,000 per air monitoring station for one 24-hour integrated sample (the actual cost depends on the number and type of target constituents). Recent advances in applied technology have facilitated the use of field gas chromatography (GCS) to automatically obtain analytical results for many organics (i. e., offsite laboratory analyses may not be necessary for some air monitoring programs). The cost for this equipment typically range from \$20,000 to over \$50,000 and one GC can generally service multiple sampling stations.

An example sampling schedule (e.g., for flat terrain sites with minimal variability of dispersion and source conditions) for meeting this objective is given below:

- Meteorological monitoring -90 days continuous monitoring.
- Initial air monitoring (Alternative 1) -90 days:
   Analysis of 24-hour time integrated samples for target constituents every day during the 90-day period (total of 90 samples)
- Additional monitoring as necessary to supplement initial air monitoring results in order to adequately characterize the release.

The 90-day monitoring program will facilitate collecting samples over a wide range of emission and dispersion conditions. The 90-day period should be selected, as previously discussed, to coincide with the expected season of highest ambient concentrations. Meteorological monitoring should be continuous and concurrent with this 90-day period to adequately characterize dispersion conditions at the site and to provide meteorological data to support interpretation of the air-quality. monitoring data.

The collection of a time-integrated sample based on continuous monitoring for several days can result in technical difficulties (e.g., poor collection efficiencies for volatile constituents or large sample volumes). The application of five-day composite samples at each station, or intermittent sampling during the five days, results in continuous monitoring coverage during the 90-day period and facilitates the characterization of long-term exposure levels.

Although there are some limitations associated with composite/intermittent sampling (e.g., the potential for sample degradation), the 24-hour samples collected every sixth day will provide a second data set for characterizing ambient concentrations. Although the results of the two data sets should not be directly combined (because of the different sampling periods) they provide a comprehensive technical basis by which to evaluate long-term exposure conditions.

## 12.6.4.4 Subsequent Monitoring

Subsequent monitoring may be necessary if initial monitoring data were not sufficient to estimate "reasonable worst case" long-term concentrations (e.g., data recovery was not sufficient or additional monitoring stations are needed).

The same schedule specified for the initial monitoring phase is also applicable to subsequent monitoring. However, when evaluating the results of subsequent monitoring and comparing them to previously collected data, potential differences in emission/dispersion conditions and other data representativeness factors should be accounted for.

#### 12.6.5 Monitoring Approach

The RFI air release characterization strategy may involve source emission monitoring and/or air monitoring. The strategy which defines the process for selection and application of these alternative monitoring approaches has been discussed previously. A summary of applicable air monitoring strategies related to source type is presented in Table 12-10.

# 12.6.5.1 Source Emissions Monitoring

Monitoring at the source to measure a rate of emission for the constituents of concern may, in many cases, offer a practical approach to characterizing air emissions. Using this technique, the emission rate is then input into a mathematical dispersion model for estimation of downwind concentrations. Monitoring interferences from sources close to the unit are eliminated because the source is isolated from the ambient atmosphere for monitoring purposes. Source monitoring techniques are also advantageous because they do not require the level of sensitivity required by air monitors. Concentrations of airborne constituents at the source are generally higher than at downwind locations due to the lack of dispersion of the constituent over a wide area. The concentrations expected in the air (generally part-per-billion levels) may be at or near the limit of detectability of the methods used. Methods for source emissions monitoring for various constituent classes are discussed in Section 12.8.

Area sources (such as landfills, land treatment units, and surface impoundments) can be monitored using the isolation flux chamber approach. This method involves isolating a small area of contamination under a flux chamber, and passing a known amount of a zero hydrocarbon carrier gas through the chamber, thereby picking up any organic emissions in the effluent gas stream from the flux chamber. Samples of this effluent stream are collected in inert sampling containers, usually stainless steel canisters under vacuum, and removed to the laboratory for subsequent analysis. The analytical results of the identified analytes can be converted through a series of calculations to direct emission rates from the source. These emission rates can be used to evaluate downwind concentrations by application of dispersion models. Multiple emission tests should be conducted to account for temporal and spatial variability of source conditions. More information on use of the isolation flux chamber and test design is provided in the following references:

U.S. EPA. 1986. <u>Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide.</u> EPA/600/8-86/008. NTIS PB 86-223161. Washington, D.C. 20460.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning. and Standards. Research Triangle Park, NC 27711.

Some area source units may not be amenable to the source sampling approach, however. A unit in which the source cannot be isolated and viable measurements taken of the parameters of concern is one example. This includes active areas of landfills and land-treatment areas, as well as aerated surface impoundments. Also, area sources in which particulate emissions are of concern cannot be measured using an isolation flux chamber due to technical limitations in the technique. For these applications, only an upwind/downwind monitoring approach should be used.

#### 12.6.5.2 Air Monitoring

Use of an upwind/downwind network of monitors or sample collection devices is the primary air monitoring approach recommended to determine release and background concentrations of the constituents of concern. Upwind/downwind air monitoring networks provide concentrations of the constituents of concern at the point of monitoring, whether at the unit boundary, facility property boundary, or at a receptor point. The upwind/downwind approach involves the placement of monitors or sample collection devices at various points around the unit of concern. Each air sample collected is classified as upwind or downwind based on the wind conditions for the sampling period. Downwind concentrations are compared to those measured at upwind points to determine the relative contribution of the unit to air concentrations of toxic compounds. This is generally accomplished by subtracting the upwind concentration (which represents background conditions) from the concurrent downwind concentrations. Applicable field methods for air monitoring are discussed in Section 12.8 as well as in Procedures for Conducting Air Pathway Analyses for Superfund Applications (U.S. EPA, December 1988). Downwind air concentrations at the facility can be extrapolated to other locations by using dispersion modeling results. This is accomplished by obtaining initial modeling results based on meteorological conditions for the monitoring period and an arbitrary emission rate. These initial dispersion modeling results along with monitoring results at the site perimeter are used to back calculate an emission rate such that modeling results can be adjusted to be equivalent to monitoring results at

the onsite monitoring station. This estimated emission rate is then used as dispersion modeling input to predict offsite concentrations.

## 12.6.6 Monitoring Locations

As with other factors associated with air monitoring, siting of the monitors should reflect the primary objective of characterizing concentrations at the facility property boundary. This section discusses monitoring locations for both upwind/downwind approaches and source monitoring techniques.

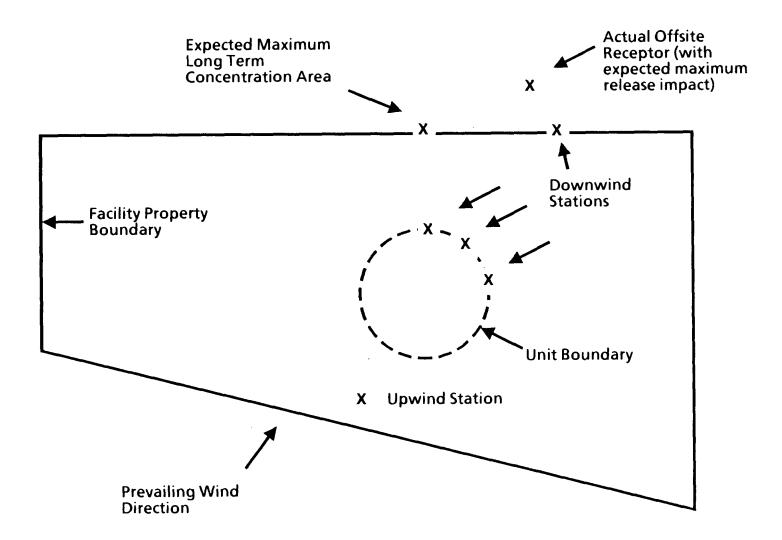
# 12.6.6.1 Upwind/Downwind Monitoring Locations

The air monitoring network design should provide adequate coverage to characterize both upwind (background) and downwind concentrations. Therefore, four air monitoring zones are generally necessary for initial monitoring. Multiple monitoring stations per zone will frequently be required to adequately characterize the release. An upwind zone is used to define background concentration levels. Downwind zones at the unit boundary, at the facility property boundary and beyond the facility property boundary, if appropriate, are used to define potential offsite exposure.

The location of air monitoring stations should be based on local wind patterns. Air monitoring stations should be placed at strategic locations, as illustrated in the following example (see Figure 12-6).

- Upwind (based on the expected prevailing wind flow during the 90-day monitoring period) of the unit' and near the facility property boundary to characterize background air concentration levels. There should be no air emission source between the upwind monitoring station and the unit boundary.
- Downwind (based on the expected prevailing wind flow during the 90-day monitoring period) at the unit boundary plus stations at adjacent sectors also at the unit boundary (the separation distance of air monitoring stations at the unit boundary should be 30° or 50 feet, whichever is greater).

FIGURE 12-6. EXAMPLE AIR MONITORING NETWORK



- Downwind (based on the expected prevailing wind flow during the 90day monitoring period) at the facility property boundary (this station may not be required if the site perimeter is within 100 meters of the unit boundary).
- Downwind (at the area expected to have the highest average concentration levels during the 90-day monitoring period) at the facility property boundary, if appropriate.
- Downwind at actual offsite receptor locations (if appropriate).
- Additional locations at complex terrain and coastal sites associated with pronounced secondary air flow paths (e.g., downwind of the unit near the facility property boundary for both primary daytime and nighttime flow paths).

The above Locations should be selected prior to initial monitoring based on the onsite meteorological survey and on evaluation of available representative offsite meteorological data. This analysis should provide an estimate of expected wind conditions during the 90-day initial monitoring period. If sufficient representative data are available, dispersion modeling can be used to identify the area of maximum long term concentration levels at the facility property boundary and, if appropriate, at actual offsite receptors. If not, the facility property boundary sector nearest to the unit of concern should be selected for initial monitoring.

The network design defined above will provide an adequate basis to define long-term concentrations based on continuous monitoring during the 90-day initial monitoring period. The monitoring stations at the unit boundary should increase the potential for release detection. The facility property boundary air monitoring stations should provide data (with the aid of dispersion modeling, if appropriate) to perform health and environmental assessment, and if appropriate, characterize offsite concentrations.

Air monitoring at offsite receptors (if deemed to be appropriate) may be impractical in many cases, because analytical detection limits may not be low

enough at offsite receptor locations to measure the release. Also, a 90-day offsite monitoring program can be problematic. Factors such as vandalism, erroneous readings due to public tampering with the equipment, public relations problems in setting up the equipment, and legal access problems may preclude the use of offsite air monitoring stations. For these cases, dispersion models may be used to extrapolate monitoring data collected at the facility to actual offsite receptor locations. This is accomplished by obtaining initial modeling results based on meteorological conditions for the monitoring period and an arbitrary emission rate. These initial dispersion modeling results along with monitoring results at the site perimeter are used to back calculate an emission rate such that modeling results can be adjusted to be equivalent to monitoring results at the onsite monitoring station. This estimated emission rate is then used as dispersion modeling input to predict offsite concentrations for the same downwind sector and exposure period as for this monitoring period.

If additional monitoring is required, a similar network design to that illustrated in Figure 12-6 will generally be appropriate. Evaluation of the meteorological monitoring data collected during the initial phase should provide an improved basis to identify local prevailing and diurnal wind flow paths. Also, the site meteorological data will provide dispersion modeling input. These modeling results should provide dilution patterns that can be used to identify areas with expected relatively high concentration levels. However, these results should account for seasonal meteorological differences between initial and additional monitoring periods.

Wind-directionally controlled air monitoring stations can also be used at sites with highly variable wind directions. These wind-directionally controlled stations should be collocated with the fixed monitoring stations. This approach facilitates determination of the unit source contribution to total constituent levels in the local area. These automated stations will only sample for a user-defined range of wind directions (e.g., downwind stations would only sample if winds were blowing from the source towards the station). Interpretation of results from wind-directionally controlled air monitoring stations should account for the lower sampling volumes (and therefore, the possibility that not enough sample would be collected for analysis) generally associated with this approach.

The inlet exposure height of the air monitors should be 2 to 15 meters to be representative of potential inhalation exposure but not unduly biased by road dust and natural wind erosion phenomena. Further guidance on air monitoring network design and station exposure criteria (e.g., sampling height and proximity to structures and air emission sources) is provided in the following reference:

U.S. EPA. September 1984. <u>Network Design and Site Exposure Criteria for Selected Non-criteria Air Pollutants.</u> EPA-450/4-84-022. Office of Air Quality Planning and Standards. Research Triangle Park, N.C.

The above referenced document recommends the use of dispersion models to identify potential relatively high concentration areas as a basis for network design. This topic is also discussed in the following document:

U.S. EPA. July 1986. <u>Guidelines on Air Quality Models (Revised)</u>. EPA-450/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Uniformity among the sampling sites should be achieved to the greatest degree possible. Descriptions should be prepared for all sampling sites. The description should include the type of ground surface, and the direction, distance, and approximate height with respect to the source of the release. Location should also be described on a facility map.

#### 12.6.6.2 Stack/Vent Emission Monitoring

Point source measurements should be taken in the vent. Both the VOST and Modified Method 5 methodologies describe the exact placement in the stack for the sampler inlet. (See Section 12.8.3). If warranted, an upwind/downwind monitoring network can be used to supplement the release rate data.

#### 12.6.6.3 Isolation Flux Chambers

Monitor placement using flux chambers (discussed earlier) is similar to conducting a characterization of any area source. Section 3 of this guidance discusses establishment of a grid network for sampling. Such a grid should be

established for an area source, with sampling points established within the grids, as appropriate. It is suggested that a minimum of six points be chosen for each monitoring effort. Once these areas are sampled, the results can be temporally and spatially averaged to provide an overall compound specific emission rate for the plot. Additional guidance on monitoring locations for isolation flux chambers is presented in Section 3.6 and in the following references:

U.S. EPA. 1986. <u>Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide.</u> EPA/600/8-86/008. NTIS PB86-223161. Environmental Monitoring Systems Laboratory. Las Vegas, NV 89114.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

#### 12.7 Data Presentation

As discussed in Section 5, progress reports will be required by the regulatory agency at periodic intervals during the investigation. The following data presentation formats are suggested for the various phases of the air investigation in order to adequately characterize concentrations at actual offsite receptors.

#### 12.7.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

- Tables of waste constituents and concentrations;
- Tables of relevant physical/chemical properties for potential air emission constituents;
- Tables and narratives describing unit dimensions and special operating conditions and operating schedules concurrent with the air monitoring program;

- Narrative description of unit operations; and
- Identification of "reasonable worst case" emission conditions that occurred during the monitoring period.

# 12.7.2 Environmental Setting Characterization

Environmental characteristics should be presented as follows:

- Climate (historical summaries from available onsite and offsite sources):
  - Annual and monthly or seasonal wind roses;
  - Annual and monthly or seasonal tabular summaries of mean wind speeds and atmospheric stability distributions; and
  - Annual and monthly or seasonal tabular summaries of temperature and precipitation.
- Meteorological survey results:
  - Hourly listing of all meteorological parameters for the entire monitoring period;
  - Daytime wind rose (at coastal or complex terrain sites);
  - Nighttime wind rose (at coastal or complex terrain sites):
  - Summary wind rose for all hours;
  - Summary of dispersion conditions for the monitoring period (joint frequency distributions of wind direction versus wind speed category and stability class frequencies); and
  - Tabular summaries of means and extremes for temperature and other meteorological parameters.

- Definition of soil conditions (if appropriate):
  - Narrative of soil characteristics (e.g., temperature, porosity and organic matter content); and
  - Characterization of soil contamination conditions (e.g., in land treatment units, etc.).
- Definition of site-specific terrain and nearby receptors:
  - Topographic map of the site area with identification of the units, meteorological and air monitoring stations, and facility property boundary;
  - Topographic map of 10-kilometer radius from site (U.S. Geological Survey 7.5 minute quadrangle sheets are acceptable); and
  - Maps which indicate location of nearest residence for each of sixteen 22.5 degree sectors which correspond to major compass points (e.g., north, north-northwest, etc.), nearest population centers and sensitive receptors (e. g., schools, hospitals and nursing homes).

Maps showing the topography of the area, location of the unit(s) of concern, and the location of meteorological monitoring equipment.

A narrative description of the meteorological conditions during the air sampling periods, including qualitative descriptions of weather events and precipitation which are needed for data interpretation.

#### 12.7.3 Characterization of the Release

Characteristics of the release should be presented as follows:

Screening sampling:

- Identification of sampling and analytical methodology;
- Map which identifies sampling locations;
- Listing of measured concentrations indicating collection time period and locations;
- Prioritization of units as air release sources which warrant monitoring based on screening results;
- Discussion of QA/QC results; and
- Listing and discussion of meteorological data during the sampling period.
- Initial and additional monitoring results:
  - Identification of monitoring constituents;
  - Discussion of sampling and analytical methodology as well as equipment and specifications;
  - Identification of monitoring zones as defined in Section 12.6.6.1;
  - Map which identifies monitoring locations relative to units;
  - Discussion of QA/QC results;
  - Listing of concentrations measured by station and monitoring period indicating concentrations of all constituents for which monitoring was conducted. Listings should indicate detection limits if a constituent is not detected:
  - Summary tables of concentration measured indicating maximum and mean concentration values for each monitoring station;

- Discussion of meteorological station locations selection, sensor height, local terrain, nearby obstructions and equipment specifications;
- Listing of all meteorological parameters concurrent with the air sampling periods;
- Daytime wind rose (only for coastal or complex terrain areas);
- Nighttime wind rose (only for coastal or complex terrain areas);
- Summary wind rose based on all wind direction observations for the sampling period;
- Summary of dispersion conditions for the sampling period (joint frequency distributions of wind direction versus wind speed category and stability class frequencies based on guidance presented in <u>Guidelines on Air Quality Models (Revised)</u>, (U.S. EPA, July 1986));
- Tabular summaries of means and extremes for temperature and other meteorological parameters;
- A narrative discussion of sampling results, indicating problems encountered, relationship of the sampling activity to unit operating conditions and meteorological conditions, sampling periods and times, background levels and identification of other air emission sources and interferences which may complicate data interpretation;
- Presentation and discussion of models used (if any), modeling input data and modeling output data (e.g., dilution or dispersion patterns based on modeling results); and

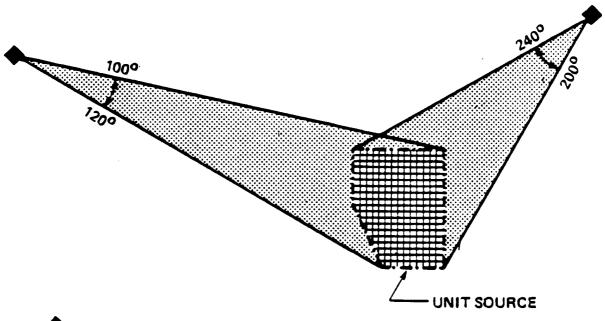
 Concentrations based on monitoring and/or modeling for actual offsite receptor locations.

Interpretation of air monitoring results should also account for additional factors such as complex terrain, variable winds, multiple contaminant sources and intermittent or irregular releases. The key to data interpretation for these cases is to evaluate monitoring results as a function of wind direction.

Terrain factors can alter wind flow trajectories especially during stable nighttime conditions. Therefore, straightline wind trajectories may not occur during these conditions if there is intervening terrain between the source and the air monitoring station. For these cases wind flows will be directed around large obstacles (such as hills) or channeled (for flows within valleys). Therefore, it is necessary to determine the representativeness of the data from the meteorological stations as a function of wind direction, wind speed and stability conditions. Based on this assessment, and results from the meteorological survey, upwind and downwind sectors (i.e., a range of wind direction as measured at the meteorological station) should be defined for each air monitoring station to aid in data interpretation, Figure 12-7 illustrates an example which classifies a range of wind directions during which the air monitoring stations will be downwind of an air emission source. Therefore, concentrations measured during upwind conditions can be used to characterize background conditions and concentrations measured during downwind conditions can be used to evaluate the air-quality impact of the release.

Complex terrain sites and coastal sites frequently have very pronounced diurnal wind patterns. Therefore, as previously discussed, the air monitoring network at these sites may involve coverage for multiple wind direction sectors and use of wind-directionally controlled air samplers. This monitoring approach is also appropriate for sites with highly variable wind conditions. Comparing results from two collocated air monitoring stations (i.e., one station which samples continuously and a second station at the same location which is wind-directionally controlled on an automated basis), facilitates determination of source contributions to ambient air concentrations.

# FIGURE 12-7 EXAMPLE OF DOWNWIND EXPOSURES AT AIR MONITORING STATIONS



**◆**= MONITORING STATIONS

= DOWNWIND SECTOR

Comparison of results from collocated (continuous versus wind-directionally controlled) air monitoring stations can also be used to assist in data interpretation at sites with multiple air emission sources or with intermittent/irregular releases. For some situations, the consistent appearance of certain air emission constituents can be used to "fingerprint" the source. Therefore, the air monitoring results can be classified based on these "fingerprint" patterns. These results can then be summarized as two separate data sets to assess background versus source contributions to ambient concentrations.

The use of collocated (continuous and wind-directionally controlled) air monitoring stations is a preferred approach to data interpretation for complex terrain, variable wind, multiple source and intermittent release sites. An alternative data interpretation approach involves reviewing the hourly meteorological data for each air sampling period. Based on this review, the results from each sampling period (generally a 24-hour period) for each station are classified in terms of downwind frequency. The downwind frequency is defined as the number of hours winds were blowing from the source towards the air monitoring station divided by the total number of hours in the sampling period. These data can then be processed (by plotting scattergrams) to determine the relationship of downwind frequency to measured concentrations.

Data interpretation should also take into account the potential for deposition, degradation and transformation of the monitoring constituents. These mechanisms can affect ambient concentrations as well as air sample chemistry (during storage). Therefore, standard technical references on chemical properties, as well as the monitoring guidance previously cited, should be consulted to determine the importance of degradation and transformation for the monitoring constituents of concern.

## 12.8 Field Methods

This section describes field methods which can be used during initial or subsequent monitoring phases. Methods are classified according to source type and area. Guidance on meteorological monitoring methods is also provided in this section.

# 12.8.1 Meteorological Monitoring

Meteorological monitoring generally should employ a 10-meter tower equipped with wind direction, wind speed, temperature and atmospheric stability instrumentation. Wind direction and wind speed monitors should exhibit a starting threshold of less than 0.5 meters per second (m/s). Wind speed monitors should be accurate above the starting threshold to within 0.25 m/sat speeds less than or equal to 5 m/s. At higher speeds the error should not exceed 5 percent of the wind speed. Wind direction monitor errors should not exceed 5 degrees. Errors in temperature should not exceed 0.5°C during normal operating conditions.

The meteorological station should be installed at a location which is representative of overall site terrain and wind conditions. Multiple meteorological station locations may be required at coastal and complex terrain sites.

Additional guidance on equipment performance specifications, station location, sensor exposure criteria, and field methods for meteorological monitoring are provided in the following references:

- U.S. EPA. February 1983. <u>Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV, Meteorological Measurement.</u> EPA-600-4-82-060. Office of Research and Development. Research Triangle Park, NC 27711.
- U.S. EPA. November 1980. <u>Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD)</u>. EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.
- U.S. EPA. July 1986. <u>Guidelines on Air Quality Models (Revised).</u> EP-450/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

#### 12.8.2 **Air Monitoring**

Selection of methods for monitoring air contaminants should consider a number of factors, including the compounds to be detected, the purpose of the method (e. g., screening or quantification), the detection limits, and sampling rates and duration required for the investigation.

Organic and inorganic constituents require different analytical methods. Within these two groups, different methods may also be required depending on the constituent and its physical/chemical properties. Another condition that affects the choice of monitoring technique is whether the compound is primarily in the gaseous phase or is found adsorbed to solid particles or aerosols.

Screening for the presence of air constituents involves techniques and equipment that are rapid, portable, and can provide "real-time" monitoring data. Air contamination screening will generally be used to confirm the presence of a release, or to establish the extent of contamination during the screening phase of the investigation. Quantification of individual components is not as important during screening as during initial and additional air monitoring, however the technique must have sufficient specificity to differentiate hazardous constituents of concern from potential interferences, even when the latter are present in higher concentrations. Detection limits for screening devices are often higher than for quantitative methods.

Laboratory analytical techniques must provide positive identification of the components, and accurate and precise measurement of concentrations. This generally means that preconcentration and/or storage of air samples will be required. Therefore, methods chosen for quantification usually involve a longer analytical time-period, more sophisticated equipment, and more rigorous quality assurance procedures.

The following list of references provides guidance on air monitoring methodologies:

U.S. EPA. June 1983. <u>Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air.</u> EPA-600/4-83-027. NTIS PB 83-239020. Office of Research and Development. Research Triangle Park, NC 27711.

U. S. EPA. April 1984. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. EPA-600/4-84-041. Office of Research and Development. Research Triangle Park, NC 27711.

NIOSH. February 1984. <u>NIOSH Manual of Analytical Methods.</u> NTIS PB 85-179018. National Institute for Occupational Safety and Health. Cincinnati, OH.

U.S. EPA. September 1983. <u>Characterization of Hazardous Waste Sites - A Methods Manual: Volume II, Available Sampling Methods.</u> EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. September 1983. <u>Characterization of Hazardous Waste Sites - A Methods Manual: Volume III, Available Laboratory Analytical Methods.</u> EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. 1986. <u>Test Methods for Evaluating Solid Waste</u>. 3rd Edition. EPA SW-846. GPO No 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

ASTM. 1982. <u>Toxic Materials in the Atmosphere.</u> ASTM, STP 786. Philadelphia, PA.

ASTM. 1980. Sampling and Analysis of Toxic Organics in the Atmosphere. ASTM. STP721. Philadelphia. PA.

ASTM. 1974. Instrumentation for Monitoring Air Quality. ASTM, STP 555. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association. Cincinnati, OH.

ACGIH. 1983. <u>Air Sampling Instruments for Evaluation of Atmospheric Contaminants.</u> American Conference of Governmental Industrial Hygienists. Washington, D.C.

U.S. EPA. December 1988 Draft. <u>Procedures for Conducting Air Pathway Analyses for Superfund Applications</u>. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

## 12.8.2.1 Screening Methods

Screening techniques for vapor-phase constituents fall into two main categories. (1) organic and non-organic compound-specific indicators, and (2) general organic detectors. Table 12-11 presents a summary of commercially available screening methods for these compounds.

Indicator tubes and other calorimetric methods--indicator tubes, also known as gas detector or Draeger tubes, are small glass tubes filled with a reagent-coated material which changes color when exposed to a particular chemical. Air is pulled through the tube with a low-volume pump. Tubes are available for 40 organic gases, and for 8 hour or 15 minute exposure periods. Indicator tubes were designed for use in occupational settings, where high levels of relatively pure gases are likely to occur. Therefore, they have only limited usefulness for ambient air sampling, where part-per-billion levels are often of concern. However, because they are covenient to use and available for a wide range of compounds, detector tubes may be useful in some screening/sampling situations.

Other calorimetric methods, such as continuous flow and tape monitor techniques, were developed to provide real-time monitoring capability with indicator methods. The disadvantages of these systems are similar to those of indicator tubes.

Instrument detection screening methods-More commonly used for volatile organic surveys, portable instrument detection methods include flame ionization detectors (FID), photoionization detectors (PID), electron capture detectors (ECD), and infrared detectors (ID). Also in use are detectors that respond to specific chemical classes such as sulfur- and nitrogen-containing organics. These instruments are used to indicate levels of total organic vapors and for identification of "hot zones" downwind of the release source(s). They can be used as real-time non-specific monitors or, by adding a gas chromatography, can provide concentration estimates and tentative identification of pollutants.

TABLE 12-11
TYPICAL COMMERCIALLY AVAILABLE SCREENING TECHNIQUES FOR ORGANICS IN AIR (FROM RIGGIN, 1983)

Technique	Manufacturers	Compounds Detected	Approximate Detection Limit	Comments	
Gas Detection Tubes	Draeger Matheson Kitagawa	Various organics and inorganics	0.1 to 1 ppmv	Sensitivity and selectivity highly dependent on component of interest.	
Continuous Flow Calorimeter	CEA Instruments, Inc.	Acrylonitrile, formaldehyde, phosgene, and various organics	0.05 to 0.5 ppmv	Sensitivity and selectivity similar to detector tubes.	
Calorimetric Tape Monitor	KHDA Scientific	Toluene, diisocyanate, dinitro toluene, phosgene, and various inorganics	0.05-0.5 ppmv	Same as above.	
Infrared Analysis	Foxboro/Wilkes	Most organics	1-10 ppmv	Some inorganic gases (H <sub>2</sub> O, CO) will be detected and therefore are potential interferences.	
FID (Total Hydrocarbon Analyzer)	Beckman HSA, Inc. AID, Inc.	Most organics	0.5 ppmv	Responds uniformly to most organic compounds on a carbon basis.	
GC/FID (portable)	Foxboro/Century AID, Inc.	Same as above except that polar compounds may not elute from the column.	0.5 ppmv	Qualitative as well as quantitative information obtained.	
PID and GC/PID (portable)	HNU, Inc. AID, Inc. Photovac, Inc.	Most organic compounds can be detected with the exception of methane	0.1 to 100 ppbv	Selectivity can be adjusted by selection of lamp energy. Aromatics most readily detected.	
GC/ECD (portable)	AID, Inc.	Halogenated and nitro- substituted compounds	0.1 to 100 ppbv	Response varies widely from compound to compound.	
GC/FPD (portable)	AID, Inc.	Sulfur or phosphorus- containing compounds	10-100 ppbv	Both inorganic and organic sulfur or phosphorus compounds will be detected.	
Chemiluminescent Nitrogen Detector	Antek, Inc.	Nitrogen-containing compounds	0.1 ppmv (as N)	Inorganic nitrogen compounds will interfere.	

Of the available detectors, those that are the most applicable to an RFI are the FID and PID. Table 12-12 summarizes four instruments (two FID and two PID versions) which are adequate for the purposes of the screening phase.

Flame Ionization Detectors--The Century OVA 100 series and AID Model 550 utilize a FID to determine the presence of vapor phase organics. The detector responds to the total of all organics present in the air at any given moment. Flame ionization detectors will respond to most organics, but are most sensitive to hydrocarbons (i.e., those chemicals which contain only carbon and hydrogen molecules such as benzene and propane). FIDs are somewhat less sensitive to compounds containing chlorine, nitrogen, oxygen, and sulfur molecules. The response is calibrated against a reference gas, usually methane. FID response is often termed "total hydrocarbons"; however, this is misleading because particulate hydrocarbons are not detected. FID detection without gas chromatography is not useful for quantification of individual compounds, but provides a useful tool for general assessment purposes. Detection limits using a FID detector alone are about 1 ppm. Addition of a gas chromatography (GC) lowers the detection limit to ppb levels, but increases the analysis time significantly.

Photoionization Detectors--Portable photoionization detectors such as the HNU Model PI-101 and the Photovac 10A10 operate by applying UV ionizing radiation to the contaminant molecules. Some selectivity over the types of organic compounds detected can be obtained by varying energy of the ionizing beam. In the screening mode this feature can be used to distinguish between aliphatic and aromatic hydrocarbons and to exclude background gases from the instrument's response. The HNU and Photovac can be used either in the survey mode (PID only), or with GC. Sensitivity with PID alone is about 1 ppm, but can go down to as low as 0.1 ppb when a GC is used.

PI and FI detectors used in the GC mode can be used for semiquantitative analysis of compounds in ambient air. However, in areas where numerous contaminants are present, identification of peaks in a complex matrix may be tentative at best.

TABLE 12-12
SUMMARY OF SELECTED ONSITE ORGANIC SCREENING METHODOLOGIES

Instrument or detector	Measurable parameters	Low range of detection	Comments
Century Series 100 or AID Model 550 (survey mode)	Volatile organic species	Low ppm	Uses Flame Ionization Detector (FID)
HNU Model PI-101	Volatile organic species	Low ppm	Photo-ionization (Pi) detector-provides especially good sensitivity to low molecular weight aromatic compounds (i.e., benzene, toluene)
Century Systems OVA-128 (GC mode)	Volatile organic species	Low ppm	Uses GC column for possible specific compound identification
Photo Vac 10A10	Volatile organic species	Low ppm	Uses PI detector. Especially sensitive to aromatic species. May be used for compound identification if interferences are not present

Another method which can be used as a survey technique is mobile mass spectrometry. Ambient air is drawn through a probe directly into the instrument, which is usually mounted in a van. Particularly in the MS/MS configuration this is a powerful technique which can provide positive identification and semiquantitative measurement of an extremely wide range of organic and inorganic gaseous contaminants.

#### 12.8.2.2 Quantitative Methods

Laboratory analysis of hazardous constituents in air includes the following standard steps:

- Preconcentration of organics (as necessary to achieve detection limit goals);
- Transfer to a gas chromatography or HPLC (High Pressure Liquid Chromatography); and
- Quantification and/or identification with a detector.

Broad-spectrum methods applicable to most common air contaminants are discussed below.

#### 12.8.2.2.1 Monitoring Organic Compounds in Air

Due to the large number of organic compounds that maybe present in air, and their wide range in chemical and physical properties, no single monitoring technique is applicable to all organic air contaminants. Numerous techniques have been developed, and continue to be developed, to monitor for specific compound classes, individual chemicals, or to address a wide range of hazardous contaminants. This last approach may be the most efficient approach to monitoring at units where a wide range of chemicals are likely to be present. Therefore, methods that apply to a broad range of compounds are recommended. In cases, where specific compounds of concern are not adequately measured by broad-spectrum methods, compound-specific techniques are described or referenced.

# 12.8.2.2.1.1 Vapor-Phase Organics

The majority of hazardous constituents of concern can be classified as gaseous or (vapor-phase) organics. These constituents include most petroleum-related hydrocarbons, organic solvents, and many pesticides, and other semivolatile organic compounds. Methods to monitor these compounds generally include on-site analysis (making use of onsite concentration techniques, where necessary), or require storage in a tightly sealed non-reactive container.

Techniques for volatile and semivolatile organics measurement include:

- Adsorption of the sample on a solid sorbent with subsequent resorption (thermal or chemical), followed by gas chromatographic analysis using a variety of detectors.
- Collection of whole air (grab) samples in an evacuated flask or in Tedlar or Teflon bags, with direct injection of the sample into a GC using high sensitivity and/or constituent-specific detectors. This analysis may or may not be preceded by a preconcentration step.
- Cryogenic trapping of samples in the field with subsequent instrumental analysis.
- Bubbling ambient air through a liquid-filled impinger, containing a chemical that will absorb or react with specific compounds to form more stable products for GC analysis.
- Direct introduction of the air into a MS/MS or other detector.

Tables 12-13 (A and B), 12-14, and 12-15 summarize sampling and analytical techniques that are applicable to a wide range of vapor phase organics, have been widely tested and validated in the literature, and make use of equipment that is readily available. A discussion of general types of techniques is given below.

TABLE 12-13A. SUMMARY OF CANDIDATE METHODOLOGIES FOR QUANTIFICATION OF VAPOR PHASE ORGANICS

Collection Technique	Analytical Technique	Applicability (See Table 12.15B)	Positive Aspects	Negative Aspects
Sorption onto Tenax- GC or carbon molecular sieve packed cartridges using low-volume pump	Thermal Resorption into GC or GC/MS	l	<ul> <li>adequate QA/QC data base</li> <li>widely used on investigations around uncontrolled waste sites</li> <li>wide range of applicability</li> <li>µ/m3 detection limits</li> <li>practical for field use</li> </ul>	<ul> <li>possibility of contamination</li> <li>artifact formation problems</li> <li>rigorous cleanup needed</li> <li>no possibility of multiple analysis</li> <li>low breakthrough volumes for some compounds</li> </ul>
Sorption onto charcoal packed cartridges using low-volume pump	Resorption with solvent-analysis by GC or GC/MS	II	<ul> <li>large data base for various compounds</li> <li>wide use in industrial applications</li> <li>practical for field use</li> </ul>	<ul> <li>problems with irreversible adsorption of some compounds</li> <li>high (mg/m³) detection limits</li> <li>artifact formation problems</li> <li>high humidity reduces retention efficiency</li> </ul>
II. Sorption onto polyurethane foam (PUF) using low-volume or high-volume pump	Solvent extraction of PUF; analysis by GUMS	1,11,111	<ul> <li>wide range of applicability</li> <li>easy to preclean and extract</li> <li>very low blanks</li> <li>excellent collection and retention efficiencies</li> <li>reusable up to 10 times</li> </ul>	. possibility of contamination  losses of more volatile compounds may occur during storage
V. Sorption on passive dosimeters using Tenax or charcoal as adsorbing medium	Analysis by chemical or thermal resorption following by GC or GC/MS	l or II	<ul> <li>samplers are small, portable, require no pumps</li> <li>makes use of analytical procedures of known precision and accuracy for a broad range of compounds</li> <li>pg/m³ detection limits</li> </ul>	<ul> <li>problems associated with sampling using sorbents</li> <li>uncertainty in volume of air sampled makes concentration calculations difficult</li> <li>requires minimum external air flow rate</li> </ul>

### TABLE 12-13A (Continued)

Collection Technique	Analytical Technique	Applicability (see Table 12-15B)	Positive Aspects	Negative Aspects
v. Cryogenic trapping of analytes in the field	Resorption into GC	II, III	<ul> <li>applicable to a wide range of compounds</li> <li>artifact formation minimized</li> <li>low blanks</li> </ul>	<ul> <li>requires field use of liquid nitrogen or oxygen</li> <li>sample is totally used in one analysis- no reanalysis possible</li> <li>samplers easily clogged with water vapor</li> <li>no large data base on precision or recoveries</li> </ul>
VI. Whole air sample taken in glass or stainless steel bottles	Cryogenic trapping or direct injection into GC or GC/MS (onsite or laboratory analysis)	11, 111	<ul> <li>useful for grab sampling</li> <li>large data base</li> <li>excellent long-term storage</li> <li>wide applicability</li> <li>allows multiple analyses</li> </ul>	<ul> <li>difficult to obtain integrated samples</li> <li>low sensitivity if preconcentration is not used</li> </ul>
VII. Whole air sample taken in Tedlar <sup>k</sup> Bag	C r y o g e n i c trapping or direct injection into GC or GC/MS (onsite or laboratory)	11, 111	<ul> <li>grab or integrated sampling</li> <li>wide applicability</li> <li>allows multiple analyses</li> </ul>	<ul> <li>long-term stability uncertain</li> <li>low sensitivity if preconcentration is not used</li> <li>adequate cleaning of containers between samples may be difficult</li> </ul>
IX. Dinitrophenyl - hydrazine Liquid Impinger sampling using a Low-Volume Pump	HPLC/UV analysis	IV	<ul> <li>specific to aldehydes and ketones</li> <li>good stability for derivatized compounds</li> <li>low detection limits</li> </ul>	<ul> <li>fragile equipment</li> <li>sensitivity limited by reagent impurities</li> <li>problems with solvent evaporation when long-term sampling is performed</li> </ul>
X. Direct introduction by probe	Mobile MS/MS	I,II, III, IV	<ul> <li>immediate results</li> <li>field identification of air contaminants</li> <li>allows "real-time" monitoring</li> <li>widest applicability of any analytical method</li> </ul>	<ul> <li>high instrument cost</li> <li>requires highly trained operators</li> <li>grab samples only</li> <li>no large data base on precision or accuracy</li> </ul>

TABLE 12-13B. LIST OF COMPOUND CLASSES REFERENCED IN TABLE 12-13A

Category	Types of Compound
	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80 to 200°C.
II	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15 to + 120°C.
III	Semivolatile organic chemicals (e.g., organochlorine pesticides and PCBs).
IV	Aldehydes and ketones.

# TABLE 12-14. SAMPLING AND ANALYSIS TECHNIQUES APPLICABLE TO VAPOR PHASE ORGANICS

Compound Name	Whole Air	Tenax Cartridge T0-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Acetophenone	х	Х						
Acrolein	х							
Acrylonitrile	х		Х	Х				
Aniline	х			Х			2002	
Arsenic and compounds							7900	Solid, use Std. Hi-Vol
Benzene	х	х	Х	Х				
Bis(2-ethylhexyl) phalate							5020	
Bromomethane	х		NP	Х			2520	
Cadmium and compounds							7048	Solid, use Std. Hi-Vol
Carbon disulfide	х		NP	Х			1600	
Carbon tetrachloride	х	В	Х	Х			1003	
Chlordane	х			Х	Х			
Chloroaniline (p)	NP			NP				No validated Method
Chlorobenzene	х	х		Х			1003	
Chloroform	х	В	Х	Х			1003	
Chloromethane (methyl chloride)	х	В	NP		NP			
Chlorophenol								Needs XAD-2 Backup
Chloroprene (Neoprene)	х	х	NP	х			1002	
Chromium and compounds	-						7024	Solid, use Std. Hi-Vol
Copper cyanide					ļ		7029	Solid, use Std. Hi-Vol.

Compound Name	Whole Air	Tenax Cartridge TO- 1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Cresol (o)							2001	Syn: methyl phenol
Cresol (p)							2001	Syn: methyl phenol
Cyanide	х						7904	
Dichloro-2-butene (1 ,4)	х	Х		х				
Dichloro benzene (1,2)	Х	Х		Х			1003	
Dichloro benzene (1,4)	Х	Х		х			1003	
Dichlorodifluoromethane	х	NP	NP					NIOSH 1012 should work
Dichloroethane (1,1) [ethylidine chloride]	х	Х	NP	Х			1003	
Dichlorophenoxyacetic acid (2,4)	Х				NP		5001	Syn: 2,4-D
Dichloropropane (1,2)	х	Х		х			1013	Method 1003 may be used
Dichioropropene (1,3)	Х	NP		х				
Diethyl phthalate								No method identified
Dinotrotoluene (2,4)								Yellow crystals, use Hi-Vol
Dioxane (1,4)	Х	Х		х			1602	
Diphenylhydrazine (1,2)								No method identified
Ethylene dibromide	х	В		х			1008	Syn: 1,2-dibromoethane
Ethylene dichloride	х	В		Х			1003	Syn: 1,2-dichloroethane
Fluorides							7902	Std. Hi-Vol for particulate fraction
Heptachlor								Waxy solid, use Std. Hi- Vol
Hexachlorobutadiene	х							

### TABLE 12-14. (continued)

Compound Name	Whole Air	Tenax Cartridge TO- 1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Hexachloroethane		NP		х			1003	Syn: perchloroethane
Isobutanol		NP		х			1401	Syn: isobutyl alcohol
Lead and compounds							7802	Mostly particulate, use Hi-Vol
Mercury and compounds							7300	Mostly particulate, use Hi-Vol
Methacrylonitrile	х		NP	х				
Methyl ethyl ketone	х	Х					2500	Syn: 2-butanone
Methyl methacrylate	х	NP		х				
Methylene chloride		В	х	х			1005	Syn: dichloromethane
Naphthalene	х				х		5515	Method TO-4 needs XAD-2
Nickel and compounds							7300	Mostly particulate, use Hi-Vol
Nitrobenzene	х	Х		х			2005	
Nitrophenol	х	NP		х				
Parathion					NP		5012	
Pentachlorobenzene	х	NP		х				
Pentachloroethane	х	Х		х				
Pentachlorophenol	х	NP						
Perchloroethylene	х	Х		х				Syn. Tetrachloroethylene
Phenol	х	Х		х			3502	
Phorate	х			Х				
Pyridine	х							
Resorcinol	х							_
Styrene	X.	ŅP		Х		]	1501	Syn Polystyrene

Compound Name	Whole Air	Tenax Cartridge T0-1	Carbon MS Cartridge TO-2	Cryogenic Trapping T0-3	Hi-Vol PUF T0-4	Liquid Impinger T0-5	NIOSH Method Number	Comments/Others
TCDD (2,3,7,8)					х			
Toluene	х	Х	х	х			1501	
Toxaphene	х				NP			Syn: Chlorinated camphene
Trichlorobenzene	х	NP		NP				
Trichloroethane (1, 1,1)	х	В	х	х			1003	Syn: Methyl Chloroform
Trichloroethylene	х	Х	х	х				
Trichloropropane (1,2,3)	х	Х		х				
Vanadium pentoxide								Mostly particulate, use Hi-Vol
Vinyl acetate	х			х				
Vinyl chloride	х		х	х			1007	Syn: 1,1-dichloroethene
Vinylidene chloride (1,1 dichloroethylene)	х		х	х				
Xylene (m, o, p)	х	Х		х			1501	Syn: dimethylbenzene
Zinc oxide							7530 and 7502	Solid, use Std. Hi-Vol

- 1. Blank spaces indicate that the method is inappropriate for that compound
- 2. B = small breakthrough volume for adsorbent
- 3. NP = not proven for this adsorbent, but may work
- 4. x = acceptable media for collection

#### **TABLE 12-15**

### COMPOUNDS MONITORED USING EMSL-RTP TENAX SAMPLING PROTOCOLS

2-Chloropropane 1-Bromo-3-chloropropane

1,1-Dichloroethene Ethylbenzene
Bromoethane Bromoform

I-Chloropropane Ethenylbenzene

Bromochloromethane o-Xylene

Chloroform 1,1,2,2-Tetrachloroethane

Tetrahydrofuran Bromobenzene 1,2-Dichloroethane Benzaldehyde

1,1,1-Trichloroethane Pentachloroethane

Benzene 4-Chlorostyrene

Carbon tetrachloride 3-Chloro-1-propene
Dibromomethane 1,4-Dichlorobutane

1,2-Dichloropropane 1,2,3-Trichloropropane

Trichloroethene 1,1-Dichloroethane

1,1,2-Trichloroethane 2-Chlorobutane

2,3-Dichlorobutane 2-Chloroethyl vinyl ether
Bromotrichloromethane 1,1,1,2-Tetrachloroethane

Toluene p-Dioxane

1,3-Dichloropropane Epichlorobutane1,2-Dibromomethane 1,3-Dichlorobutane

Tetrachloroethene p-Dichlorobenzene

Chlorobenzene cis-1,4-Dichloro-2-butene

1,2-Dibromopropane n-Butyl benzene

Nitrobenzene 3,4-Dichloro-1-butene

Acetophenone 1,3,5-Trimethyl benzene

Benzonitrite

Isopropylbenzene

p-Isopropyltoluene

Sorbent techniques--A very common technique used to sample vapor-phase organics involves sorption onto a solid medium. Methods of this type usually employ a low- or high-volume pump to pull air through a glass tube containing the sorbent material. Organic compounds are trapped (removed from the air) by chemical attraction to the surface of the adsorbent material. After a predetermined volume of air has been pulled through the trap, the tube is capped and returned to the laboratory for analysis. Adsorbed organics are then thermally or chemically desorbed from the trap prior to GC or GC/MS analysis.

Thermal resorption is accomplished by rapidly heating the sorbent tube while a stream of inert gas flushes desorbed organics directly onto the GC column. Generally a secondary trap (either another sorbent or a cryogenically cooled loop) is used to hold the organics until injection into the GC column, but this step precludes multiple analyses of the sample.

Chemical resorption involves flushing the sorbent tube with an organic solvent, and analysis of the desorbed organics by GC or GC/MS. Since only a portion of the solvent is injected into the GC, sensitivity is lower than with thermal adsorption. However, reanalysis of samples is possible. The most common application of chemical resorption is for analysis of workplace air samples, where relatively high concentrations of organics are expected.

The primary advantages of sorbent techniques are their ease of use and ability to sample large volumes of air. Sorbent cartridges are commercially available for many applications, and can easily be adapted to portable monitoring pumps or personal samplers. A wide variety of sorbent materials are available, and sorbent traps can be used singly or in series for maximum retention of airborne pollutants. Sorbent methods are especially applicable to integrated or long-term sampling, because large volumes of air can be passed through the sampling tube before breakthrough occurs.

In choosing a sorbent method, the advantages and limitations of specific methods should be considered along with general limitations of sorbents. Some important considerations are discussed below.

- Sorbents can be easily contaminated during manufacturing, shipping or storage. Extensive preparation (cleaning) procedures are generally needed to insure that the sorbent is free from interfering compounds prior to sampling. Tenax, for example, is often contaminated with benzene and toluene from the manufacturing process, requiring extensive solvent extraction and thermal conditioning before it is used. Once prepared, sampling cartridges must be protected from contamination before and after sampling.
- No single adsorbent exists that will retain all vapor phase organics. The efficiency of retention of a compound on a sorbent depends on the chemical properties of both compound and sorbent. Generally, a sorbent that works well for nonpolar organics such as benzene will perform poorly with polar organics such as methanol, and vice versa. Highly volatile compounds such as vinyl chloride will not be retained on weakly adsorbing materials such as Tenax, while less volatile compounds will be irreversibly retained on strong absorbents such as charcoal. The optimal approach involves use of a sorbent that will retain a wide range of compounds with good efficiency, supplemented by techniques specifically directed towards "problem" compounds.
- Tenax-GC is a synthetic polymeric resin which is highly effective for volatile nonpolar organics such as aliphatic and aromatic hydrocarbons, and chlorinated organic solvents. Table 12-15 lists compounds that have been successfully" monitored using a Tenax sorption protocol. Tenax has the important advantage that it does not retain water. Large amounts of water vapor condensing on a sorbent reduces collection efficiency and interferes with GC and GC/MS analysis. Another advantage of this material is the ease of thermal or chemical resorption.

The major limitation of Tenax is that certain highly volatile or polar compounds are poorly retained (e.g., vinyl chloride, methanol). Formation of artifacts (i.e., degradation products from the air contaminant sample collected due to hydrolysis, oxidation, photolysis or other processes) on Tenax has also been noted, especially the oxidation

of amines to form nitrosamines, yielding false positive results for the latter compounds.

Carbon sorbents include activated carbon, carbon molecular sieves, and carbonaceous polymeric resins. The major advantage of these materials is their strong affinity for volatile organics, making them useful for highly volatile compounds such as vinyl chloride. The strength of their sorptive properties is also the major disadvantage of carbon sorbents because some organic compounds may become irreversibly adsorbed on the carbon. Thermal resorption of compounds with boiling points above approximately 80°C is not feasible due to the high temperature (400°c) required. Carbon absorbents will retain some water, and therefore may not be useful in high humidity conditions.

In addition to the Tenax and carbon tube sampling methods shown above, passive sorption devices for ambient monitoring can be used. These passive samplers consist of a portion of Tenax or carbon held within a stainless steel mesh holder. Organics diffuse into the sampler and are retained on the sorbent material. The sampling device is designed to fit within a specially constructed oven for thermal resorption. Results from these passive samplers were reported to compare favorably with pump-based sorbent techniques. Because of the difficulty of determining the volume of air sampled via passive sampling, these devices would appear to be mainly applicable for screening purposes.

 Polyurethane foam (PUF) has been used extensively and effectively for collection of semivolatile organics from ambient air. Semivolatiles include PCBs and pesticides. Such compounds are often of concern even at very low concentrations. A significant advantage of PUF is its ability to perform at high flow rates, typically in excess of 500 liters per minute (I/m). This minimizes sampling times.

PUF has been shown to be effective for collection of a wide range of semivolatile compounds. Tables 12-16 and 12-17 list compounds that have been successfully quantified in ambient air with PUF. Compounds

# TABLE 12-16. SUMMARY LISTING OF ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER AND SUBSEQUENT ANALYSIS WITH AN ELECTRON CAPTURE DETECTOR (GC/ECD)<sub>2</sub>

Polychlorinated Biphenyls (PCBs)	p, p¹-DDTa	<b>Chlorinated Phenols</b>
	Endosulfan la	
Aroclor 1221c	Heptachlor d	2,3-Dichlorophenolb
Aroclor 1232d	Aldrina	2,4-Dichlorophenolb
Aroclor 1242a		2,5-Dichlorophenolb
Aroclor 1016c		2,6-Dichlorophenolb
Aroclor 1248d	Polychlorinated Napthalenes (PCNs)	3,4-Dichlorophenolb
Aroclor 1254a		3,5-Dichlorophenolb
Aroclor 1260a	Halowax 1001c	2,3,4-Trichlorophenol d
	Halowax 1013c	2,3,5-Trichlorophenol d
		2,3,6-Trichlorophenol d
Chlorinated Pesticides		2,4,5-Trichlorophenol a
	Chlorinated Benzene	2,4,6-Trichlorophenol d
α-chlordanea		3,4,5-Trichlorophenol d
Y-chlordane a	1,2,3-Trichlorobenzene a	2,3,4,5-Tetrachlorophenold
Chlordane (technical)a	1,2,4-Trichlorobenzene d	2,3,4,6-Tetrachlorophenold
<u>M</u> irex <sub>a</sub>	1,3,5-Trichlorobenzene d	2,3,5,6-Tetrachlorophenold
α -BHCa	1,2,3,4-Tetrachlorobenzene a	Pentachlorophenol a
β-BHCd	1,2,3,5-Tetrachlorobenzene d	
-BHC (Lindane)a	1,2,4,5-Tetrachlorobenzene d	
-BHCd	Pentachlorobenzene a	
p,p¹-DDDd	Hexachlorobenzene a	
p,p¹-DDEa	Pentachloronitrobenzene a	

- Method validation data for all components, unless otherwise noted, are available in the literature. This includes collection efficiency data and/or retention efficiency data, method recovery data, and in some cases, storage stability data on selected isomers from this compound class.
- Method validation data not presently available in the literature for either a low or high volume sampling procedure. Dichlorophenols, however, are amenable to the same analytical protocols suggested for the higher molecular weight clorophenol isomers (trichloro, tetrachloro, and pentachloro). Users are cautioned that sample collection efficiencies may not be as high for dichlorophenols as for the higher molecular weight chlorophenols. Collection/retention efficiency data should be generated for each specific program.
- Validation data employing low volume sampling conditions not presently available in literature. Component has, however, been evaluated using high volume PUF sampler.
- d Actual validation data for isomer(s) employing low volume PUF sampler not available in literature. Behavior under low volume sample conditions should be similar to other structural isomers listed. Component is amenable to analytical scheme employing GC/ECD.

TABLE 12-17. SUMMARY LISTING OF ADDITIONAL ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER

Polynuclear Aromatic Hydrocarbons <sup>a</sup>	Herbicide Esters	<u>Urea Pesticides</u>
Napthalene	2,4-D Esters, isopropyl°	Monuron°
Biphenyl	2,4-D Esters, butyl <sup>c</sup>	Diuron°
Fluorene	2,4-D Esters, isobutyl°	Linuron°
Dibenzothiophene	2,4-D Esters, isooctyl°	Terbuthiuron°
Phenanthrene		Fluometuron °
Anthracene	Organophosphorous Pesticides	Chlorotoluron°
Carbazole		
2-Methylanthracene	Mevinphos <sup>b</sup>	Triazine Pesticides
I-Methylphenanthrene	Dichlorvos °	
Fluoranthene	Ronnel°	Simazine°
Pyrene	Chlorpyripos <sup>c</sup>	Atrazine°
Benzo(a)fluorene	Diazinon °	Propazine°
Benzo(b)fluorene	Methyl parathion <sup>c</sup>	
Benzo(a)anthracene	Ethyl parathion°	Pyrethrin Pesticides
Chrysene/triphenylene		
Benzo(b)fluoranthene	Carbamate Pesticides	Pyrethrin I°
Benzo(e)pyrene		Pyrethrin II°
Benzo(a)pyrene	Propoxur°	Allethrin°
Perylene	Carbofuran°	d-trans-Allethrin °
o-Phenylenepyrene	Bendiocarb <sup>c</sup>	Dicrotophos°
Dibenzo(ac)/(ah)anthracene	Mexacarbate <sup>°</sup>	Resmethrin °
Benzo(g,h,i)perylene	CarbaryI°	Fenvalerate °
Coronene		

These components have been reported in the literature using polyurethane foam samplers. Users are cautioned that this listing is provided solely as a working reference. Method validation studies including collection efficiencies, retention efficiencies, etc., employing the sampling procedures cited in this document have not been conducted. Procedures other than those noted in this document may be more applicable in routine use.

<sup>&</sup>lt;sup>b</sup> Validation data employing low volume sampling conditions not presently available in literature. Component, however, has been evaluated using high volume PUF sampler.

sample evaluation data for these compound classes using a low volume PUF sampler contained in the literature.

that have shown poor retention or storage behavior with PUF include hexachlorocyclohexane, dimethyl and diethylphthalates, mono- and dichlorophenols, and trichloro- and tetrachlorobenzenes. These compounds have higher vapor pressures, and may be collected more effectively with Tenax or with resin sorbents such as XAD-2.

PUF is easy to handle, pre-treat, and extract. Blanks with very low contaminant concentrations can be obtained, as long as precautions are taken against contamination after pretreatment. Samples have been shown to remain stable on PUF during holding times of up to 30 days. PUF concentration methods have shown excellent collection efficiency and recovery of sorbed compounds from the material.

Most PUF methods specify the use of a filter ahead of the PUF cartridge, to retain particulate. The filter prevents plugging of the PUF which would reduce air flow through the sorbent. Some methods recommend extracting the filter separately to obtain a value for particulate organics. However, because most semivolatile compounds have sufficient vapor pressure to volatilize from the filter during the collection period, particulate measurements may not be representative of true particulate concentrations. Therefore, results from the PUF analyses may overestimate gaseous concentrations of semi-volatile compounds due to volatilization of semi-volatiles originally collected on the sampler inlet filter and subsequently collected by the PUF cartridge.

Cryogenic methods for capturing and collecting volatile organics involve pulling air through a stainless steel or nickle U-tube immersed in liquid oxygen or liquid argon. After sampling, the tube is sealed, stored in a coolant, and returned to the laboratory for analysis. The trap is connected to a GC, rapidly heated, and flushed into a GC or GC/MS for analysis.

The major advantage of cryogenic concentration is that all vapor phase organics, except the most volatile, are concentrated. This is a distinct advantage over sorbent concentration, which is especially selective for particular chemical

classes. Contamination problems are minimal with cryogenic methods because a collection media is not required.

Several disadvantages limit the current usefulness of cryogenic methods, including:

- Samplers rapidly become plugged with ice in high humidity conditions.
   This limits the volume of air that can be sampled.
- The entire sample is analyzed at once, enhancing sensitivity but making multiple analyses of a sample impossible.
- The necessity of handling and transporting cryogenic liquids makes this method cumbersome for many sampling applications.
- There is a possibility of chemical reactions between compounds in the cryogenic trap.

Whole air sampling--Air may be collected without preconcentration for later use in direct GC analysis or for other treatment. Samples may be collected in glass or stainless steel containers, or in inert flexible containers such as Tedler bags. Rigid containers are generally used for collection of grab samples, while flexible containers or rigid containers may be used to obtain integrated samples. Using a flexible container to collect whole air samples requires the use of a sampling pump with flow rate controls. Sampling with rigid containers is performed either by evacuating the container and allowing ambient air to enter, or by having both inlet and outlet valves remain open while pumping air through the container until equilibrium is achieved.

Whole air sampling is generally simple and efficient. Multiple analyses are possible on samples, allowing for good quality control. This method also has the ability to be used for widely differing analyses on a single sample. The method has been widely used, and a substantial data base has been developed.

Problems may occur using this method due to decomposition of compounds during storage and loss of some organics by adsorption to the container walls.

Sample stability is generally much greater in stainless steel containers than in glass or plastic. Whole-air sampling is limited to relatively small volumes of air (generally up to 20 liters due to the impracticality of handling larger sample collection containers), and has higher detection limits than some sorbent techniques.

Impinger collection -- Impinger collection involves passing the air stream through an organic solvent. Organics in the air are dissolved in the solvent, which can then be analyzed by GC/MS. Large volumes of air sampled cause the collection solvent to evaporate. In addition, collection efficiency is dependent on flow rate of the gas, and on the gas-liquid partition coefficients of the individual compounds. However, there are certain specialized applications of impinger sampling that have been found to be preferable to alternate collection techniques (e.g., sampling for aldehydes and ketones).

Certain compounds of interest are highly unstable or reactive, and will decompose during collection or storage. To concentrate and analyze these compounds, they must be chemically altered (derivatized) to more stable forms. Another common reason for derivatization is to improve the chromatographic behavior of certain classes of compounds (e.g., phenols). Addition of the derivatization reagent to impinger solvent is a convenient way to accomplish the necessary reaction.

A widely used method for analysis of aldehydes and ketones is a DNPH (dinitrophenylhydrazine) impinger technique. Easily oxidized aldehydes and ketones react with DNPH to form more stable hydrazone derivatives, which are analyzed by high performance liquid chromatography (HPLC) with a UV detector. This method is applicable to formaldehyde as well as less volatile aldehydes and ketones.

<u>Direct analysis</u> -- A method not requiring preconcentration or separation of air components is highly desirable, because it avoids component degradation or loss during storage. Air is drawn through an inert tube or probe directly into the instrument detector. Several portable instruments exist that can provide direct air analysis, including infrared spectrophotometers, mobile MS instruments, and portable FID detectors. Some of these instruments have been discussed in the section on screening methods.

Mobile mass spectrometry has been used to compare upwind and downwind concentrations of organic pollutants at hazardous waste management facilities. The advantage of the multiple mass spectrometer configuration (MS/MS or triple MS) over a single MS system is that multiple systems can identify compounds in complex mixtures without pre-separation by gas chromatography. Major limitations of MS/MS methods are low sensitivity and high instrument cost.

In summary, of the methods described in this subsection, the majority of vapor-phase organics can be monitored by use of the following sampling methods:

- Concentration on Tenax or carbon absorbents, followed by chemical or thermal resorption onto GC or GC/MS.
- Sorption on polyurethane foam (PUF) cartridges, followed by solvent extraction.
- Cryogenic trapping in the field.
- Whole-air sampling.

### 12.8.2 .2.1.2 Particulate Organics

Certain hazardous organic compounds of concern in ambient air are primarily associated with airborne particles, rather than in the vapor phase. Such compounds include dioxins, organochlorine pesticides, and polyaromatic hydrocarbons. Therefore, to measure these compounds accurately, it is necessary to monitor particulate emissions from units of concern.

Measurement of particulate organics is complicated because even relatively nonvolatile organics exhibit some vapor pressure, and will volatilize to a certain extent during sampling. The partitioning of a compound between solid and gaseous phases is highly dependent on the sampling conditions (e.g., sampling flow rate, temperature). Particulate sampling methods generally include a gas phase collection device after the particulate collector to trap those organics that become desorbed during sampling.

The most common methods used for collection of particles from ambient air are:

#### Filtration

- Cellulose Fiber
- Glass or Quartz Fiber
- Teflon Coated Glass Fiber
- Membranes
- Centrifugal Collection (e.g., cyclones)
- Impaction
- Electrostatic Precipitation

The standard sampling method for particulate is filtration. Teflon-coated glass membranes generally give the best retention without problems with separating the particulates sampled from the filter. Problems, however, may be caused by resorption of organics from the filter, by chemical transformation of organics collected on the filter, and with chemical transformation of organics due to reaction with atmospheric gases such as oxides of nitrogen and ozone. These problems are magnified by the large volumes of air that must be sampled to obtain sufficient particulate material to meet analytical requirements. For example, to obtain 50 milligrams of particulate from a typical air sample, 1000 cubic meters of air must be sampled, involving about 20 hours of sampling time with a high-volume sampling pump.

Despite the drawbacks mentioned above, filtration is currently the simplest and most thoroughly tested method of collecting particulates for organic analysis. Other methods, such as electrostatic precipitation, make use of electrical charge or mechanical acceleration of the particles. The effect of these procedures on compound stability is poorly understood.

### 12.8.2.2.2 Monitoring Inorganic Compounds in Ambient Air

#### 12.8.2 .2.2.1 Particulate Metals

Metals in ambient air can occur as particulate or can be adsorbed on other particulate material. Metals associated with particulate releases are effectively collected by use of filter media allowing for the collection of adequate samples for analysis of a number of particulate contaminants.

<u>Collection on filter media</u>--Sampling methods for particulate metals are generally based on capture of the particulate on filter media. For the most part, glass fiber filters are used; however, organic and membrane filters such as cellulose ester and Teflon can also be used. These membrane filters demonstrate greater uniformity of pore size and, in many cases, lower contamination levels of trace metals than are found in glass fiber filters. Analytical procedures described in the following reference can be utilized to analyze particulate samples.

U.S. EPA. 1986. <u>Test Methods for Evaluating Solid Waste</u>. 3rd Edition. EPA SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

<u>Hi-Vol collection devices</u>--The basic ambient air sampler is the high volume sampler which can collect a 2000 cubic meter sample over a 24-hour period and capture particulates on an 8 x 10 inch filter (glass fiber) as described in 40 CFR Part 50. It has a nominal cut point of 100μm for the maximum diameter particle size captured. A recent modification involves the addition of a cyclone ahead of the filter to separate respirable and non-respirable particulate matter. Health criteria for particulate air contaminants are based on respirable particulate matter.

<u>Personnel samplers</u>--Another particulate sampling method involves the use of personnel samplers according to NIOSH methods (NIOSH, 1984). The NIOSH methods are intended to measure worker exposure to particulate metals for comparison to OSHA standards. A 500-liter air volume is sampled at approximately 2 liters per minute. This method is most efficient when less than 2 mg total particulate weight are captured. Capture of more than 2 mg may lead to sample

losses during handling of the sample. The preferred filter medium is cellulose ester (47 mm diameter) which will dissolve during the standard acid digestion.

The NIOSH method, however, is not recommended for the RFI for several reasons. The NIOSH analytical methods (and good QA/QC practices) require several aliquots of the sample to be prepared for best analytical results. The 47 mm filter is too small for aliquoting; therefore, use of the NIOSH method would require the simultaneous operation of several sampling systems. More importantly, the 500 liter sample volume generally does not provide sufficient particulate matter for the analytical methods to detect trace ambient levels of metals. The method is best suited for industrial hygiene applications.

<u>Dichotomous Samplers</u> -- Dichotomous samplers (virtual impactors) have been developed for particle sizing with various limit cutpoints for use in EPA ambient monitoring programs. These samplers collect two particulate fractions on separate 37 mm diameter filters from a total air volume of about 20 cubic meters. The standard sampling period is 24 hours. Teflon filters are generally recommended by sampler manufacturers because they exhibit negligible particle penetration and result in a low pressure drop during the sampling period. However, glass fiber and cellulose filters are also acceptable.

The need for multiple extractions would require multiple sampling trains. If the two filters are combined to form one aliquot and extracted together, they will provide sufficient sensitivity for some but not all analytical procedures and defeat the purpose of fractioning the sample. The use of the dichotomous sampler is, therefore, limited.

### 12.8.2 .2.2.2 Vapor Phase Metals

Most metallic elements and compounds have very low volatilizes at ambient temperatures. Those that are relatively volatile, however, require a different sampling method than used for collection of particulate forms, although analytical techniques may be similar. For the purpose of ambient monitoring, vapor-phase metals are defined as all elements or compounds that are not effectively captured by standard filter sampling procedures. Available methods for the measurement of vapor phase metals are presented in Tables 12-18 and 12-19. These available

TABLE 12-18. SAMPLING AND ANALYSIS METHODS FOR VOLATILE MERCURY

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
*NIOSH P&CAM 6000	Particulate, organic and elemental mercury	Sampling train consists of membrane filter to capture particulate Hg, followed by Carbosieve B to trap organic Hg, and then silver coated Chromosorb P (CP) to collect elemental Hg. Each section is analyzed separately by thermal resorption into a flameless AA. Filters are acid digested, reduced to Hg and amalgamated on Ag CP prior to the AA analysis step.	Standard method Permits measurement of all three types of mercury - Method selective to mercury	<ul> <li>Requires use of complex resorption unit</li> <li>Cl<sub>2</sub> interferes with sampling Separation of organic and metallic mercury is uncertain at 0.001 Hg/total Hg Requires preparation of special sorbents</li> </ul>
NIOSH SCP-S342	Organic mercury	Filter to separate particulate; adsorb organic Hg on Carbosieve B; thermally desorb into flameless AA unit	- Standard method - Option to P&CAM 175 if organic mercury is only concern Range is 20-80 µg/m3 with a 3 liter sample volume	- Requires complex thermal resorption unit
PA Method 101	Particulate and vaporous mercury	Collection in acidified 0.1 N HCI impinger solution; analysis by NAA or optionally by cold vapor AA	- Standard method - Detection limit of 1 μg/m3 Fairly stable reagent Same reagent has been used for volatile Pb (Ref. 572)	<ul> <li>NAA expensive and not routinely available         Ice interferes with cold vapor         AA method at low concentrations of Hg</li> <li>Instability of collected Hg compounds in solution has been reported</li> </ul>
Canadian EPS Standard Method	Particulate and vaporous mercury	Collection in impinger solution of 10% H <sub>2</sub> SO <sub>4</sub> /2% KMnO <sub>4</sub> ; analysis by cold vapor AA	- Standard method - Collection efficiency ≥90% KMn0₄ and AA compatible AA costs = \$30/sample Reagent gives low blank levels	<ul> <li>KMn0₄ reagent must be prepared within 12 hours of use</li> <li>Short sample holding time Reagent can be easily expended in oxidizing and organic matrices</li> </ul>

TABLE 12-18. (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
environment Canada	Vaporous mercury or particulate mercury	Vaporous mercury is collected by amalgamation on silver. Particulate is collected on microquartz filters. Both are analyzed by thermal resorption and/or pyrolysis with reamalgamation; then thermal resorption for determination by UV absorption at 253.7	<ul> <li>Standard method for ambient air Used in range of 4- 22 mg/m³</li> <li>Claimed to be "inexpensive"</li> </ul>	- Complex desorption/amalgamation unit
3M Badge	Elemental Hg vapor	Passive device-diffusion of Hg through membrane, amalgamation on gold, analysis of badges performed by 3M	- Very simple and mercury specific method Requires no analysis to be performed by users Gives 8-hour time weighted average and concentrations of up to 20 µg/m³	<ul> <li>CI₂ interferes with sampling efficiency High H₂S and SO₂ also interfere</li> <li>Temperature variations affect diffusion rates and must be corrected for</li> </ul>
MSA Method	Elemental and organic mercury	Adsorb mercury on iodine impregnated charcoal; place in tantalum boat and volatilize	Simple equipment requirements Range of 50-200 µg/m³tested	<ul> <li>Large coefficient of variation</li> <li>Quality of results are very much operator dependent Only works well at 200 µg/m³</li> </ul>
Hopcalite Method	Elemental and organic mercury	Adsorb on hopcalite; dissolve sorbent and mercury in HNO <sub>3</sub> + HCI; analyze by cold vapor AA	<ul> <li>Simple equipment requirement</li> <li>Evaluated in range of 50-200 µg/m³</li> </ul>	<ul> <li>Does not provide for analysis of particulate mercury</li> <li>Insufficient performance data in available literature</li> </ul>

### TABLE 12-18 (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
*Silver amalgamation and APHA	Vaporous elemental mercury	Amalgamation on silver wool or silver <b>gauge</b> ; thermal resorption with analysis by flameless AA or UV absorption	- Substantial information on the method; interferences provided in the references - Ag wool-24 hour sample can be used with 15 ng-10 pg/m³ levels - Ag gauge ≤ 2 hour sample can give concentrations of 5 ng-100 µg/m³	<ul> <li>Collection efficiency for organic mercury is in question</li> <li>Oxidants could interfere with sampling procedure unless removed before reaching silver</li> </ul>
Impinger/Dithizone	Organic, particulate and vaporous mercury	Collect in impinger solution of <b>0.1</b> NiCl and <b>0.5 m</b> HCl; analyze by the dithizone calorimetric method	- Efficient capture of all three types of volatile mercury	<ul> <li>Dithizone method suffers from high blanks, interference from SO₂ and interference from several other metals</li> <li>Mercury compounds collected in HCl are unstable</li> </ul>
Jerome instrument Corp., Model <b>411</b> , old Film Hg Vapor Analyzer	Elemental mercury	Onsite monitor-amalgamation of Hg on <b>gold</b> , measure concentration by change in gold foil resistance	<ul> <li>Selective for mercury</li> <li>Direct reading eliminates sample transport and analysis         Concentration range from μg/m³ to mg/m³</li> </ul>	<ul> <li>Monitor costs \$3500-\$4000</li> <li>May suffer interference from oxidants as noted for 3M badges</li> </ul>

<sup>\*</sup> Recommended methods

TABLE 12-19. SAMPLING AND ANALYSIS OF VAPOR STATE TRACE METALS (EXCEPT MERCURY)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
Antimony	NIOSH S243	Stibine (SbH <sub>3</sub> )	Adsorb on mercuric chloride impregnated silica gel; extract with concentration HCl; oxidize Sb(111) to Sb(V) with eerie sulfate; calorimetric analysis by Rhodamine	- Standard method	- Range only 0.1-1.0 ng/m³ using a 20-liter sample Analytical interferences by Pb(III), Tl(I), and Sb(II)
Arsenic	NIOSH P&CAM 6001	Arsine (AsH <sub>3</sub> )	Adsorb on charcoal; desorb with HNO <sub>3</sub> ; analyze by furnace AA	- Standard method	<ul> <li>Possible breakthrough at high concentrations</li> </ul>
	NIOSH S229 NIOSH 7900	Arsine (AsH <sub>3</sub> )	Same as P&CAM 265 except that HNO <sub>3</sub> resorption is performed with 10 ml rather than 1 ml	<ul> <li>Standard method</li> <li>Working range 0.09- 0.1 mg/m³</li> </ul>	<ul> <li>Possible breakthrough at high concentrations</li> <li>Earlier version of P&amp;CAM 265</li> </ul>
		As <sub>2</sub> O <sub>3</sub> and others	Absorb in dilute NaOH solution; analytical procedure not specified but it may be suitable to use arsine generation or furnace AA	<ul> <li>Only method proposed for AS<sub>2</sub>O<sub>3</sub> in available literature Relatively simple</li> </ul>	- No supporting data available
*Lead	NIOSH S383 and S384	Tetraethyl lead and tetramethyl lead	Adsorb on XAD-2; desorb with pentane; analysis by GC	<ul> <li>Standard method</li> <li>Permits separation of the various alkyl lead compounds</li> <li>Range 0.045-0.20 ng/m³ (as Pb)</li> <li>Can alter GC conditions to remove interferences with analysis</li> </ul>	- Compound identification only by GC retention times; must verify
		Alkyl lead compounds	Collect in HCI/NiCI impinger solution; analyze by dithizone calorimetric method when 8-hour sampling period or by AA for 24 hour sample	- Near 100% collection efficiency - Dithizone detection limit - 10 µg/m³ AA detection limit - 0.2 - 10 µg/m³	<ul> <li>Very little information in literature</li> <li>Dithizone method may have same problems noted elsewhere for other elements</li> </ul>

### TABLE 21-19. (continued)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
		Alkyl lead compounds	Adsorb on activated carbon; digest with HN0 <sub>3</sub> + HCl0 <sub>4</sub> ; analyze by dithizone method	- Good collection efficiency Low detection limits possible	<ul> <li>No data available         Dithizone method may have interferences as noted above     </li> </ul>
Nickel	N 10SH P&CM 344	Nickel tetracarbonyl (Ni(CO) <sub>4</sub> )	Adsorb on charcoal; desorb with dilute HNO <sub>3</sub> ; analyze by furnace AA	- Standard method - AA specific for . Nickel Range 2-60 µg/m³	- Sorbent capacity limits upper concentration
	Ref. 120, 142	Nickel tetracarbonyl (Ni(CO)₄)	Absorb in 3% HCI impinger solution; analyze by calorimetric method in which color development in chloroform phase is measured	- Detection limit - 0.001 ppm	<ul> <li>Not a standard method Interference may occur from other Nickel compounds, Cu, Pb, Cr, Se and V</li> </ul>
Selenium		SeO <sub>2</sub> , H <sub>2</sub> SeO <sub>3</sub>	Collect in impinger with aqueous solution of Na <sub>2</sub> SO <sub>3</sub> , Na <sub>2</sub> S, or NaOH, analyze by NAA, AA, GC, colorimetry, fluorimetry, ring oven techniques, or catalytic methods	- Only method suggested in literature for volatile Se	No data to support this method

methods are generally developed for industrial hygiene applications by NIOSH.

The methods for measuring vapor-phase metals presented in Tables 12-18 and 12-19 have undergone limited testing for precision and accuracy and have had matrix interferences documented. Therefore, they should be used in lieu of any methods which have no supporting data.

Several methods are suitable for quantification of vapor-phase mercury. If elemental mercury is to be measured, the silver amalgamation technique with thermal resorption and flameless AA (atomic absorption) analysis is recommended. This technique is presented in American Public Health Association (APHA) Method 317, which can achieve nanogram per cubic meter detection limits. If organic and/or particulate mercury are also to be determined, NIOSH methods (NIOSH, 1984) are recommended. These methods can measure all three airborne mercury species, but require a complex two stage thermal resorption apparatus.

### 12.8.2.2.2.3 Monitoring Acids and Other Compounds in Air

Monitoring for acids and other inorganic/non-metal compounds (e.g., hydrogen sulfide) in the ambient air will generally require application of industrial hygiene technologies. Applicable methods have been compiled in the following references:

NIOSH. February 1984. <u>NIOSH Manual of Analytical Methods.</u> NTIS PB 85-179108. National Institute for Occupational Safety and Health. Cincinnati, OH.

ASTM. 1981. <u>Toxic Materials in the Atmosphere.</u> ASTM, STP 786. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association.

ACGIH. 1983. <u>Air Sampling Instruments for Evaluation of Atmospheric Contamination.</u> American Conference of Governmental industrial Hygienists. Cincinnati. OH.

### 12.8.3 Stack/Vent Emission Sampling

EPA methods for source-sampling and analysis are documented in the following reference:

Code of Federal Regulations. 40 CFR Part 60, Appendix A: Reference Methods. Office of the Federal Register, Washington, D.C.

Additional guidance is available in the following references:

- U.S. EPA. 1978. Stack Sampling Technical Information, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042 a, b, c. NTIS PB 80-161672, 80-1616680, 80-161698. Office of Air Quality Planning and Standards Research Triangle Park, NC 27711.
- U.S. EPA. February 1985. <u>Modified Method 5 Train and Source Assessment Sampling System Operators Manual.</u> EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, NC 27711.
- U.S. EPA March 1984. <u>Protocol for the Collection and Analysis of Volatile POHC's Using VOST.</u> EPA-600/8 -84-007. NTIS PB 84-177799. Office of Research and Development. Research Triangle Park, NC 27711.
- U.S. EPA. February 1984. <u>Sampling and Analysis Methods for Hazardous Waste Combustion.</u> EPA-600/8 -84-002. NTIS PB 84-155845. Washington, D.C. 20460.
- U.S. EPA. November 1985. <u>Practical Guide Trial Burns for Hazardous Waste Incinerators.</u> NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.
- U.S. EPA. 1981. <u>Source Sampling and Analysis of Gaseous Pollutants.</u> EPA-APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1979. <u>Source Sampling for Particulate Pollutants.</u> EPA-APTI Course Manual 450. NTIS PB 80-188840, 80-174360, 80-182439. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1986. <u>Test Methods for Evaluating Solid Waste</u>. 3rd Edition. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

### 12.8.3.1 Vapor-Phase and Particulate Associated Organics

Generally, point source vapor-phase samples are obtained from the process vents and effluent streams either by a grab sample technique or by an integrated sampling train. Careful planning is necessary to insure that sampling and analytical techniques provide accurate quantitative and qualitative data for measurement of vapor-phase organics. Considerations such as need for real-time (continuous) versus instantaneous or short-term data, compatibility with other compounds/parameters to be measured, and the need for onsite versus offsite analysis may all be important in the selection process.

Monitoring for complex organic compounds generally requires detailed methods and procedures for the collection, recovery, identification, and quantification of these compounds. The selection of appropriate sampling and analytical methods depends on a number of important considerations, including source type and the compounds/parameters of interest. Table 12-20 lists several sampling methods for various applications and compound classess (applicable to combustion sources). The first three methods listed are fixed-volume, grab-sampling methods. Grab sampling is generally the simplest technique to obtain organ emission samples.

Sample collection by the bag and canister sampling methods can be used to collect time-integrated samples. These methods also allow for a choice of sample volumes due to a range of available bag sized (6, 12, and 20 liter capacities are typical). Bags of various materials are available, including relatively inert and noncontaminating materials such as Teflon, Tedlar, and Mylar. All sample collection bag types may have some sample loss due to adsorption of the contaminants collected to container walls. The bag sample is collected by inserting the bag into

### TABLE 12-20. SAMPLING METHODS FOR TOXIC AND HAZARDOUS ORGANIC MATERIALS FROM POINT SOURCES

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Syringe Flow-through bottle Evacuated canister Tedlar bag EPA Method 3)	Instantaneous grab Instantaneous grab Integrated grab Integrated grab	Non-combustion (storage tanks spray booths paint bake ovens, etc.) Low moisture content combustion emissions (boilers, incinerators, etc.).	Volatiles, C1-C10  Volatiles, C1-C10  Volatiles, C1-C10  Volatiles, C1-C10	GC-FID <sup>a</sup> GC-MS <sup>b</sup> or GC-PID <sup>c</sup>	Sample size and therefore detectable concentration are limited by container size; ≥1 ppm.  Bag samples are subject to absorptive losses of sample components.
EPA method 25	Two stage integrated grab train consisting of cold trap followed by evacuated S.S. tank.	Non-combustion and low moisture content combustion emissions as above.	Volatiles and semi-volatiles, C1-C16	Oxidation/ reduction followed by GC/FID.	Sample size is limited by tank volume. C0 <sub>2</sub> and H <sub>2</sub> 0 can produce significant interferences. System is complex/cumbersome.
-VOST <sup>d</sup>	Water-cooled sample gas, including condensate, is passed through dual in-series sorbent traps. Tenax GC in first tube followed by Tenax GC backed-up by charcoal in second tube.	Combustion emissions (boilers, hazardous waste incinerators, etc.).	Volatiles and semi volatiles, C1 C16, C1 C10	GC-MS GC-ECD GC-PID	Sample size is limited to 20 liters per pair of sorbent tubes. Sorbent tubes are susceptible to contamination from organics in ambient air during installation and removal from train.

### TABLE 12-20 (continued)

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Modified Method 5	Water-cooled sample gas, with condensate is passed through single sorbent trap. Sorbent type dependent on compound(s) of interest.	Combustion emission as for VOST.	Semi - volatiles, PCB's, other halogenated organics, C <sub>1</sub> -c <sub>1b</sub> , c1-1-c110	GC-ECD, GC-HECD, GC-MS	Single trap system does not provide check for breakthrough. Flow rate limited to approximately 1 cpm.
High Volume Modified Method 5	Sample gas is passed through condensers where moisture is removed before passing through two sorbent traps, primary followed by back-up. Flow rates of up to 5 cpm are achievable. Sorbent type dependent on compounds of interest."	Combustion emissions.	Semi-volatiles, PCBS, other halogenated organics, c7-c16, c1-c10	GC-ECD, GC-HECD, GC-MS	High flow rate results in high sampling train pressure drop requiring large pump capacity.
SASS Train	Sample gas passes through a cold trap followed by an XAD-2 sorbent trap. Train is all stainless steel construction.	Combustion emissions (boilers, hazardous waste incinerators).	Semi-volatiles, and other, non- halogenated organics, c7-c-16	GC-ECD, GC-HECD, GC-MS	System is complex, large and cumbersome. Recovery of organics from cold trap can be difficult. S.S. construction makes train components highly susceptible to corrosion from acidic gases especially HCI.

- a GC-FID gas chromatography with flame ionization detector.
- b GC-MS gas chromatography-mass spectrometry.
- c GC-PID gas chromatography-photoionization detector.
- d VOST . volatile organic sampling train.
  e Sorbents include Florisil, XAD-2 resin, and Tenax-GC among the most commonly used.

Source: Hazardous Waste Management, Vol. 35, No. 1, January 1985

an airtight, rigid container (lung) and evacuating the container. The sample is drawn into the bag because reduced pressure in the container provides adequate suction to fill the bag. This procedure is presented in detail in 40 CFR Part 60, Appendix A (Method 3).

Evacuated canisters are conventionally constructed of high grade polished stainless steel. There are many versions available ranging from units with torque limiting needle valves, purge free assemblies, internal electropolished surfaces and versions utilizing stainless steel beakers with custom designed tops and fittings. Also, different container materials may react differently with the sample. Therefore, sample storage time or sample recovery studies to determine or verify inertness of the sampling canister should be considered.

Canisters are generally used to collect samples by slowly opening the sample valve, allowing the vacuum to draw in the sample gas. In less than a minute, the container should equilibrate with the ambient atmospheric pressure. At that time, the sample valve is closed to retain the sample. To collect composite samples over longer intervals, small calibrated orifices can be inserted before the inlet valve to extend the time required for equilibration of pressure once the sample valve is opened.

The sample collection procedure for EPA Method 5 (U.S. EPA, 1981) is similar in principle to that for the evacuated canister. The train consists of a polished stainless steel canister with a cold condensate trap in series and prior to the canister to collect a higher boiling point organic fraction. This two fraction apparatus provides for separate collection of two concentration ranges of volatile organic compounds based on boiling point.

The following four sampling methods utilize sample concentration techniques using one or more sorbent traps. The advantages of these methods is an enhanced limit of detection for many toxic and hazardous organic compounds. These techniques are preferred due to their lower detection limit. The Modified Method 5 (MM5) sampling train (U.S. EPA, 1981) is used to sample gaseous effluents for vaporphase organic compounds that exhibit vapor pressures of less than 2 mm Hg (at 20°C). This system is a modification of the conventional EPA Method 5 particulate sampling train. The modified system consists of a probe, a high efficiency glass or

quartz fiber filter, a sorbent module, impingers, and related control hardware. The sample gas is passed through a single sorbent trap, containing XAD-2. The MM5 train is limited due to the single sorbent trap design that does not provide a backup for breakthrough. This is especially important when large volumes of sample are collected.

To minimize the potential for breakthrough, the MM5 train can be modified to provide a backup trap. However, this dual trap modification increases the pressure drop across the train, reducing the range of flow rates possible for sample collection. To overcome this pressure drop and maintain the desired flow rate, the high-volume MM5 train utilizesa much larger capacity pump.

The Source Assessment Sampling System (SASS) train is another comprehensive sampling train, consisting of a probe that connects to three cyclones and a filter in a heated oven module, a gas treatment section, and a series of impingers to provide large collection capacities for particulate matter, semivolatiles, and other lower volatility organics. The materials of construction are all stainless steel making the system very heavy and cumbersome. The stainless steel construction is also very susceptible to corrosion. This system can, however, be used to collect and concentrate large sample volumes, providing for a much lower detection limit. Because of the sorbents used (generally XAD-2), its use is limited to the same class of lower volatility organics and metals as the MM5 train.

The Volatile Organic Sampling Train (VOST) has proven to be a reliable and accurate method for collection of the broad range of organic compounds. By using a dual sorbent and dual in-series trap design, the VOST train can supplement either the MM5 or SASS methods allowing for collection of more volatile species. However, VOST has several limitations, including a maximum sample flow rate of 1.0 liter/minute, and **a** total sample volume of 20 liters per trap pair. Therefore, frequent changes of the trap pairs are required for test periods that exceed 20 minutes. The frequent change of traps makes the samples more susceptible to contamination.

Any of the point source monitoring techniques described above can be adapted for use with the isolation flux chamber techniques described previously. For point sources where particulate emissions are of concern, the Modified Method

5 or SASS train (originally designed to measure particle emissions from combustion effluents) are also applicable and proven technologies.

Analytical methodologies for the techniques discussed above will vary with the technique used. While certain techniques will offer advantages over others in the measurement of specific contaminants, the investigator is advised to utilize standard methodologies whenever possible in performing the RFI. For example, use of the VOST and/or the MM5 train, and their associated analytical methodologies is recommended for point source monitoring of the applicable compounds. Descriptions for both of these methods are included in the 3rd Edition of "Test Methods for Evaluating Solid Waste" (EPA SW-846), 1986 (GPO No. 955-001-00000-1). Although these methods are designed for the evaluation of incinerator efficiencies, they are essentially point-source monitoring methods which can be adapted to most point sources.

### 12.8.3.2 Metals

Although the emission of metallic contaminants is primarily associated with particulate emission from area sources caused by the transfer of material to and from different locations, wind erosion, or general maintenance and traffic activities at the unit, point source emission of particulate or vapor-phase metals can exist. Metallic constituents may exist in the atmosphere as solid particulate matter, as dissolved or suspended constituents of liquid droplets (mists), and as vapors.

Metals specified as hazardous constituents in 40 CFR Part 261, Appendix VIII are generally noted as the element and compounds "not otherwise specified (NOS)", as shown in Table 12-21, indicating that measurement of the total content of that element in the sample is required.

<u>Vapor phase metals</u>--For the purpose of point-source monitoring, vapor-phase metals will be defined as all elements or compounds thereof, that are not quantitatively captured by standard filter sampling procedures. These include volatile forms of metals such as elemental and alkyl mercury, arsine, antimony, alkyl lead compounds, and nickel carybonyl.

### **Table 12-21.**

## RCRA APPENDIX VIII HAZARDOUS METALS AND METAL COMPOUNDS

Antimony and compounds NOS<sup>a</sup>
Arsenic and compounds NOS<sup>b</sup>
Barium and compounds NOS
Beryllium and compounds NOS
Cadmium and compounds NOS
Chromium and compounds NOS
Lead and compounds NOS
Mercury and compounds NOS<sup>b</sup>
Nickel and compounds NOS<sup>b</sup>
Selenium and compounds NOS<sup>b</sup>
Silver and compounds NOS<sup>b</sup>
Thallium and compounds NOS<sup>b</sup>

<sup>&</sup>lt;sup>a</sup> NOS = not otherwise specified.

<sup>&</sup>lt;sup>b</sup>Additional specific compound(s) listed for this element.

The sampling of point sources for vapor phase metals has not been a common or frequent activity for the investigation of air releases from solid waste management units. If a point source of vapor-phase metals is identified, the sampling approach should identify the best available monitoring techniques, considering that many have been developed which are specific to single species rather than multiple species of many different metal elements. The primary references for identifying available techniques include National Institute of Occupational Safety and Health (NIOSH, 1984) methods, EPA methods such as those presented in SW-846 and in the <a href="Federal Register">Federal Register</a> under the National Emissions Standards for Hazardous Air Pollutants (NESHAPs), and American Public Health Association (APHA, 1977) methods. The basic monitoring techniques include collection on sorbents and in impinger solutions. The particular sorbent or impinger solution utilized should be selected based on the specific metal species under investigation.

Particulate Metals--Point-source releases to air could also require investigation of particulate metals. Source sampling particulate procedures such as the Modified Method 5 or SASS methods previously discussed are appropriate for this activity. EPA Modified Method 5 is the recommended approach. Modification of this basic technique involving the collection of particulate material on a filter with subsequent analysis of the collected particulate material on a filter for the metals of concern, could include higher or lower flow rates and the use of alternate filter media. Such modifications may be proposed when standard techniques prove to be inadequate. Several important particulate metal sampling methods are available in the NIOSH methods manuals (NIOSH, 1984); however, these methods were designed for ambient or indoor applications and may require modification if used on point sources.

### 12.9 Site Remediation

Although the RFI Guidance is not intended to provide detailed guidance on site remediation, it should be recognized that certain data collection activities that may be necessary for a Corrective Measures Study may be collected during the RFI. EPA has developed a practical guide for assessing and remediating contaminated sites that directs users toward technical support, potential data requirements and

technologies that may be applicable to EPA programs such as RCRA and CERCLA. The reference for this guide is provided below.

U.S. EPA. 1988. <u>Practical Guide for Assessingl and Remediating Contaminated Sites.</u> Office of Solid Waste and Emergency Response. Washington, D.C. 20460.

The guide is designed to address releases to ground water as well as soil, surface water and air. A short description of the guide is provided in Section 1.2 (Overall RCRA Corrective Action Process), under the discussion of Corrective Measures Study.

### **RFI CHECKLIST - AIR**

	Name/Loca of Unit						
1.	Does was	te characterization include the following information?	(Y/N)				
	•	Physical form of the waste					
	•	Identification of waste components					
	•	Concentrations of constituents of concern					
	•	Chemical and physical properties of constituents of concern					
2.	Does unit	characterization include the following information?	(Y/N)				
	•	Type of unit					
	•	Types and efficiencies-of control devices					
	•	Operational schedules					
	•	Operating logs					
	•	Dimensions of the unit					
	•	Quantities of waste managed					
	•	Locations and spatial distribution/					
		variation of waste in the unit					
	•	Past odor complaints from neighbors					
	•	Existing air monitoring data					
	•	Flow rates from vents					
3.	Does env	Does environmental setting characterization include					
	the	following information?	(Y/N)				
	•	Definition of regional climate					
	•	Definition of site-specific meteorological conditions					
	•	Definition of soil conditions					

	<ul> <li>Definition of site-specific terrain</li> </ul>	
	<ul> <li>Identification of potential release receptors</li> </ul>	
4.	Have the following data on the initial phase of the release characterization been collected?	(Y/N)
	<ul> <li>Conceptual model of release developed</li> <li>Concentrations of released constituent at unit, facility property boundary and, if appropriate, at nearby offsite receptors (based on screening assessment or available modeling/monitoring data)</li> <li>Screening monitoring data (as warranted)</li> <li>Additional waste/unit data (as warranted)</li> </ul>	
5.	Have the following data on the subsequent phase(s) of the release characterization been collected?	(Y/N)
	<ul> <li>Identification of "reasonable worst case" conditions</li> </ul>	
	<ul> <li>Meteorological conditions during monitoring</li> </ul>	
	Release source conditions during monitoring	
	<ul> <li>Basis for selection of monitoring constituents</li> </ul>	
	Concentrations of released constituents at unit,	
	facility property boundary and, if appropriate,	
	at nearby offsite receptors (based on	
	monitoring or modeling and representative of reasonable "worst case" conditions)	

#### 12.11 References

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#### **SECTION 13**

#### **SURFACE WATER**

#### 13.1 Overview

The objective of an investigation of a release to surface water is to characterize the nature, extent, and rate of migration of the release to this medium. This section provides the following:

- An example strategy for characterizing releases to the surface water system (e.g., water column, bottom sediments, and biota), which includes characterization of the source and the environmental setting of the release, and conducting a monitoring program that will characterize the release;
- A discussion of waste and unit source characteristics and operative release mechanisms;
- A strategy for the design and conduct of monitoring programs considering specific requirements of different wastes, release characteristics, and receiving water bodies;
- Formats for data organization and presentation;
- Appropriate field and other methods that may be used in the investigation; and
- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be facility and site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all

instances; however, it identifies the information that is likely to be needed to perform release characterizations and identifies methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information collection for release characterization. This list is not a list of requirements for all releases to surface water. Some releases will involve the collection of only a subset of the items listed, while others will involve the collection of additional data.

Case Study Numbers 27, 28, 29, 30 and 31 in Volume IV (Case Study Examples) illustrate various aspects of surface water investigations which are described below.

## 13.2 Approach for Characterizing Releases to Surface Water

## 13.2.1 General Approach

A conceptual model of the release should be formulated using all available information on the waste, unit characteristics, environmental setting, and any existing monitoring data. This model (not a computer or numerical simulation model) should provide a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any). The model should be testable/verifiable and flexible enough to be modified as new data become available. For surface water investigations, this model should account for the release mechanism (e.g., overtopping of an impoundment), the nature of the source area (e.g., point or non-point), waste type and degradability, climatic factors (e.g., history of floods), hydrologic factors (e.g., stream flow conditions), and fate and transport factors (e.g., ability for a contaminant to accumulate in stream bottom sediments). The conceptual model should also address the potential for the transfer of contaminants in surface water to other environmental media (e. g., soil contamination as a result of flooding of a contaminated creek on the facility property).

An example strategy for characterization of releases to surface waters is summarized in Table 13-1. These steps outline a phased approach, beginning with evaluation of existing data and proceeding to design and implementation of a monitoring program, revised over time, as necessary, based on findings of the previous phase. Each of these steps is discussed briefly below.

#### **TABLE 13-1**

#### **EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO SURFACE WATER\***

#### INITIAL PHASE

- 1. Collect and review existing information on:
  - Waste
  - Unit
  - Environmental setting
  - Contaminant releases, including inter-media transport
- 2. Identify any additional information necessary to fully characterize release:
  - Waste
  - Unit
  - Environmental setting
  - Contaminant releases, including inter-media transport
- Develop monitoring procedures: 3.
  - Formulate conceptual model of release
  - Determine monitoring program objectives
  - Select monitoring constituents and indicator parameters
  - Select monitoring locations

  - Determine monitoring frequency Incorporate hydrologic monitoring as necessary
  - Determine role of biomonitoring and sediment monitoring
- 4. Conduct initial monitoring:
  - Collect samples under initial monitoring phase procedures and complete field analyses
  - Analyze samples for selected parameters and constituents
- 5. Collect, evaluate, and report results:
  - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
  - Summarize and present data in appropriate format
  - Determine if monitoring program objectives were met
  - Determine if monitoring locations, constituents and frequency were adequate to characterize release (nature, extent, and rate)
  - Report results to regulatory agency

## **TABLE 13-1 (continued)**

#### **EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO SURFACE WATER\***

## SUBSEQUENT PHASES (If necessary)

- 1. Identify additional information necessary to characterize release:
  - Identify additional information needs
  - Determine need to include or expand hydrologic, and sediment and biomonitoring
  - Evaluate potential role of inter-media transport
- 2. Expand initial monitoring as necessary:
  - Relocate, decrease, or increase number of monitoring locations
  - Add or delete constituents and parameters of concern
  - Increase or decrease monitoring frequency
  - Delete, expand, or include hydrologic, sediment or bio-monitoring
- 3. Conduct subsequent monitoring phases:
  - Collect samples under revised monitoring procedures and complete field analyses
  - Analyze samples for selected parameters and constituents
- 4. Collect, evaluate and report results/identify additional information necessary to characterize release:
  - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
  - Determine if monitoring program objectives were met
  - Determine if monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)
  - Identify additional information needs
  - Determine need to include or expand hydrologic, sediment, or biomonitoring
  - Evaluate potential role of inter-media transport
  - Report results to regulatory agency

Surface water system is subject to inter-media transport. Monitoring program should incorporate the necessary procedures to characterize the relationship, if any, with ground water, sediment deposition, fugitive dust and other potential release migration pathways.

The first step in the general approach is the collection and review of available information on the contaminant source and the environmental setting. Some information on the contaminant source will be available from several reports and other documents. The RCRA permit, compliance order, or RFA report will provide a summary of information regarding actual or suspected releases from the various units. The facility owner or operator should be familiar with this information as a basis for further characterization of the release(s) in the RFI. In addition, a thorough understanding of the environmental setting is essential to an adequate determination of the nature and extent of releases to surface waters. Monitoring data should also be reviewed focusing on the quality of the data. If the quality is determined to be acceptable, then the data may be used in the design of the monitoring program. Guidance on obtaining and evaluating the necessary information on the contaminant source and the environmental setting is given in Section 13.3.

During the initial investigation particular attention should be given to sampling run-off from contaminated areas, leachate seeps and other similar sources of surface water contamination, as these are the primary overland release pathways for surface water. Releases to surface water via ground-water discharge should be addressed as part of the ground-water investigation, which should be coordinated with surface water investigations, for greater efficiency.

Based on the collection and review of existing information, the design of the monitoring program is the next major step in the general approach. The monitoring program should include clear objectives, monitoring constituents and indicator parameters, monitoring locations, frequency of monitoring, and provisions for hydrologic monitoring. in addition to conventional water quality and hydrologic monitoring, sediment monitoring and biomonitoring may also have a role in the surface water evaluation for a given RFI. Guidance on the design of the monitoring program is given in Section 13.4.

Implementation of the monitoring program is the next major step in the general strategy for characterizing releases to surface water. The program may be implemented in a phased manner that allows for modifications to the program in subsequent phases. For example, initial monitoring results may indicate that

downstream monitoring locations have been placed either too close to or too far from the contaminant source to accurately define the complete extent of downstream contamination. In this case, the program should be modified to relocate monitoring stations for subsequent monitoring phases. Similarly, initial monitoring may indicate that biomonitoring of aquatic organisms is needed in the next phase. Guidance on methods that can be used in the implementation of the program is given in Section 13.6.

Finally, the results of the characterization of releases to surface waters must be evaluated and presented in conformance with the requirements of the RFI. Section 13.5 provides guidance on data presentation. Table 13-2 summarizes techniques and data-presentation methods for the key characterization tasks.

As monitoring data become available, both within and at the conclusion of discrete investigation phases, they should be repot-ted to the regulatory agency as directed. The regulatory agency will compare the monitoring data to applicable health and environmental criteria to determine the need for (1) interim corrective measures; and/or (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the monitoring data with respect to adequacy and completeness to determine the need for any additional monitoring efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are supplied in Section 8. A flow diagram illustrating RFI decision points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is directed to follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

# TABLE 13-2 RELEASE CHARACTERIZATION TASKS FOR SURFACE WATER

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs			
Waste/Unit     Characterization					
- Waste Composition and Analysis	- See Section 13.3.1	- Data Tables			
- Unit or Facility Operations	- Review waste handling and disposal practices and schedules	- Schematic diagrams of flow paths, narrative			
	- Review environmental control strategies				
- Release Mechanisms	- See Section 13.3.1, Review operational information	- Site-specific diagrams, maps, narrative			
Environmental Setting     Characterization					
- Geographic Description	- Review topographic, soil and geologic setting	- Maps, Tables, Narrative			
- Classification of Surface Water and Receptors	information - See Section 13.3.3.1	- Maps, Cross Sections, Narrative			
- Define Hydrologic Factors	- See Section 13.3.3.1	- Tables, Graphs, Map			
3. Release Characterization					
- Delineate Areal Extent of Contamination	- Sampling and Analysis	- Tables of Results, Contour Maps, Maps of Sampling Locations			
<ul> <li>Define Distribution         Between Sediment,         Biota and Water         Column</li> </ul>	- Sampling and Analysis	- Graphs and Tables			
- Determine Rate of Migration	- Flow Monitoring	- Graphs and Tables			
- Describe Seasonal Effects	- Repetitive Monitoring	- Graphs and Tables			

## 13.2.2 Inter-media Transport

Surface waters are subject to inter-media transport, both as a receptor of contamination and as a migration pathway. For example, surface waters are generally engaged in a continual dynamic relationship with ground water. Ground water may discharge to a surface water body that may, in turn, recharge an aquifer. Hence, contamination may be transported from ground water to surface water and from surface water to ground water. Release of contaminants from a receiving water body to soil can also occur through deposition of the contaminants in floodplain sediments. These sediments may be exposed to wind erosion and become distributed through fugitive dust. Sediments may be exposed to air during periods of low flow of water in streams and lakes and when sediments are deposited by overland flow during rainfall-runoff events. Contaminants may also enter the air from surface water through volatilization.

#### 13.3 Characterization of the Contaminant Source and Environmental Setting

The initial step in developing an effective monitoring program for a release to surface waters is to investigate the unit(s) that is the subject of the RFI, the waste within the unit(s), the constituents within the waste, the operative release mechanisms and migration pathways to surface water bodies, and the surface water receptors. From this information, a conceptual model of the release can be developed for use in designing a monitoring program to characterize the release.

#### 13.3.1 Waste Characterization

Knowledge of the general types of wastes involved is an important consideration in the development of an effective monitoring program. The chemical and physical properties of a waste and the waste constituents are major factors in determining the likelihood that a substance will be released. These waste properties may also be important initially in selecting monitoring constituents and indicator parameters. Furthermore, once the wastes are released, these propeties play a major role in controlling the constituent's migration through the environment and its fate. Table 13-3 lists some of the significant properties in evaluating environmental fate and transport in a surface water system. Without data on the wastes, the investigator may have to implement a sampling program

#### **TABLE 13-3**

## IMPORTANT WASTE AND CONSTITUENT PROPERTIES AFFECTING FATE AND TRANSPORT IN A SURFACE WATER ENVIRONMENT

Bulk waste properties affecting mobility<sup>a</sup>

- Physical state (solid, liquid, gas) of waste
- Chemical nature (e.g., aqueous vs non-aqueous) of waste
- Density (liquid)
- Viscosity (liquid)
- Interracial tension (with water and minerals) (liquid)

#### Properties to assess mobility of constituents

- Volubility
- Vapor pressure
- Henry's law constant (or vapor pressure and water volubility)
- Bioconcentration factor
- Soil adsorption coefficient
- Diffusion coefficient (in air and water)
- Acid dissociation constant
- Octanol-water partition coefficient
- Activity coefficient
- Mass transfer coefficients (and/or rate constants) for intermedia transfer
- Boiling point
- Melting point

## Properties to assess persistence

- Rate of biodegradation (aerobic and anaerobic)
- Rate of hydrolysis
- Rate of oxidation or reduction
- Rate of photolysis

Sources of values for these and other parameters include Mabey, Smith, and Podall, (1982), and Callahan, et al. (1979). Parameter estimation methods are described by Lyman, Riehl, and Rosenblatt, (1982), and Neely and Blau (1985).

These waste properties will be important when it is known or suspected that the waste itself has migrated into the environment (e.g., due to a spill).

b These properties are important in assessing the mobility of constituents present in low concentrations in the environment.

For these properties, it is generally important to know (1) the effect: of key parameters on the rate constants (e.g., temperature, concentration, pH) and (2) the identity of the reaction products.

involving many constituents to ensure that all potential constituents have been addressed. General guidance on defining physical and chemical properties and identifying possible monitoring constituents and indicator parameters is provided in Sections 3 and 7.

Below are brief synopses of several of the key release, mobility, and fate parameters summarized in Table 13-3. Figure 13-1 shows the qualitative relationship between various environmental partitioning parameters. Neely and Blau (1985) provide a description of environmental partitioning effects of constituents and application of partition coefficients.

#### Physical State:

Solid wastes would appear to be less susceptible to release and migration than liquids. However, processes such as dissolution (i.e., as a result of leaching or runoff), and physical transport of waste particulate can act as significant release mechanisms.

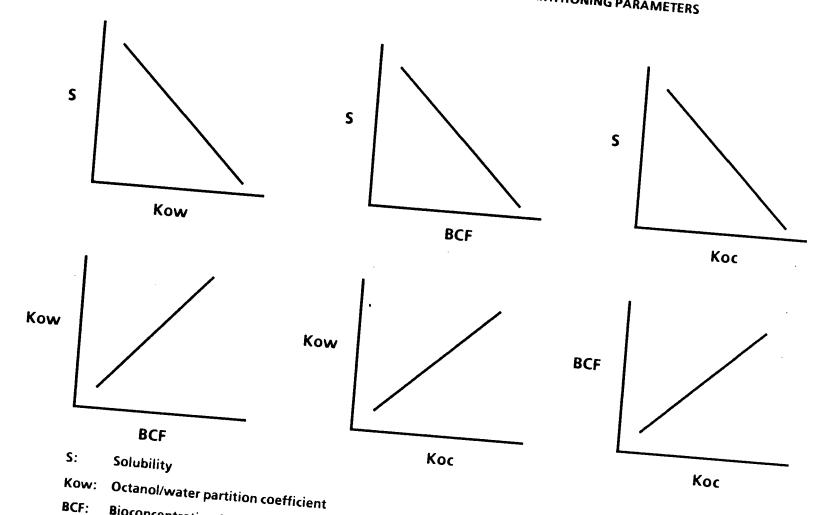
## Water Volubility:

Volubility is an important factor affecting a constituent's release and subsequent migration and fate in the surface water environment. Highly soluble contaminants (e.g., methanol at 4.4 x 106 mg/L at 77°F) are easily and quickly distributed within the hydrologic cycle. These contaminants tend to have relatively low adsorption coefficients for soils and sediments and relatively low bioconcentration factors in aquatic life. An example of a less soluble constituent is tetrachloroethylene at 100 mg/L at 77°F.

#### Henry's Law Constant:

Henry's Law Constant indicates the relative tendency of a constituent to volatilize from aqueous solution to the atmosphere based on the competition between its vapor pressure and water volubility. Contaminants with low Henry's Law Constant values (e.g., methanol, 1.10 x 10<sup>6</sup> atm-m<sup>3</sup>/mole at 77°F) will tend to favor the aqueous phase

FIGURE 13-1 QUALITATIVE RELATIONSHIP BETWEEN VARIOUS PARTITIONING PARAMETERS



BCF: **B**ioconcentration factor

Koc: Soil/sediment adsorption coefficient and volatilize to the atmosphere more slowly than constituents with high values (e.g., carbon tetrachloride,  $2.3 \times 10^{-2}$  atm-m³/mole at 770 F). This parameter is important in determining the potential for inter-media transport to the air media.

## Octanol/Water Partition Coefficient (K<sub>ow</sub>):

The octanol/water partition coefficient  $(K_{ow})$  is defined as the ratio of an organic constituent's concentration in the octanol phase (organic) to its concentration in the aqueous phase in a two-phase octanol/water system. Values of  $K_{ow}$  carry no units.  $K_{ow}$  can be used to predict the magnitude of an organic constituent's tendency to partition between the aqueous and organic phases of a two phase system such as surface water and aquatic organisms. The higher the value of  $K_{ow}$ , the greater the tendency of an organic constituent to adsorb to soil or waste matrices containing appreciable organic carbon or to accumulate in biota. Generally, constituents with  $K_{ow}$  values greater than or equal to 2.3 are considered potentially bioaccumulative (Veith, et al., 1980).

## Soil-Water Partition Coefficient (K<sub>d</sub>):

The mobility of contaminants in soil depends not only on properties related to the physical structure of the soil, but also on the extent to which the soil material will retain, or adsorb, the hazardous constituents. The extent to which a constituent is adsorbed depends on chemical properties of the constituent and of the soil. Therefore, the sorptive capacity must be determined with reference to a particular constituent and soil pair. The soil-water partition coefficient ( $K_d$ ) is generally used to quantify soil sorption.  $K_d$  is the ratio of the adsorbed contaminant concentration to the dissolved concentration, at equilibrium.

#### Bioconcentration Factor (BCF):

The bioconcentration factor is the ratio of the concentration of the constituent in an organism or whole body (e.g., a fish) or specific tissue (e.g., fat) to the concentration in water. Ranges of BCFs for various constituents and organisms are reported in the literature (Callahan, et al., 1979) and these values can be used to predict the potential for

bioaccumulation, and therefore to determine whether sampling of the biota may be necessary. Another source of BCFs for constituents is contained in EPA's Ambient Water Quality Criteria (for priority pollutants). BCFs can also be predicted by structure-activity relationships. Constituents exhibiting a BCF greater than 1.0 are potentially bioaccumulative. Generally, constituents exhibiting a BCF greater than 100 cause the greatest concern.

## • The Organic Carbon Adsorption Coefficient (K<sub>sc</sub>):

The extent to which an organic constituent partitions between the solid and solution phases of a saturated or unsaturated soil, or between runoff water and sediment, is determined by the physical and chemical properties of both the constituent and the soil (or sediment). The tendency of a constituent to be adsorbed to soil is dependent on its properties and on the organic carbon content of the soil or sediment.  $K_{\rm oc}$  is the ratio of the amount of constituent adsorbed per unit weight of organic carbon in the soil or sediment to the concentration of the constituent in aqueous solution at equilibrium.  $K_{\rm oc}$  can be used to determine the partitioning of a constituent between the water column and the sediment. When constituents have a high  $K_{\rm oc}$ , they have a tendency to partition to the soil or sediment. In such cases, sediment sampling would be appropriate.

#### Other Equilibrium Constants:

Equilibrium constants are important predictors of a compound's chemical state in solution. In general, a constituent which is dissociated (ionized) in solution will be more soluble and therefore more likely to be released to the environment and more likely to migrate in a surface water body. Many inorganic constituents, such as heavy metals and mineral acids, can occur as different ionized species depending on pH. Organic acids, such as the phenolic compounds, exhibit similar behavior. R should also be noted that ionic metallic species present in the release may have a tendency to bind to particulate matter, if present in a surface water body, and settle out to the sediment over time and distance. Metallic species also generally exhibit bioaccumulative properties. When metallic

species are present in a release, both sediment and biota sampling would be appropriate.

#### Biodegradation:

Biodegradation results from the enzyme-catalyzed transformation of organic constituents, primarily from microorganisms. The ultimate fate of a constituent introduced into a surface water or other environmental system (e.g., soil), could be a constituent or compound other than the species originally released. Biodegradation potential should therefore be considered in designing monitoring programs. Section 9.3 (Soils) presents additional information on biodegradation.

#### Photolysis:

Photodegradation or photolysis of constituents dissolved in aquatic systems can also occur. Similar to biodegradation, photolysis may cause the ultimate fate of a constituent introduced into a surface water or other environmental system (e. g., soil) to be different from the constituent originally released. Hence, photodegradation potential should also be considered in designing sampling and analysis programs.

#### • Chemical Degradation (Hydrolysis and Oxidation/Reduction):

Similar to photodegradation and biodegradation, chemical degradation, primarily through hydrolysis and oxidation/reduction (REDOX) reactions, can also act to change constituent species once they are introduced to the environment. Hydrolysis of organic compounds usually results in the introduction of a hydroxyl group (-OH) into a chemical structure. Hydrated metal ions, particularly those with a valence of 3 or more, tend to form ions in aqueous solution, thereby enhancing species solubility. Mabey and Mill (1978) provide a critical review of the hydrolysis of organic compounds in water under environmental conditions. Stumm and Morgan (1982) discuss the hydrolysis of metals in aqueous systems. Oxidation may occur as a result of oxidants being formed during photochemical processes in natural waters. Similarly, in some surface water environments (primarily those with low oxygen levels) reduction of constituents may take place.

Degradation, whether biological, physical or chemical, is often reported in the literature as a half-life, which is usually measured in days. It is usually expressed as the time it takes for one half of a given quantity of a compound to be degraded. Long half-lives (e.g., greater than a month or a year) are characteristic of persistent constituents. It should be noted that actual half-life can vary significantly over reported values based on site-specific conditions. For example, the absence of certain microorganisms at a site, or the number of microorganisms, can influence the rate of biodegradation, and therefore, half-life. Other conditions (e. g., temperature) may also affect degradation and change the half-life. As such, half-life values should be used only as general indications of a chemical's persistence.

In addition to the above, reactions between constituents present in a release may also occur. The owner or operator should be aware of potential transformation processes, based on the constituents' physical, chemical and biological properties, and account for such transformations in the design of monitoring procedures and in the selection of analytical methods.

Table 13-4 provides an application of the concepts discussed above in assessing the behavior of waste material with respect to release, migration, and fate. The table gives general qualitative descriptors of the significance of some of the more important properties and environmental processes for the major classes of organic compounds likely to be encountered.

Table 13-4 can be used to illustrate several important relationships.

- Generally, water volubility varies inversely with sorption, bioconcentration, and to a lesser extent, volatilization.
- Oxidation is a significant fate process for some classes of constituents which can volatilize from the aqueous phase.
- Variations in properties and environmental processes occur within classes as indicated by the pesticides, monocyclic aromatics, polycyclic aromatics, and the nitrosamines and other nitrogen-containing compounds.

TABLE 13-4

GENERAL SIGNIFICANCE OF PROPERTIES AND ENVIRONMENTAL PROCESSES FOR CLASSES OF ORGANIC CHEMICALS UNDER ENVIRONMENTAL CONDITIONS

Chemical Class	Solubility	Sorption	Bioconcentration	Volatilization	Photolysis	Oxidation	Hydrolyses
Pesticides							
Organochlorines Organophosphates Carbamates	Low Moderate Moderate	High Moderate Moderate	High Low Moderate	High Low Low	Moderate High Moderate	Low High Moderate	Low Moderate-High Moderate
Polychlorinated Biphenyls	Low	High	High	Moderate	Low	Low	Low
Halogenated Aliphatics	Moderate	Low	Low	High	Low	High*	Low
Halogenated Ethers	High	Low	Low	Low	Low	High*	High
Monocyclic Aromatics							
Toluene Phenol	Moderate High	Moderate Low	Low Low	High Low-Moderate	Low Moderate	High* Moderate	Low Low
Phthalate Esters	Low	High	High	Low	Low	Low	Low
Polycyclic Aromatics							
Naphthalene Benzo(K)Fluoranthene	Moderate Low	High High	Low Low	Moderate Low	High** High**	Low Low	Low Low
Nitrosamines and other Nitrogen - Containing Compounds							
Benzedine Di-n-propylnitrosamine	Moderate-High High	High Low	Low Low	Low Low	High High	High Low	Low Low

<sup>\*</sup> Atmospheric oxidation (volatile organic chemicals).

Table entries are qualitative only and based on a typical chemical within the class. Variations are observed within each class.

Dissolved portion only.

Characterizing the environmental processes and properties of inorganic waste constituents takes a similar approach to that shown on Table 13-4 for organics. However, characterizing the metals on a class-by-class basis is not advisable because of the complex nature of each metal and the many species in which the metals generally occur. The interaction of each metal species with the surface water environment is generally a function of many parameters including pH, REDOX potential, and ionic strength. See Stumm and Morgan (1982) for additional discussions on this subject. Generally, however, when metal species are present in a release, it is advisable to monitor the sediment and biota, in addition to the water column. This is due to likely deposition of metals as particulate matter, and to potential bioaccumulation.

#### 13.3.2 Unit Characterization

The relationship between unit characteristics and migration pathways provides the framework in this section for a general discussion of release mechanisms from units of concern to surface waters.

## 13.3.2.1 Unit Characteristics

Information on design and operating characteristics of a unit can be helpful in characterizing a release. Unsound unit design and operating practices can allow waste to migrate from a unit and possibly mix with runoff. Examples include surface impoundments with insufficient freeboard, allowing for periodic overtopping; leaking tanks or containers; or land-based units above shallow, low-permeability materials which, if not properly designed and operated, can fill with water and spill over. In addition, precipitation failing on exposed wastes can dissolve and thereby mobilize hazardous constituents. For example, at uncapped active or inactive waste piles and landfills, precipitation and leachate are likely to mix at the toe of the active face or the low point of the trench floor. Runoff may then flow into surface water through drainage pathways.

## 13.3.2.2 Frequency of Release

Releases to surface waters may be intermittent, continuous, or a past occurrence. It is important to consider the anticipated frequency of a release to establish an effective monitoring program.

Most direct releases to surface waters are intermittent. Intermittent discharges may be periodic, but may occur more often in a non-periodic manner, for example, in response to rainfall runoff. Other common factors affecting intermittent releases include fluctuations in water levels and flow rates, seasonal conditions (e.g., snow melt), factors affecting mass stability (e. g., waste pile mass migration), basin configuration, quantity/quality of vegetation, engineering control practices, integrity of the unit, and process activities.

Erosion of contaminated materials from a unit (e.g., a landfill) is generally intermittent, and is generally associated with rainfall-runoff events. Similarly, breaches in a dike are generally short-term occurrences when they are quickly corrected following discovery. Leaks, while still predominantly intermittent in nature, may occur over longer spans of time and are dependent on the rate of release and the quantity of material available.

Direct placement of wastes within surface waters (e.g., due to movement of an unstable waste pile) has the potential to continuously contribute waste constituents until the wastes have been removed or the waste constituents exhausted. Direct placement is usually easily documented by physical presence of wastes within the surface water body.

The frequency of sample collection should be considered in the design of the monitoring program. For example, intermittent releases not associated with precipitation runoff may require more frequent or even continuous sample collection to obtain representative data on the receiving water body. Continuous monitoring is generally feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available. Intermittent releases that are associated with precipitation runoff may require event sample collection. With event sampling, water level or flow-activated automatic sampling/recording equipment can be used. For continuous releases, less

frequent sample collection is generally adequate to obtain representative data on the receiving water body.

Previous intermittent releases may be identified through the analysis of bottom sediments, and whole body or tissue analyses of relatively sessile and long-lived macroinvertebrates (e.g., clams), or other species, such as fish. These analyses may identify constituents that may have adsorbed onto particulate and settled to the sediment, as well as bioaccumulative contaminants. In addition, intermittent releases may be detected through the use of in situ bioassays. Using these procedures, the test specie(s) is held within the effluent or stream flow and periodically checked for survival and condition.

#### 13.3.2.3 Form of Release

Releases to surface waters may be generally categorized as point sources or non-point sources. Point sources are those that enter the receiving water at a definable location, such as piped discharges. Non-point source discharges are ail other discharges, and generally cover large areas.

In general, most unit releases to surface waters are likely to be of a point source nature. Most spills, leaks, seeps, overtopping episodes, and breaches occur within an area which can be easily defined. Even erosion of contaminated soil and subsequent deposition to surface water can usually be identified in terms of point of introduction to the surface water body, through the use of information on drainage patterns, for example. However, the potential for both point and non-point sources should be recognized, as monitoring programs designed to characterize these types of releases can be different. For example, the generally larger and sometimes unknown areal extent of non-point source discharges may require an increase in the number of monitoring locations from that routinely required for point source discharges. The number of monitoring locations must be carefully chosen to ensure representative monitoring results.

#### 13.3.3 Characterization of the Environmental Setting

The environmental setting includes the surface water bodies and the physical and biological environment. This section provides a general classification scheme for surface waters and discusses collection of hydrologic data that may be important in their characterization. Collection of specific geographical and climatological

data are also discussed. Characterization of the biotic environment is treated in Section 13.4.

Note that individual states have developed water quality standards for surface waters pursuant to the Clean Water Act. These standards identify the designated uses (e. g., drinking, recreation, etc.) of a surface water and a maximum contaminant level to support the use. If applicable, the owner or operator should report such standards.

#### 13.3.3.1 Characterization of Surface Waters

Surface waters can be classified into one of the following categories. These are obviously not pure classifications; intergrades are common.

- Streams and rivers;
- Lakes and impoundments;
- Wetlands; and
- Marine environments.

#### 13.3.3.1.1 Streams and Rivers

Streams and rivers are conduits of surface water flow having defined beds and banks. The physical characteristics of streams and rivers greatly influence their reaction to contaminant releases and natural purification (i. e., assimilative capacity). An understanding of the nature of these influences is important to effective planning and execution of a monitoring program. Important characteristics include depth, velocity, turbulence, slope, changes in direction and in cross sections, and the nature of the bottom.

The effects of some of these factors are so interrelated that it is difficult to assign greater or lesser importance to them. For example, slope and roughness of the channel influence depth and velocity of flow, which together control turbulence. Turbulence, in turn, affects rates of contaminant dispersion,

reaeration, sedimentation, and rates of natural purification. The nature of contaminant dispersion is especially critical in the location of monitoring stations. All these factors may be of greater or lesser importance for specific sites. It should also be noted that these factors may differ at the same site depending on when the release occurred. For example, differences between winter and summer flow may greatly influence the nature of contaminant dispersion.

Of further relevance to a surface water investigation are the distinctions between ephemeral, intermittent, and perennial streams, defined as follows:

- Ephemeral streams are those that flow only in response to precipitation in the immediate watershed or in response to snow melt. The channel bottom of an ephemeral stream is always above the local water table.
- Intermittent streams are those that usually drain watersheds of at least one square mile and/or receive some of their flow from baseflow recharge from ground water during at least part of the year, but do not flow continually.
- Perennial streams flow throughout the year in response to ground water discharge and/or surface water runoff.

The distinction between ephemeral, intermittent and perennial streams will also influence the selection of monitoring frequency, monitoring locations and possibly other monitoring program design factors. For example, the frequency of monitoring for ephemeral streams, and to a lesser extent intermittent streams, will depend on rainfall runoff. For perennial-stream monitoring, the role of rainfall runoff in monitoring frequency may be of less importance under similar release situations.

The location of ephemeral and intermittent streams may not be apparent to the owner or operator during periods of little or no precipitation. Generally, intermittent and ephemeral streams may be associated with topographic depressions in which surface water runoff is conveyed to receiving waters. In addition to topography, a high density of vegetation in such areas may be an indicator of the presence of ephemeral or intermittent drainage.

Perennial streams and rivers are continually engaged in a dynamic relationship with ground water, either receiving ground-water discharge (gaining stream) or recharging the ground water (losing stream) over any given stream reach. These characteristics should be considered in the evaluation of contaminant transport and fate.

The Ecology of Running Waters (Hynes 1970) and Introduction to Hydrology (Viessman et al., 1977) may be reviewed for basic discussions of surface water hydrology.

## 13.3.3.1.2 Lakes and Impoundments

Lakes are typically considered natural, while impoundments may be manmade. The source for lakes and impoundments may be either surface water or ground water, or both. Impoundments may be either incised into the ground surface or may be created via the placement of a dam or embankment. As with streams and rivers, the physical characteristics of lakes and impoundments influence the transport and fate of contaminant releases and therefore the design of the monitoring program. The physical characteristics that should be evaluated include dimensions (e.g., length, width, shoreline, and depth), temperature distribution, and flow pathways.

Especially in the case of larger lakes and impoundments, flow paths are not clearcut from inlet to outlet. Not only is the horizontal component of flow in question, but as depth of the water body increases in the open water zone, chemical and more commonly physical (i. e., temperature) phenomena create a vertical stratification or zonation. Figure 13-2 provides a typical lake cross section, showing the various zones of a stratified lake.

Because of stratification, deeper water bodies can be considered to be comprised of three lakes. The upper lake, or epilimnion, is characterized by good light penetration, higher levels of dissolved oxygen, greater overall mixing due to wave action, and elevated biological activity. The lower lake, or hypolimnion, is the opposite of the epilimnion. Lying between these is what has been termed the

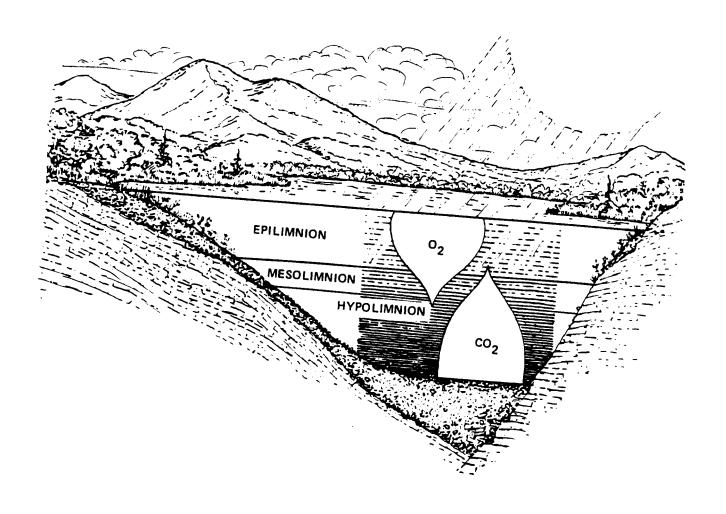


FIGURE 13-2. TYPICAL LAKE CROSS SECTION

(Source: Adapted from Cole, 1975).

middle lake or mesolimnion, characterized by a rapid decrease in temperature with depth. Were it not for the phenomenon of lake over-turn, or mixing, contaminants with specific gravities greater than water might be confined to the lowermost lake strata, where they might remain for some time. Due to the potential importance of lake mixing to contaminant transport, it is discussed below.

Temperatures within the epilimnion are relatively uniform because of the mixing that occurs there. Water is most dense at 4° Centigrade (C); above and below 4°C its density decreases. In temperate climates, lake mixing is a seasonal occurrence. As the surface of the epilimnion cools rapidly in the fall, it becomes denser than the underlying strata. At some point, the underlying strata can no longer support the denser water and an "overturn" occurs, resulting in lake mixing. A similar phenomenon occurs in the spring as the surface waters warm to 4°C and once again become denser than the underlying waters.

Because of the influence of stratification on the transport of contaminants within a lake or reservoir, the location of monitoring points will largely depend on temperature stratification. The monitoring points on water bodies that are not stratified will be more strongly influenced by horizontal flowpaths, shoreline configuration and other factors. The presence of temperature stratification can be determined by establishing temperature-depth profiles of the water body.

More information on lakes and impoundments may be found in the following references:

A Treatise on Limnology, Volumes I and II (Hutchinson, 1957, 1967) or

Textbook of Limnology (Cole, 1975)

#### 13.3.3.1.3 Wetlands

Wetlands are those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands include, but are not limited to, swamps, marshes, bogs, and similar areas.

Wetlands are generally recognized as one of the most productive and sensitive of biological habitats, often associated with critical. habitat for State or Federally listed special-status species of plants or wildlife. Wetlands also may play a significant role in basin hydrology, moderating peak surface water flows and providing recharge to the ground water system. The definition of the extent and sensitivity of wetlands that may be affected by a release is essential to release characterization.

High organic content, fine-grained sediments, slow surface water movement and lush vegetative growth and biological activity contribute to a high potential for wetlands to concentrate contaminants from releases. This is especially true for bioaccumulative contaminants, such as heavy metals. The pH/Eh conditions encountered in many wetlands are relatively unique and can have a significant effect on a contaminant's toxicity, fate, etc. Seasonal die-off of the vegetation and flooding conditions within the basin may result in the wetlands serving as a significant secondary source of contaminants to downstream surface water receptors.

#### 13.3.3.1.4 Marine Environments

For the purpose of this guidance, marine environments are restricted to estuaries, intermediate between freshwater and saline, and ocean environments. Industrial development near the mouths of rivers and near bays outletting directly into the ocean is relatively widespread, and the estuarine environment may be a common receptor of releases from industrial facilities.

Estuaries are influenced by both fresh water and the open ocean. They have been functionally defined as tidal habitats that are partially enclosed by land but have some access to the open sea, if only sporadically, and in which ocean water is partially diluted by fresh water. Estuaries may also experience conditions where salinities are temporarily driven above the ocean levels due to evaporative losses. Because of the protection afforded by encircling land areas, estuaries are termed "low-energy" environments, indicating that wave energy and associated erosive and mixing processes are reduced.

The physical characteristics of an estuary that will influence the design of a monitoring program are similar to those considered for lakes and impoundments (i.e., length, width, shoreline, depth, and flow pathways). However, the increased probability for chemical stratification due to varying salinities may be most pronounced in areas where freshwater streams and rivers discharge into the estuary. The monitoring program design should also consider tidal influences on stratification and contaminant dispersion.

In addition, estuaries, or some portions of estuaries, can be areas of intergrained sediment deposition. These sediments may contain a significant organic fraction, which enhances the opportunity for metal/organic adsorption, and subsequent bioaccumulation. Hence, biomonitoring within an estuary may also be appropriate. The ionic strength of contaminants may also have an important effect on their toxicity, fate, etc., in the marine environment.

## 13.3.3.2 Climatic and Geographic Conditions

A release to the surface water system will be influenced by local climatological/meteorological and geographic conditions. The release may be associated only with specific seasonal conditions like spring thaws or meteorological events such as storms. If the release is intermittent, the environmental conditions at the time of the release may help identify the cause of and evaluate the extent of the release. If the release is continuous, seasonal variations should also be evaluated.

The local climatic conditions should be reviewed to determine:

- The annual precipitation distribution (monthly averages);
- Monthly temperature variations;
- Diurnal temperature range (daytime/nighttime difference);
- Storm frequency and severity;
- Wind direction and speed; and

Snowfall and snowpack ranges (if applicable),

This information will be useful in developing a sampling schedule and in selecting sampling methods. From these data, it should be possible to anticipate the range of climatic conditions at the site. These conditions may be far more complex than simple cold/hot or wet/dry seasons. Some areas have two or more "wet seasons", one characterized by prolonged showers, another by brief intense storms, and perhaps a third as a result of snowmelt. Cold/hot seasons may overlap these wet/dry seasons to create several climatologically identifiable seasons. Each season may affect the release differently and may require a separate characterization. The unique climatological seasons that influence the site should be identified. Typical winter, spring, summer and fall seasonal descriptions may not be appropriate or representative of the factors influencing the release. Sources of climatological data are given in Section 12 (Air).

In addition to the climatological/meteorological factors, local geographic conditions will influence the design of the sampling program. Topographic conditions and soil structure may make some areas prone to flash floods and stream velocities that are potentially damaging to sampling equipment. In other areas (e.g., the coastal dune areas of the southeastern states), virtually no runoff occurs. Soil porosity and vegetation are such that all precipitation either enters the ground water or is lost to evapotranspiration. (See Section 9 (Soil) for more information).

A description of the geographic setting will aid in developing a sampling program that is responsive to the particular conditions at the facility. When combined with a detailed understanding of the climatological/meteorological conditions in the area, a workable monitoring framework can be created.

## 13.3.4 Sources of Existing Information

Considerable information may already be available to assist in characterizing a release. Existing information should be reviewed to avoid duplication of previous efforts and to aid in focusing the RFI. Any information relating to releases from the unit, and to hydrogeological, meteorological, and environmental factors that could influence the persistence, transport or location of contaminants should be reviewed. This information may aid in:

- Delineating the boundaries of the sampling area;
- Choosing sampling and analytical techniques; and
- Identifying information needs for later phases of the investigation.

Information may be obtained from readily available sources of geological and meteorological data, waste characteristics, and facility operations records. (See also Sections 2,3,7 and Appendix A).

## 13.4 Design of a Monitoring Program to Characterize Releases

Following characterization of the contaminant source and environmental setting, a monitoring program is developed. This section outlines and describes factors that should be considered in design of an effective surface water monitoring program. The characterization of contaminant releases may take place in multiple phases. While the factors discussed in this section should be carefully considered in program design, each of these generic approaches may require modification for specific situations.

The primary considerations in designing a surface water monitoring program are:

- Establishing the objectives of the monitoring program;
- Determining the constituents of concern;
- Establishing the hydrologic characteristics of the receiving water and characteristics of the sediment and biota, if appropriate;
- Selecting constituents and/or indicators for monitoring;
- Selecting monitoring locations and monitoring frequency; and

• Determining the need for sediment monitoring and, hydrologic and biomonitoring.

## 13.4.1 Objectives of the Monitoring Program

The principal objectives of a monitoring program are to:

- Identify the characteristics of releases (e.g., continuous vs intermittent);
- Identify the fate of constituents;
- Identify the nature, rate, and extent of the release and actual or potential effects on water quality and biota; and
- Identify the effect of temporal variation on constituent fate and identify impacts on water quality and biota.

Periodic monitoring of the surface water system is often the only effective means of identifying the occurrence of releases and their specific effects. Releases can be continuous or intermittent, point source, or non-point source. The concept of monitoring is the same, regardless of the frequency or-form of the release. A series of measurements, taken over time, better approximate the actual release to surface waters than a one-time grab sample.

The functional difference between monitoring the various types of discharges is the point of measurement. Point source discharges may be monitored at and/or near the discharge point to surface waters. The fate and potential effects of non-point source discharges should be inferred through measurement of the presence of constituents of concern or suitable indicators of water quality within the receiving water body.

The monitoring program should also establish the background condition against which to measure variations in a continuous release or the occurrence of an intermittent release. Such information will enable the facility owner or operator to compile data that will establish trends in releases from a given unit(s) as well as to identify releases from other sources.

Monitoring programs should characterize contaminant releases as a function of time. Climatologic factors such as frequency of intense rainfall, added effects of snowmelt, temperature extremes, and mixing in lakes and estuaries should be evaluated and quantified as causative agents for intermittent contaminant release.

Important concepts to consider in designing the monitoring program for surface water to help meet the above-stated objectives are described below.

#### 13.4.1.1 Phased Characterization

The initial phase of a surface water release characterization program may be directed toward verification of the occurrence of a release identified as suspected by the regulatory agency. It may also serve as the first step for characterizing surface water systems and releases to those systems in cases where a release has already been verified.

The initial characterization will typically be a short-duration activity, done in concert with evaluation of other media that may either transport contaminants to surface waters, or may themselves be affected by discharges from surface waters (i.e., inter-media transport). It may be particularly difficult to define intermittent discharges in the initial characterization effort, especially if the contaminants from these releases are transient in the surface water body.

If the waste characterization is adequate, the initial characterization phase may rely upon monitoring constituents and suitable indicator parameters to aid in defining the nature, rate, and extent of a release. Subsequent phases of release characterization will normally take the form of an expanded environmental monitoring program and hydrologic evaluation, sensitive to seasonal variations in contaminant release and loading to the receiving water bodies, as well as to natural variation in hydrologic characteristics (e.g., flow velocity and volume, stream cross section).

# 13.4.1.2 Development of Conceptual Model

To effectively design a monitoring program, it is important to develop a conceptual model or understanding of the fate of constituents of the release in the receiving water body. This conceptual understanding will assist in answering the following questions.

- What portion of the receiving water body will be affected by the release and what conditions (e. g., low flow, immediate stormwater runoff) represent reasonable worst case conditions under which sampling should occur?
- What should the relative concentrations of contaminants be at specific receptor points within the water body (e.g., public water supply intakes downstream of a site)?
- How does the release of concern relate to background contamination in the receiving water body as a result of other discharges?
- How might the monitoring program be optimized, based on contaminant dispersion and relative concentrations within the receiving water body?

The fate of waste constituents entering surface waters is highly dependent on the hydrologic characteristics of the various classifications of water bodies, (i.e., streams and rivers, lakes and impoundments, wetlands, and estuaries, as discussed earlier). Because of their complexity, methods for characterization of contaminant fate in wetlands and estuaries is not presented in detail in this guidance. The reader is referred to Mills (1985) for further detail on characterizing contaminant fate in wetlands and estuaries.

### 13.4.1.3 Contaminant Concentration vs Contaminant Loading

Concentration and loading are different means of expressing contaminant levels in a release or receiving water body. The concept is important in the selection of constituents for monitoring. Both concentration and loading should be

evaluated with respect to the release and the receiving waters. Basing an evaluation solely on concentration may obscure the actual events. In addition, it is essential to quantify individual sources of contaminants and the relationships between media, as well as the loading found in the receiving water body, to effectively define the nature and extent of the contaminant release.

Contaminant concentrations in receiving waters have specific value in interpreting the level of health or environmental effects anticipated from the release. Contaminant loading provides a common denominator for comparison of contaminant inputs between monitoring points. In addition, especially in the case of contaminants that are persistent in sediments (e. g., heavy metals), loadings are a convenient means of expressing ongoing contributions from a specific discharge. The distinction between concentration and loading is best drawn through the following example.

A sample collected from a stream just upgradient of a site boundary (Station A) has a concentration of 50 micrograms per liter ( $\mu$ g/I) of chromium. A second sample collected just downstream of the site (Station B) has a chromium concentration of 45  $\mu$ g/1. From these data it appears that the site is not releasing additional chromium to the stream. If, however, the stream flow is increasing between these two sampling locations, a different interpretation is apparent. If the stream flow at the upstream location is 1,000 gallons per minute (gpm) and the downstream location is 1,300 gpm, the actual loading of chromium to the stream at the two locations is as follows:

#### Station A

Chromium =  $(50.0 \mu g/l)(1,000 \text{ gal/min})(10^{-9} \text{kg/}\mu\text{g})(60 \text{ min/hr})(3.785 l/gal = 0.0114 kg/hr$ 

#### Station B

Chromium =  $(45.0 \mu g/1)(1,300 \text{ gal/min})(10^{-9} \text{kg/}\mu\text{g})(60 \text{ min/hr})(3.785 \text{ l/gal}) = 0.0133 \text{kg/hr}$ 

It is now apparent that somewhere between the two sampling stations is a source(s) contributing 0.0019 kg/hr of chromium. If all of the flow difference (i.e.,

300 gpm) is from a single source, then this source would have a chromium concentration of 27.9  $\mu g/l$ :

Chromium =  $[(0.0019 \text{ kg/hr})(10^{\circ} \mu\text{g/kg})(1\text{hr/60min})(1 \text{ min/300 gal})(1 \text{ gal/3.785 l})] = 27.9 \mu\text{g/l}$ 

If, however, 90 percent of this flow difference (i.e., 270 gpm) was due to ground-water discharge with a chromium concentration below detectable limits and the remaining 10 percent (i.e., 30 gpm) was the result of a direct discharge from the facility, this discharge could have a chromium concentration of 279  $\mu$ g/1.

# 13.4.1.4 Contaminant Dispersion Concepts

Contaminant dispersion concepts and models of constituent fate can be used to define constituents to be monitored and the location and frequency of monitoring. Dispersion may occur in streams, stratified lakes or reservoirs, and in estuaries. Dispersion may be continuous, seasonal, daily, or a combination of these.

The discussion below is based on information contained in the <u>Draft Superfund Exposure Assessment Manual</u> (EPA, 1987) relative to simplified models useful in surface water fate analyses. The reader is directed to that document for a more in-depth discussion of models. The equations presented below are based on the mixing zone concept originally developed for EPA's National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act. To avoid confusion over regulatory application of these concepts in the NPDES program, and the approach presented below (basically to aid in the development of a monitoring program), the following discussion refers to use of the "Dispersion Zone".

The following equation provides an approximate estimate of the concentration of a substance downstream from a point source release, after dilution in the water body:

$$C_{,} = \frac{C_{,}Q_{,} + C_{,}Q_{,}}{Q_{,} + Q_{,}}$$

where:

C<sub>r</sub> = downstream concentration of substance following complete dispersion (mass/volume)

C<sub>u</sub> = upstream concentration of substance before effluent release point (mass/volume)

C<sub>w</sub> = concentration of substance in effluent (mass/volume)

Q<sub>w</sub> = effluent flow rate (volume/time)

Q<sub>11</sub> = upstream flow rate before effluent release point (volume/time)

The following equation may be used to estimate instream concentrations after dilution in situations where waste constituents are introduced via inter-media transfer or from a non-point source, or where the release rate is known in terms of mass per unit time, rather than per unit effluent volume:

$$C = \frac{T_r + M_u}{Q_t}$$

where:

 $T_r$  = inter-media transfer rate (mass/time)

M<sub>u</sub> = upstream mass discharge rate (mass/time)

Q<sub>t</sub> = stream flow rate after inter-media transfer or non-point source release (volume/time)

The above two equations assume the following:

- Dispersion is instantaneous and complete;
- The waste constituent is conserved (i.e., all decay or removal processes are disregarded); and
- Stream flow and rate of contaminant release to the stream are constant (i.e., steady-state conditions).

For a certain area downstream of the point of release, the assumption of complete dispersion-may not be valid. Under certain situations, the dispersion zone can extend downstream for a considerable distance, and concentrations can be considerably higher within the dispersion zone than those estimated by the equation. The length of this zone can be approximated by the following equation:

$$DZ = \frac{0.4 \text{ w}^2\text{u}}{0.6 \text{ d}\sqrt{\text{gds}}}$$

where:

DZ = dispersion zone length (length units)

w = width of the water body (length units)

u = stream velocity (length/time)

d = stream depth (length units)

s = slope (gradient) of the stream channel (length/length)

g = acceleration due to gravity (32 ft/sec<sup>2</sup>)

Within the dispersion zone, contaminant concentrations will show spatial variation. Near the release point the contaminant will be restricted (for a discharge along one shoreline) to the nearshore area and (depending on the way the discharge is introduced and its density) can be vertically confined. As the water moves downstream, the contaminant will disperse within surrounding ambient water and the plume will widen and deepen. Concentrations will generally decrease along the plume centerline and the concentration gradients away from the centerline will decrease. Eventually, as described above, the contaminant will become fully dispersed within the stream; downstream from this point concentration will be constant throughout the stream cross-section, assuming that the stream flow rate remains constant.

It is important to understand this concentration variability within the dispersion zone if measurements are to be made near the release. Relatively straightforward analytical expressions (See Neely, 1982) are available to calculate the spatial variation of concentration as a function of such parameters as stream width, depth, velocity, and dispersion coefficients. Dispersion coefficients characterize the dispersion between the stream water and contaminated influx;

they can, in turn, be estimated from stream characteristics such as depth, gradient, and path (i.e., straight or bends).

The above considerations are for instream concentrations resulting from the releases of concern. If total instream concentrations are required, the concentrations determined from background water samples should also be considered. In addition, if introduction of the contaminant occurs over a fixed stream reach, as might be the case with a non-point discharge, it should be assumed that the dispersion zone begins at the furthest downstream point within this reach.

# 13.4.1.5 Conservative vs Non-Conservative Species

The expressions presented thus far have assumed that the contaminant(s) of concern is conservative (i.e., that the mass loading of the contaminant is affected only by the mechanical process of dilution). For contaminants that are non-conservative, the above equations would provide a conservative estimate of contaminant loading at the point of interest within the receiving water body.

In cases where the concentration after dilution of a non-conservative substance is still expected to be above a level of concern, it may be useful to estimate the distance downstream where the concentration will remain above this level and at selected points in between. The reader is referred to the <u>Draft Superfund Exposure Assessment Manual</u> (EPA, 1987), for details regarding this estimation procedure and to specific State Water Quality Standards for determination of acceptable instream concentrations.

### 13.4.2 Monitoring Constituents and Indicator Parameters

#### 13.4.2.1 Hazardous Constituents

The facility owner or operator should propose a list of constituents and indicator parameters, if appropriate, to be included in the Surface Water investigation. This list should be based on a site-specific understanding of the composition of the release source(s) and the operative release mechanisms, as well as the physical and chemical characteristics of the various classes of contaminants. These factors, as well as potential release mechanisms and migration pathways,

have been discussed in Sections 13.3 and 13.4.1. Also refer to Sections 3 and 7 of this guidance, and to the lists of constituents provided in Appendix B.

### 13.4.2.2 Indicator Parameters

Indicator parameters (e.g., chemical and biochemical oxygen demand, pH, total suspended solids, etc.) may also play a useful role in release characterization. Though indicators can provide useful data for release verification and characterization, specific hazardous constituent concentrations should always be monitored. Furthermore, many highly toxic constituents may not be detected by indicators because they do not represent a significant amount of the measurement.

Following are brief synopses of some common indicator parameters and field tests that can be used in investigations of surface water contamination. The use of biomonitoring as an indicator of contamination is discussed in Section 13.4.5.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)--BOD is an estimate of the amount of oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It may also measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Because the complete stabilization of a BOD sample may require an extended period, 5 days has been accepted as the standard incubation period. While BOD measures only biodegradable organics, non-biodegradable materials can exert a demand on the available oxygen in an aquatic environment. COD measures the total oxygen demand produced by biological and chemical oxidation of waste constituents. Availability of results for the COD in approximately 4 hours, versus 5 days for the BOD, may be an important advantage of its use in characterizing releases of a transient nature.

COD values are essentially equivalent to BOD when the oxidizable materials present consist exclusively of organic matter. COD values exceed BOD values when non-biodegradable materials that are susceptible to oxidation are present. The reverse is not often the case; however, refinery wastes provide a notable exception. There are some organic compounds, such as pulp and paper mill cellulose, that are non-biodegradable, yet oxidizable. Nitrogenous compounds, which may place a

significant drain on available oxygen in aquatic environments, are not measured **in** the COD test. In addition, chlorides interfere with the COD test, leading to overestimates of the actual COD. BOD/COD ratios, as an indicator of biodegradability, are discussed in Section 9 (Soil). BOO and COD may be useful indicator parameters if the release is due primarily to degradable organic wastes.

<u>Total Organic Carbon (TOC)</u>--Total organic carbon is valuable as a rapid estimator of organic contamination in a receiving water. TOC, however, is not specific to a given contaminant or even to specific classes of organics. In addition, TOC measurements have little use if the release is primarily due to inorganic wastes.

<u>Dissolved Oxygen (DO)</u> --Measurements of DO may be readily made in the field with an electronic DO meter, which has virtually replaced laboratory titrations. Especially in lake environments, it is valuable to know the DO profile with depth. The bottoms of lakes are often associated with anoxic conditions (absence of oxygen) because of the lack of mixing with the surface and reduced or non-existent photosynthesis. Influx of a contaminant load with a high oxygen demand can further exacerbate oxygen deficiencies under such conditions. In addition, low DO levels favor reduction, rather than oxidation reactions, thus altering products of chemical degradation of contaminants. DO levels less than 3 mg/liter (ppm) are considered stressful to most aquatic vertebrates (e.g., fish and amphibians).

pH--pH is probably one of the most common field measurements made of surface waters. It is defined as the inverse log of the hydrogen ion concentration of an aqueous medium. pH is generally measured in the field with analog or digital electronic pH meters.

As an indicator of water pollution, pH is important for two reasons:

- The range within which most aquatic life forms are tolerant is usually quite narrow. Thus, this factor has significant implications in terms of impact to aquatic communities; and
- The pH of a solution may be a determining factor in moderating other constituent reactions.

<u>Temperature-</u>-Along with pH, temperature is a fundamental parameter that should always be recorded in the field when a water sample is collected. Temperature is most often measured by electronic meters that can simultaneously record pH and/or specific conductance. Temperature is a significant parameter because:

- Most aquatic species are sensitive to elevated temperatures;
- Elevated temperatures can bean indication of a contaminant plume;
- Most chemical reactions are temperature-dependent; and
- Temperature defines strata in thermally-stratified lakes.

<u>Alkalinity--</u>Alkalinity is the capacity of water to resist a depression in pH. It is, therefore, a measure of the ability of the water to accept hydrogen ions without resulting in creation of an acid medium. Most natural waters have substantial buffering capacity (a resistance to any alteration in pH, toward either the alkaline or acid side) through dissolution of carbonate-bearing minerals, creating a carbonate/bicarbonate buffer system.

Alkalinity is usually expressed in calcium carbonate (CaCO<sub>3</sub>) equivalents and is the sum of alkalinities provided by the carbonate, bicarbonate, and hydroxide ions present in solution. Alkalinities in the natural environment usually range from 45 to 200 milligrams per liter (mg/l). Some limestone streams have extremely high buffering capacities, while other natural streams are very lightly buffered and are extremely sensitive to acid (or alkaline) loadings.

<u>Hardness</u>--The sum of carbonate and bicarbonate alkali nities is also termed carbonate hardness. Hardness is generally considered a measure of the total concentration of calcium and magnesium ions present in solution, expressed as CaCO<sub>2</sub> equivalents.

Calcium and magnesium ions play a role in plant and animal uptake of contaminants; knowledge of the hardness of a surface water is necessary for evaluation of the site-specific bioaccumulative potential of certain contaminants (e.g., heavy metals).

<u>Total Solids--</u>Analytically, the total solids (TS) content of a water is that remaining after evaporation at 103-115°C or 180°C, depending on the method. The residue remaining represents a sum of the suspended, colloidal, and dissolved solids. Hazardous constituents with high vapor pressures (i.e., volatiles, semi-volatiles) will not remain after evaporation, and will not contribute to the TS determination.

<u>Suspended Solids</u>--Suspended solids are those materials that will not pass a glass-fiber filter. Suspended solids contain both organic and inorganic compounds. For the purpose of comparison to water samples, the average domestic wastewater contains about 200 ppm (mg/l) of suspended solids.

<u>Volatile Suspended Solids</u>--Volatile suspended solids are the volatile organic portion of the suspended solids. Volatile suspended solids are the components of suspended solids that volatilize at a temperature of 600°C. The residue or ash is termed fixed suspended solids and is a measure of the inorganic fraction (i. e., mineral content). The only inorganic salt that will degrade below 600°C is magnesium carbonate.

<u>Total Dissolved Solids</u>--Total dissolved solids context is obtained by subtracting suspended solids from total solids. Its significance lies in the fact that it cannot be removed from a surface water or effluent stream through physical means or simple chemical processes, such as coagulation.

<u>Salinity</u> --The major salts contributing to salinity are sodium chloride (NaCl) and sulfates of magnesium and calcium (MgSO<sub>4</sub>, CaSO<sub>4</sub>). The following represents an example of classification of saline waters on the basis of salt content.

Type of Water	Total Dissolved Solids (As Salts)
brackish	1,000 to 35,000 mg/l
seawater	35,000 mg/l
brine	>35,000 mg/l

<u>Specific Conductance</u>--Conductivity measures the capacity to conduct current. Its counterpart is, of course, resistance, measured in ohms. The unit of conductivity has been defined as the mho. Specific conductance is conductivity/unit length. The most common units for specific conductance are mho/cm. Specific conductance can be

The nature and concentrations of naturally-occurring ions in surface waters are a function of the geologic setting of the area, and may be temporarily affected by stormwater runoff, which may cause resuspension of streambed sediments.

In reference to their inertness with respect to constituent and biological degradation, ionic species are termed "conservative." The fact that their mass is not altered (i.e., is conserved) in surface waters permits them to be used in simple dilution modeling.

# 13.4.3 Selection of Monitoring Locations

The selection of monitoring locations should be addressed. prior to sample acquisition because it may affect the selection of monitoring equipment and because monitoring locations will affect the representativeness of samples taken during the monitoring program. Samples must be taken at locations representative of the water body or positions in the water body with specific physical or chemical characteristics. As discussed in Section 13.4.1.2 (Development of Conceptual Model), one of the most important preliminary steps in defining monitoring locations in a surface water monitoring program is developing a conceptual model of the manner in which the release is distributed within the receiving water body. This is dependent on the physical and chemical characteristics of the receiving water, the point source or non-point source nature of the discharge, and the characteristics of the constituents themselves.

As a practical example, if a release contains contaminants whose specific gravities exceed that of water, it may behave almost as a separate phase within the receiving water body, traveling along the bottom of the water body. As another example, certain contaminants may be found in comparatively low concentrations in sediments or within the water column, yet may accumulate in aquatic biota via bioaccumulation. In this case monitoring of the biota would be advised. If the facility owner or operator is unaware of these phenomena, it would be possible for the monitoring program to show no evidence of contamination.

In general, it will be desirable to locate monitoring stations in three areas relative to the discharge in question:

Background monitoring stations:

Background monitoring should be performed in an area known not to be influenced by the release of concern (e. g., upstream of a release).

Monitoring stations at the release point(s) or area:

If the release is a point source or area source, periodic monitoring should be performed at monitoring stations near the discharge origin to determine the range of contaminant concentrations. The contaminant stream (e.g., leachate seep, runoff) should also be subjected to monitoring.

Monitoring of the receiving water body within the area of influence:

One means of evaluating the water quality effects of a discharge is to monitor the discharge point and model its dispersion (e.g., using dispersion zone concepts discussed previously) within the receiving water body. The results of this modeling may be used to determine appropriate sampling locations. Actual sampling of the area thought to be influenced by the release is required. The "area of influence" may be defined as that portion of the receiving water within which the discharge would show a measurable effect. As described previously, the area to be sampled is generally defined in a phased fashion, based on a growing base of monitoring data. It is usually prudent to start with a conservatively large area and continually refine its boundaries. This is particularly true where sensitive receptors (e. g., public water supply intakes, sensitive wetlands, recreation areas) lie downstream of the release. In addition, in order to determine the full extent of the release (and its effects), samples should be taken at locations beyond the perceived area of influence.

The majority of the effort of the monitoring program will take place within the area of influence, as defined above. Many factors are involved in selecting monitoring stations within this area, the most critical being:

- The homogeneity of the water body in terms of temperature, flow, salinity, and other physical and chemical characteristics;
- The representativeness of the monitoring point, in terms of both contaminant characteristics and use factors;
- The presence of areas of pronounced water quality degradation; and
- Defensible monitoring design, including the choice of the monitoring scheme (random, stratified random, systematic, etc.), the experimental design, and adequate sample size determination.

Estuarine areas are particularly difficult in terms of selecting monitoring locations that will allow an adequate evaluation of constituent distribution, because detailed knowledge of the hydrologic characteristics of the estuary is required to accurately locate representative monitoring points. Freshwater - salt water stratification is a particularly important consideration. If stratification is known to occur or is suspected, sampling should be conducted at a range of depths within the estuary as well as at surface locations.

The selection of sampling locations is described in much greater detail in EPA (1973, 1982).

# 13.4.4 Monitoring Schedule

The monitoring schedule or frequency should be a function of the type of release (i.e., intermittent vs continuous), variability in water quality of the receiving water body (possibly as a result of other sources), stream flow conditions, and other factors causing the release (e.g., meteorological or process design factors). Therefore, frequency of monitoring should be determined by the facility owner or operator on a site-specific basis. Sampling points with common monitoring

objectives should be sampled as close to simultaneously as possible, regardless of the monitoring frequency established.

Factors important in determining the required frequency of monitoring include:

- The homogeneity of the receiving water in terms of factors that may affect the fate of constituents. The most important of these are flow and seasonal or diurnal stratification.
- The characteristics of the releases. Releases may be continuous or event-associated.

As an example, continuous, point source releases of low variability subject to few, if any, additional releases may require relatively infrequent monitoring. On the other hand, releases known to be related to recurrent causes, such as rainfall and runoff, may require monitoring associated with the event. Such monitoring is termed "event" sampling. To evaluate the threshold event required to trigger sampling, as well as the required duration of the monitoring following the event, it is necessary that the role of the event in creating a release from the unit be well understood. In what is probably a very common example, if stormwater runoff is the event of concern, a hydrography for various storm return intervals and durations should be estimated for the point or area of interest and the magnitude and duration of its effects evaluated.

Continuous monitoring can be accomplished through <u>in situ</u> probes that provide frequent input to field data storage units. However, continuous monitoring is feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available.

In estuaries, samples are generally required through a tidal cycle. Two sets of samples are taken from an area on a given day, one at ebb or flood slack water and another at three hours earlier or later at half tide interval. Sampling is scheduled such that the mid-sampling time of each run coincides with the calculated occurrence of the tidal condition.

Where investigating discharges of contaminated ground water to streams or rivers, it is important to sample during low flow conditions (e. g., using State critical low flow designations) to better assess the possible effects of the release(s) of concern.

# 13.4.5 Hydrologic Monitoring

The monitoring program should also include provisions for hydrologic monitoring. Specifically, the program should provide for collection of data on the hydrologic condition of the surface water body at the time of sampling.

For example, some indication of the stage and discharge of a stream being monitored needs to be recorded at the time and location each water sample is collected. Similarly, for sampling that occurs during storms, a record of rainfall intensity over the duration of the storm needs to be obtained. Without this complementary hydrologic data, misinterpretation of the water quality data in terms of contaminant sources and the extent of contamination is possible.

The techniques for hydrologic monitoring that could be included in a monitoring program range in complexity from use of simple qualitative descriptions of streamflow to permanent installation of continuously-recording stream gages. The techniques appropriate in a given case will depend on the characteristics of the unit and of the surface waters being investigated. Guidance on hydrologic monitoring techniques can be found in the references cited in Section 13.6.1.

# 13.4.6 The Role of Biomonitoring

The effects of contaminants may be reflected in the population density, species composition and diversity, physiological condition, and metabolic rates of aquatic organisms and communities. Biomonitoring techniques can provide an effective complement to detailed chemical analyses for identifying chemical contamination of water bodies. They may be especially useful in those cases where releases involve constituents with a high propensity to bioaccumulate. This includes most metal species and organics with a high bioconcentration factor (e.g., > 10) or a high octanol/water partition coefficient (e.g., > 2.3). These properties were discussed in Section 13.3.

# Biomonitoring techniques may include:

- Community ecology studies;
- Evaluation of food chain/sensitive species impacts; and
- Bioassays.

These techniques are discussed below.

# 13.4.6.1 Community Ecology Studies

Indicator species are useful for evaluating the well-being of an aquatic community that may be stressed by the release of contaminants. For example, the condition of the benthic macroinvertebrate community is commonly used as an indicator of the presence of contaminants. The objective of studying the naturally-occurring biological community is to determine community structure that would be expected, in an undisturbed habitat. If significant changes occur, perturbations in the community ecology may be linked to the disturbance associated with release of contaminants to the water body.

EPA is engaged in research to develop rapid bioassessment techniques using benthic macroinvertebrates. Although protocols are being considered, in general these techniques suffer from lack of data on undisturbed aquatic communities and associated water quality information. For some areas (e.g., fisheries), however, indices to community health based on benthic invertebrate communities are available (Hilsenhoff 1982, Cummins and Wilgbach, 1985).

Because species diversity is a commonly-used indicator of the overall health of a community, depressed community diversity may be considered an indicator of contamination. For example, if a release to surface waters has a high chemical oxygen demand (COD) and, therefore, depresses oxygen levels in the receiving water body, the number of different species of organisms that can colonize the water body may be reduced. In this case the oxygen-sensitive species (e.g., the mayfly), is lost from the community and is replaced by more tolerant species. The number of tolerant species is small, but the number of individuals within these species that can colonize the oxygen-deficient waters may be quite large. Therefore,

the overall species diversity could be low, even though the numbers of organisms may be high.

Evaluations of community ecology should however, be sensitive to the role that habitat variability may play in altering community structure. Diversity of habitat may be altered by natural physical conditions (e.g., a rapid increase in stream gradient), substrate characteristics (e. g., silty versus rocky substrate), and so forth. It may also be difficult to directly link contaminant levels with the presence or absence of aquatic organisms, unless there is a secondary impact that is more self-evident, such as high oxygen demand, turbidity, or salinity.

### 13.4.6.2 Evaluation of Food Chain Sensitive/Species Impacts

At this level of biomonitoring, the emphasis is actually on the threat to specific fish or wildlife species, or man, as a result of bioaccumulation of constituents from the release being carried through the food web. Bioaccumulative contaminants are not rapidly eliminated by biological processes and accumulate in certain organs or body tissues. Their effect may not be felt by individual organisms that initially consume the contaminated substrate or take up the contaminants from the water. However, organisms at higher trophic levels consume the organisms of the lower trophic levels. Consequently, contaminants may become bioaccumulated in organisms and biomagnified through the food web.

Examination of the potential for bioaccumulation and biomagnification of contaminants requires at least a cursory characterization of the community to define its trophic structure, that is, which organisms occupy which relative positions within the community. Based on this definition, organisms representative of the various trophic levels may be collected, sacrificed, and analyzed to determine the levels of the contaminants of interest present.

If a specific trophic level is of concern, it may be possible to short-cut the process by selectively collecting and analyzing organisms from that level for the contaminants of concern. This may be the case, for instance, if certain organisms are taken by man either commercially or through recreational fishing, for consumption. It may also be necessary to focus on the prey of special-status fish or wildlife (e. g., eagles and other birds of prey) to establish their potential for

exposure. This type of biomonitoring may be especially useful if constituents released have a relatively high potential to bioaccumulate. A discussion of indicators that are generally predictive of constituents which have a significant potential for bioaccumulation was presented in Section 13.3.

In addition, in the selection of organisms it is important to consider the ability of a given organism to accumulate a class of contaminants and the residential vs migratory nature of the organisms. For example, bullfrogs are superior for accumulating metals but poor for organics; spawning (thus migratory) salmon would be much less useful for characterizing a release from a local facility than would resident fish.

# 13.4.6.3 Bioassay

Bioassay may be defined as the study of specially selected representative species to determine their response to the release of concern, or to specific constituents of the release. The organisms are "monitored" for a period of time established by the bioassay method. The objective of bioassay testing is to establish a concentration-response relationship between the contaminants of concern and representative biota that can be used to evaluate the effects of the release. Bioassay testing may involve the use of indigenous organisms (U.S. EPA, 1973) or organisms available commercially for this purpose. Bioassays have an advantage over strict constituent analyses of surface waters and effluents in that they measure the total effect of all constituents within the release on aquatic organisms (within the limits of the test). Such results, therefore, are not as tightly constrained by assumptions of contaminant interactions. Discussions of bioassay procedures are provided by Peltier and Weber (1985) and Horning and Weber (1985).

The criterion commonly used to establish the endpoint for a bioassay is mortality of the test organisms, although other factors such as depressed growth rate, reproductive success, behavior alteration, and flesh tainting (in fish and shellfish) can be used. Results are commonly reported as the LC50 (i.e., the lethal concentration that resulted in 50 percent mortality of the test organisms within the time frame of the test) or the EC50 (i.e., the effective concentration that resulted in 50 percent of the test organisms having an effect other than death within the time frame of the test).

One potential use of bioassays during the RFI is to predict the effect of a release on sensitive species residing in the affected surface water(s). Bioassay may be especially useful if the release is intermittent. In this case, samples of the waste may be taken from the unit of concern and used to conduct bioassay tests. The bioassay may be conducted using the waste at 100 percent strength, and in diluted form, to obtain a concentration response relationship. The results of this testing may then be used to predict the effects of a release on the surface water biota.

Bioassays can serve as important complements to the overall monitoring program. In considering the role and design of bioassays in a monitoring program, the facility owner or operator should be aware of the advantages and limitations of toxicity testing. The study design must account for factors such as species sensitivity and frequency of monitoring which may be different from the considerations that feed into chemical monitoring programs. Toxicity testing techniques are an integral part of the Clean Water Act program to control the discharge of toxic substances. Many issues associated with toxicity testing have been addressed in this context in the <u>Technical Support Document for Water Quality-Based Toxics Control</u> (Brandes et al. 1985).

# 13.5 Data Management and Presentation

The owner or operator will be required to report on the progress of the RFI at appropriate intervals during the investigation. The data should be reported in a clear and concise manner, and interpretations should be supported by the data. The following data presentation methods are suggested for the various phases of the surface water investigation. Further information on the various procedures is given in Section 5. Section 5 also provides guidance on various reports that may be required.

#### 13.5.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

 Tables of waste constituents, concentrations, effluent flow and mass loadings;

- Tables of relevant physical and chemical properties of potential contaminants (e.g., solubility);
- Narrative description of unit operations;
- Surface map and plan drawings of facility, unit(s), and surface waters; and
- Identification of "reasonable worst case" contaminant release to surface waters.

# 13.5.2 Environmental Setting Characterization

The environment of the waste unit(s) and surface waters should be described in terms of physical and biological environments in the vicinity. This description should include:

- A map of the area portraying the location of the waste unit in relation to potential receiving waters;
- A map or narrative classification of surface waters (e.g., type of surface water, uses of the surface water, and State classification, if any);
- A description of the climatological setting as it may affect the surface hydrology or release of contaminants; and
- A narrative description of the hydrologic conditions during sampling periods.

### 13.5.3 Characterization of the Release

The complex nature of the data involving multiple monitoring events, monitoring locations, matrices (water, sediment, biota), and analytes lends itself to graphic presentation. The most basic presentation is a site map or series of maps

that locate the monitoring stations for each monitoring event. These maps may also be adapted to include isopleths for specific analytes; however, since the isopleths imply a continuity within their borders, they may not be appropriate unless they are based on an adequate number of monitoring points and representative data. The contours should be based on unit intervals whose accuracy ranges do not overlap. in most situations, two separate reporting formats are appropriate. First, the data should be included as tables. These tables should generally be used to present the analytical results for a given sample. Each table could include samples from several locations for a given matrix, or could include samples from each location for all sample matrices. Data from these tables can then be summarized for comparison purposes using graphs.

Graphs are most useful for displaying spatial and temporal variations. Spatial variability for a given analyte can be displayed using bar graphs where the vertical axis represents concentration and the horizontal axis represents downstream distance from the discharge. The results from each monitoring station can then be presented as a concentration bar. Stacked bar graphs can be used to display these data from each matrix at a given location or for more than one analyte from each sample.

Similarly, these types of graphs can be used to demonstrate temporal variability if the horizontal axis represents time rather than distance. In this configuration, each graph will present the results of one analyte from a single monitoring location. Stacked bars can then display multiple analytes or locations. Line graphs, like isopleths, should be used cautiously because the line implies a continuity, either spatial or temporal, that may not be accurately supported by the data.

Scatter plots are useful for displaying correlations between variables. They can be used to support the validity of indicator parameters by plotting the indicator results against the results for a specific constituent.

Graphs are used to display trends and correlations. They should not be used to replace data tables, but rather to enhance the meaning of the data.

#### 13.6 Field and Other Methods

The purpose of this section is to provide an overview of methods that can be used to characterize the nature, rate, and extent of contaminant releases to surface water. Detailed descriptions of specific methods can be found in the indicated references.

The methods presented in this section relate to four specific areas, as follows:

- Surface Water Hydrology;
- Sampling and Constituent Analysis of Surface Water, Sediments, and Biota;
- Characterization of the Condition of the Aquatic Community; and
- Bioassay Methods.

# 13.6.1 Surface Water Hydrology

The physical attributes of the potentially affected water body should be characterized to effectively develop a monitoring program and to interpret results. Depending on the characteristics of the release and the environmental setting, any or all of the following hydrologic measurements may need to be undertaken.

#### Overland flow:

- Hydraulic measurement;
- Rainfall/runoff measurement;
- Infiltration measurement; and
- Drainage basin characterization (including topographic characteristics, soils and geology, and land use).

# Open channel flow:

- Measurement of stage (gaging activities);
- Measurement of width, depth, and cross-sectional area;
- Measurement of velocity;

- Measurement of channel discharge;
- Measurement of channel discharge at controls (e.g., dams and weirs); and
- Definition of flow pathways solute dispersion studies.
- Closed conduit flow:
  - Measurement of discharge.
- Lakes and impoundments:
  - Morphometric mapping;
  - Bathymetric mapping;
  - Temperature distributions; and
  - Flow pathways.

The following references provide descriptions of the measurements described above.

National Oceanic and Atmospheric Administration. Rainfall Atlas of the U.S.

Viessman, et al., 1977. Introduction to Hydrology.

USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition Chapter 1 (Surface Water) and Chapter 7 (Physical Basin Characteristics for Hydrologic Analyses).

U.S Department of Interior. 1981.' <u>Water Measurement Manual</u>. Bureau of Reclamation. GPO No. 024-003-00158-9. Washington, D.C.

Chow. 1964. Open Channel Hydraulics. McGraw-Hill. New York, N.Y.

In addition, the following monographs in the <u>Techniques of Water Resources</u> <u>Investigations</u> series of the USGS (USGS-WSP-1822, 1982) give the reader more detailed information on techniques for measuring discharge and other characteristics of various water bodies and hydrologic conditions:

Benson and Dalrymple. 1967. <u>General Field and Office Procedures for Indirect</u> Discharge Measurement.

Bodhaine, 1968. <u>Measurement of Peak Discharge at Culverts by Indirect Methods.</u> USGS-TWI-03-AS.

Buchanan and Somers. 1968. Stage Measurements at Gaging Stations.

Carter and Davidian. 1968. <u>General Procedure for Gaging Streams.</u> USGS-TWI-03-AL.

# 13.6.2 Sampling of Surface Water, Runoff, Sediment, and Biota

### 13.6.2.1 Surface Water

The means of collecting water samples is a function of the classification of the water body, as discussed in Section 13.3.3.1. The following discussion treats lakes and impoundments separately from streams and rivers although, as indicated below, the actual sampling methods are similar in some cases. Wetlands are considered an intergrade between these waters. Stormwater and snowmelt runoff is also treated as a separate category (Section 13.6.2.2). Although estuaries also represent somewhat of an intergrade, estuary sampling methods are similar to those for large rivers and lakes.

# 13.6.2.1.1 Streams and Rivers

These waters represent a continuum from ephemeral to intermittent to perennial. Streams and rivers may exhibit some of the same characteristics as lakes and impoundments. The degree to which they are similar is normally a function of channel configuration (e.g., depth, cross sectional area and discharge rate). Larger rivers are probably more similar to most lakes and impoundments, with respect to sampling methods, than to free-flowing headwater streams. In general, however, streams and rivers exhibit a greater degree of mixing due to their free-flowing characteristics than **can** be achieved in lakes and impoundments. Mixing and dilution of inflow can be slow to fast, depending on the point of discharge to the stream or river and the flow conditions.

Stream and river sampling methods do not differ appreciably from those outlined in the following section (Lakes and Impoundments). However, the selection of monitoring stations must consider additional factors created by differential flow velocities within the stream cross section. Strong currents and turbulence as a result of channel configuration may affect the amount of mixing and the distribution of contaminants in the stream. The reader may wish to refer to the references provided in Section 13.3.1 for a discussion of the manner in which differential velocities are handled in stream gaging studies to obtain representative discharge measurements.

### 13.6.2.1.2 Lakes and Impoundments

These waters are, by definition, areas where flow velocity is reduced, limiting the circulation of waters from sources such as discharging streams or ground water. They often include a shoreline wetland where water circulation is slow, dilution of inflowing contaminants is minimal, and sediments and plant life become significant factors in sampling strategies. The deeper zones of open water may be vertically stratified and subject to periodic turnover, especially in temperate climates. Sampling programs should be designed to obtain depth-specific information as well as to-characterize seasonal variations.

Access to necessary monitoring stations may be impeded by both water depth and lush emergent or floating aquatic vegetation, requiring the use of a floating sampling platform or other means to appropriately place the sampling apparatus. [t is common to employ rigid extensions of monitoring equipment to collect surface samples at distances of up to 30 or 40 feet from the shoreline. However, a boat is usually the preferred alternative for distances over about six feet. A peristaltic pump may also be used to withdraw water samples, and has the added advantage of being able to extract samples to a depth of 20 to 30 feet below the surface.

Many sampling devices are available in several materials. Samples for trace metals should not be collected in metal bottles, and samples for organics should not be collected in plastic bottles. Teflon or Teflon-coated sampling equipment, including bottles, is generally acceptable for both types of constituents. EPA (1982) and EPA (1986) provide an analysis of the advantages and disadvantages of many

sampling bottles for specific sampling situations. Detailed descriptions of the use of dippers/transfer devices, pond samplers, peristaltic pumps, and Kemmerer bottles are provided by EPA (1984).

Depth-specific samples in lake environments are usually collected with equipment such as Kemmerer bottles (commonly constructed of brass), Van Dorn samplers (typically of polyvinyl chloride or PVC construction), or Nansen tubes. The depth-specific sample closure mechanism on these devices is tripped by dropping a weight (messenger) down the line. Kemmerer bottles and Nansen tubes may also be outfitted with a thermometer that records the temperature of the water at the time of collection.

#### 13.6.2.1.3 Additional Information

Additional information regarding specific surface water sampling methods may be found in the following general references:

- U.S. EPA. 1986. Methods for Evaluating Solid Wastes. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.
- U.S. EPA. 1984. <u>Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods.</u> EPA-600/4-84-076. NTIS PB-168771. Washington, D.C. 20460.
- U.S. EPA. 1986. <u>Handbook of Stream Sampling for Wasteload Allocation</u> <u>Applications.</u> EPA/625/6-83/013.
- U.S. EPA. 1982. <u>Handbook for Sampling and Sample Preservation of Water and Wastewater</u>. NTIS PB 83-124503.
- USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition.

# 13.6.2.2 Runoff Sampling

Runoff resulting from precipitation or snowmelt creates an intermittent release situation that requires special treatment for effective sampling. The contaminant release mechanism in runoff situations may be overflow of ponds containing contaminants or erosion of contaminated soils. Based on an evaluation of the waste characteristics and the environmental setting, the facility owner or operator can determine whether waste constituents will be susceptible to this . release mechanism and migration pathway.

Once it has been determined that erosion of contaminated soils is of concern, the quantity of soil transported to any point of interest, such as the receiving water body, can be determined through application of an appropriate modification of the Universal Soil Loss Equation (USLE). The USLE was initially developed by the U.S. Department of Agriculture, Agricultural Stabilization and Conservation Service (ASCS) to assist in the prediction of soil loss from agricultural areas. The initial formula is reproduced below:

#### A = RKLSCP

#### where:

A = Estimated annual average soil loss (tons/acre)

R = Rainfall intensity factor

K = Soil erodibility factor

L = Slope-length factor

\$ = Slope-gradient factor

C = Cropping management factor\*

P = Erosion control practice factor\*

\*C and P factors can be assumed to equal unity in the equation if no specific crop or erosion management practices are currently being employed. Otherwise, these factors can be significantly less than unity, depending on crop or erosion control practices.

Section 2.6 (Soil Contamination) of the <u>Draft Superfund Exposure Assessment Manual</u> (EPA, 1987) provides a discussion of the application of a modified USLE to characterization of releases through soil erosion. This discussion is summarized in Appendix H (Soil Loss Calculation).

If the potential for a significant contaminant release exists, based on analysis of the hydrologic situation and waste site characteristics, event samples should be taken during high runoff periods. In situations where high runoff is predictable, such as spring runoff or the summer thundershower season, automatic samplers may be set to sample during these periods. Perhaps the most effective way to ensure sampling during significant events is to have personnel available to collect samples at intervals throughout and following the storm. Flow data should be collected coincident with sample collection to permit calculation of contaminant loading in the runoff at various flows during the period. Automated sampling equipment is available that will collect individual samples and composite them either over time or with flow amount, with the latter being preferred. Flow-proportional samplers are usually installed with a flow-measuring device, such as a weir with a continuous head recorder. Such devices are readily available from commercial manufacturers and can be rented or leased. Many facilities with an NPDES discharge permit routinely use this equipment in compliance monitoring.

Automated samplers are discussed in Section 8 of <u>Handbook for Sampling and Sample Preservation of Water and Wastewater</u> (EPA, 1982) (NTIS PB 83-124503); this publication also includes other references to automated samplers and a table of devices available from various manufacturers.

#### 13.6.2.3 Sediment

Sediment is traditionally defined as the deposited material underlying a body of water. Sediment is formed as waterborne solids (particulate) settle out of the water column and build up as bottom deposits.

Sedimentation is greatest in areas where the stream velocity decreases, such as behind dams and flow control structures, and at the inner edge of bends in stream channels. Sediments also build up where smaller, fast-flowing streams and runoff discharge into larger streams and lakes. These areas can be important investigative

areas. Some sections of a streambed may be virtually without sediments. In some streams or some areas of streams, water velocity may be too fast for sediments to deposit and actually may scour the bottom, transporting material and depositing it further downstream. The stream bed in such an area will be primarily rocks and debris.

In some situations, such as low-flow conditions, the overlying water temporarily recedes, exposing sediments to the air. Runoff channels, small lakes, and small streams and rivers may on occasion dry completely. In these cases, samples can be collected using the same procedures described in the Soils section (Section 9) of this document,

For this discussion, the definition of sediment will be expanded to include any material that may be overlain by water at any time during the year. This definition then includes what may otherwise be considered submerged soils and sludges. Submerged soils are found in wetlands and marshes. They may be located on the margins of lakes, ponds, and streams, or may be isolated features resulting from collected runoff, or may appear in areas where the ground-water table exists at or very near the land surface. In any instance they are important investigative areas.

Sludges are included for discussion here because many RCRA facilities use impoundments for treatment or storage and these impoundments generally have a sludge layer on the bottom. Sampling these sludges involves much the same equipment and techniques as would be used for sediments.

There are essentially two ways to collect sediment samples, either by coring or with grab/dredges. Corers are metal tubes with sharpened lower edges. The corer is forced vertically into the sediment. Sediments are held in the core tube by friction as the corer is carefully withdrawn; they can then be transferred to a sample container. There are many types and modifications of corers available. Some units are designed to be forced into the sediments by hand or hydraulic pressure; others are outfitted with weights and fins and are designed to free fall through the water column and are driven into the sediment by their fall-force.

Corers sample a greater thickness of sediments than do grab/dredges and can provide a profile of the sediment layers. However, they sample a relatively small

surface area. Most corers are less than four inches in diameter and are more commonly two inches in diameter.

Grab/dredges are basically clamshell-type scoops that sample a larger surface area but offer less depth of penetration. Typical grab/dredge designs are the Ponar, Eckman, and Peterson versions; each has a somewhat different operating mechanism and slightly different advantages. Some use spring force to close the jaws while others are counter-levered like ice tongs.

In sediment sampling, vertical profiling is not normally required because deposition of hazardous material is often a recent activity in terms of sedimentary processes. Grab/dredges that sample a greater surface area may be more appropriate than corers. Similarly, shallow sludge layers contained in surface impoundments should be sampled with grab/dredges because corer penetration could damage the impoundment liner, if present. Thicker sludge layers which may be present in surface impoundments, maybe sampled using coring equipment if it is important to obtain vertical profile information.

Submerged soils are generally easier to sample with a corer, than with a grab/dredge because vegetation and roots can prevent the grab/dredges from sealing completely. Under these conditions, most of the sample may wash out of the device as it is recovered. Corers can often be forced through the vegetation and roots to provide a sample. In shallow water, which may overlie submerged soils, sampling personnel can wade through the water (using proper equipment and precautions) and choose sample locations in the small, clear areas between vegetative stems and roots.

A wide variety of sampling devices are available for collection of sediment samples. Each has advantages and disadvantages in a given situation, and a variety of manufacturers produce different versions of the same device. As with water sampling, it is important to remember that metal samplers should not be used when collecting samples for trace metal analysis, and sampling devices with plastic components should not be used when collecting samples for analysis of organics.

The following references describe the availability and field use of sediment samplers:

U.S. EPA. 1982. <u>Handbook for Sampling and Sample Preservation of Water and Wastewater.</u> Environmental Monitoring and Support Laboratory, EPA-600/4-82-029. NTIS PB 83-124503.

U.S. EPA. 1985. Methods Manual for Bottom Sediment Sample Collection. NTIS PB 86-107414.

USGS. 1977, update June 1983. <u>National Handbook of Recommended Methods for Water-Data Acquisition.</u>

U.S. EPA. 1984. <u>Characterization of Hazardous Waste Sites -- A Methods</u>

<u>Manual: Volume II. Available Sampling Methods.</u> EPA-600/4-84-076. NTIS PB 85-168771.

### 13.6.2.4 Biota

Collection of biota for constituent analysis (whole body or tissue) may be necessary to evaluate exposure of aquatic organisms or man to bioaccumulative contaminants. For the most part, collection should be restricted to representative fish species and sessile macroinvertebrates, such as mollusks. Mollusks are filter-feeders; bioaccumulative contaminants in the water column will be extracted and concentrated in their tissues. Fish species may be selected on the basis of their commercial or recreational value, and their resultant probability of being consumed by man or by special status-species of fish or wildlife.

The literature on sampling aquatic organisms is extensive. Most sampling methods include capture techniques that be collected using sampling bottles (as for water samples) or nets of appropriate mesh sizes. Periphyton may be most easily collected by scraping off the substrate to which the organisms are attached. Other techniques using artificial substrates are available if a quantitative approach is required. Aquatic macroinvertebrates may be collected using a wide variety of methods, depending on the area being sampled; collection by hand or using forceps may be efficient. Grab sampling, sieving devices, artificial substrates and drift nets may also be used effectively. EPA (1973) provides a discussion of these techniques, as well as a method comparison and description of data analysis techniques.

Fish collection techniques may be characterized generally as follows (USGS, 1977):

Entangling gear:

Gill nets and trammel nets.

Entrapping gear:

Hoop nets, basket traps, trap nets, and fyke and wing nets.

Encircling gear:

Haul seine, purse seine, bay seine, and Danish seine.

Electroshocking gear:

Boat shockers, backpack shockers, and electric seines.

Selection of sampling equipment is dependent on the characteristics of the water body, such as size and conditions, the size of the fish to be collected, and the overall objectives of the study. <u>Fisheries Techniques</u> (Nielsen and Johnson, 1983) and <u>Guidelines for Sampling Fish in Inland Waters</u> (Backiel and Welcomme, 1980) provide basic descriptions of sampling methods and data interpretation from fisheries studies.

# 13.6.3 Characterization of the Condition of the Aquatic Community

Evaluation of the condition of aquatic communities may proceed from two directions. The first consists of examining the structure of the lower trophic levels as an indication of the overall health of the aquatic ecosystem. With respect to RFI studies, a healthy water body would be one whose trophic structure indicates that it is not impacted by contaminants. The second approach focuses on a particular group or species, possibly because of its commercial or recreational importance or because a substantial historic data base already exists.

The first approach emphasizes the base of the aquatic food chain, and may involve studies of plankton (microscopic flora and fauna), periphyton (including bacteria, yeast, molds, algae, and protozoa), macrophyton (aquatic plants), and benthic macroinvertebrates (e.g., insects, annelid worms, mollusks, flatworms, roundworms, and crustaceans). These lower levels of the aquatic community are

studied to determine whether they exhibit any evidence of stress. If the community appears to have been disturbed, the objective is to characterize the source(s) of the stress and, specifically, to focus on the degree to which the release of waste constituents has caused the disturbance or possibly exacerbated an existing problem. An example of the latter would be the further depletion of already low dissolved oxygen levels in the hypolimnion of a lake or impoundment through the introduction of waste with a high COD and specific gravity.

The sampling methods referenced in Section 13.6.2.4 may be adapted (by using them in a quantitative sampling scheme) to collect the data necessary to characterize aquatic communities. Hynes (1970) and Hutchinson (1967) provide an overview of the ecological structure of aquatic communities.

Benthic macroinvertebrates are commonly used in studies of aquatic communities. These organisms usually occupy a position near the base of the food chain. Just as importantly, however, their range within the aquatic environment is restricted, so that their community structure may be referenced to a particular stream reach or portion of lake substrate. By comparison, fish are generally mobile within the aquatic environment, and evidence of stress or contaminant load may not be amenable to interpretation with reference to specific releases.

The presence or absence of particular benthic macroinvertebrate species, sometimes referred to as "indicator species," may provide evidence of a response to environmental stress. Several references are available in this regard. For more information, the reader may consult <u>Selected Bibliography on the Toxicology of the Benthic Invertebrates and Periphyton (EPA, 1984).</u>

A "species diversity index" provides a quantitative measure of the degree of stress within the aquatic community, and is an example of a common basis for interpretation of the results of studies of aquatic biological communities. The following equation (the Sannon-Wiener Index) demonstrates the concept of the diversity index:

$$H = \sum_{i=1}^{s} (Pi) (log_2 Pi)$$

where:

H = species diversity index

s = number of species

Pi = proportion of total sample belonging to the <u>i</u> th species

Measures of species diversity are most useful for comparison of streams with similar hydrologic characteristics or for the analysis of trends over time within a single stream. Additional detail regarding the application of other measures of community structure may be found in the following references:

U.S. EPA. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Water and Effluents.

USGS. 1977, Update May, 1983. National Handbook of Recommended Methods of Water-Data Acquisition.

Curns, J. Jr., and K.L. Dickson, eds. 1973. <u>ASTM STP 528: Biological Methods for the Assessment of Water Quality</u>. American Society for Testing and Materials. STP528. Philadelphia, PA.

The second approach to evaluating the condition of an aquatic community is through selective sampling of specific organisms, most commonly fish, and evaluation of standard "condition factors" (e.g., length, weight, girth). In many cases, receiving water bodies are recreational fisheries, monitored by state or federal agencies. In such cases, it is common to find some historical record of the condition of the fish population, and it may be possible to correlate operational records at the waste management facility with alterations in the status of the fish population.

Sampling of fish populations to evaluate condition factors employs the same methodologies referenced in Section 13.6.2.4. Because of the intensity of the effort usually associated with obtaining a representative sample of fish, it is common to coordinate tissue sampling for constituent analysis with fishery surveys.

### 13.6.4 Bioassay Methods

The purpose of a bioassay, as discussed is more detail infection 13.4.6 .3, is to predict the response of aquatic organisms to specific changes within the environment. In the RFI context, a bioassay may be used to predict the potential adverse environmental effects of releases to surface water. Thus, bioassay is not generally considered to be an environmental characterization or monitoring technique. As indicated below, bioassay may be required for Federal water quality programs or state programs, especially where stream classification (e. g., warmwater fishery, cold-water fishery) is involved.

Bioassays may be conducted on any aquatic organism including algae, periphyton, macroinvertebrates, or fish. Bioassay includes two main techniques, acute toxicity tests and chronic toxicity tests. Each of these may be done in a laboratory setting or using a mobile field laboratory. Following is a brief discussion of acute and chronic bioassay tests.

Acute Toxicity Tests--Acute toxicity tests are used in the NPDES permit program to identify effluents containing toxic wastes discharged in toxic amounts. The data are used to predict potential acute and chronic toxicity in the receiving water, based on the LC50 and appropriate dilution, and application of persistence factors. Two types of tests are used; static and flow-through. The selection of the test type will depend on the objectives of the test, the available resources, the requirements of the test organisms, and effluent characteristics. Special environmental requirements of some organisms may preclude static testing.

It should be noted that a negative result from an acute toxicity test with a given effluent sample does not preclude the presence of chronic toxicity, nor does it negate the possibility that the effluent may be acutely toxic under different conditions, such as variations in temperature or contaminant loadings.

There are many sources of information relative to the performance of acute bioassays. Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Pettier and Weber, 1985) provides a comprehensive treatment of the subject.

<u>Chronic Toxicity Tests</u>--Chronic toxicity tests may include measurement of effluent effects on growth and reproductive success. These tests usually require long periods of time, depending on the life cycles of the test organisms. Chronic bioassays are generally relatively sophisticated procedures and are more intensive in terms of manpower, time and expense than are acute toxicity tests. The inherent complexity of these tests dictate careful planning with the regulatory agency prior to initiation of the work. <u>Methods for Measuring the Chronic Toxicity of Effluents to Aquatic Organisms</u> (Horning and Weber, 1985) is a companion volume to the methods document noted above, and contains method references for chronic toxicity tests. A discussion of bioassay procedures is also provided in <u>Protocol for Bioassessment of Hazardous Waste Sites</u>, NTIS PB 83-241737. (Tetra Tech, 1983).

Chronic toxicity tests are also used in the NPDES permit program to identify and control effluents containing toxic wastes in toxic amounts.

#### 13.7 Site Remediation

Although the RFI Guidance is not intended to provide detailed guidance on site remediation, it should be recognized that certain data collection activities that may be necessary for a Corrective Measures Study may be collected during the RFI. EPA has developed a practical guide for assessing and remediating contaminated sites that directs users toward technical support, potential data requirements and technologies that may be applicable to EPA programs such as RCRA and CERCLA. The reference for this guide is provided below.

U.S. EPA. 1988. <u>Practical Guide for Assessing and Remediating Contaminated Sites</u>. Office of Solid Waste and Emergency Response. Washington, D.C. 20460.

The guide is designed to address releases to ground water as well as soil, surface water and air. A short description of the guide is provided in Section 1.2 (Overall RCRA Corrective Action Process), under the discussion of Corrective Measures Study.

# 13.8 Checklist

# RFI CHECKLIST- SURFACE WATER

Site	Name/Location	
Туре	of Unit	
1.	<ul> <li>Does waste characterization include the following information?</li> <li>Constituents of concern</li> <li>Concentrations of constituents</li> <li>Mass of the constituent</li> </ul>	(Y/N)
	<ul> <li>Physical state of waste (e.g., solid, liquid, gas)</li> <li>Water volubility</li> <li>Henry's Law Constant</li> </ul>	
	<ul> <li>Octanol/Water Partition Coefficient (K<sub>ow</sub>)</li> <li>Bioconcentration Factor (BCF)</li> <li>Adsorption Coefficient (Koc)</li> </ul>	
2.	<ul> <li>Physical, biological, and chemical degradation</li> <li>Does unit characterization include the following information?</li> <li>Age of unit</li> </ul>	(YIN)
(	<ul> <li>Type of unit</li> <li>Operating practices</li> <li>Quantities of waste managed</li> <li>Presence of cover</li> </ul>	
	Dimensions of unit  Presence of natural or engineered barriers  Release frequency  Release volume and rate  Non-point or point source release  Intermittent or continuous release	

# RFI CHECKLIST-SURFACE WATER (Continued)

Do	es environmental setting information include the following?	(YIN)
•	Areal extent of drainage basin	
•	Location and interconnection of all streams, lakes	
	and other surface water features	
•	Flow identification as ephemeral, intermittent or perennial	
•	Channel alignment, gradient and discharge rate	
•	Flood and channel control structures	
•	Source of lake and impoundment water	
•	Lake and impoundment depths and surface area	
•	Vertical temperature stratification of lakes and impoundments	
•	Wetland presence and role in basin hydrology	
•	NPDES and other discharges	
•	USGS gaging stations or other existing flow monitoring systems	
•	Surface water quality characteristics	
•	Average monthly and annual precipitation values	
•	Average monthly temperature	
•	Average monthly evaporation potential estimates	
•	Storm frequency and severity	
•	Snowfall and snow pack ranges	
На	ve the following data on the initial phase of the release	
ch	aracterization been collected?	(YIN)
•	Monitoring locations	
•	Monitoring constituents and indicator parameters	
•	Monitoring frequency	
•	Monitoring equipment and procedures	
•	Concentrations of constituents and locations	
	at which they were detected	
•	Background monitoring results	

# RFI Checklist - SURFACE WATER (Continued)

	Hydrologic and biomonitoring results	(YIN)
	Inter-media transfer data	
	Analyses of rate and extent of contamination	
5.	Have the following data on the subsequent phase(s) of the release characterization been collected?	(Y/N)
	<ul> <li>New or relocated monitoring locations</li> <li>Constituents and indicators added or deleted for monitoring</li> </ul>	
	<ul> <li>Modifications to monitoring frequency, equipment or procedures</li> </ul>	
	<ul> <li>Concentrations of constituents and locations at which they were detected</li> </ul>	
	<ul> <li>Background monitoring results</li> </ul>	
	<ul> <li>Hydrologic and biomonitoring results</li> </ul>	
	Inter-media transfer data	
	<ul> <li>Analyses of rate and extent of contamination</li> </ul>	

### 13.9 References

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# **APPENDIX G**

# AIR RELEASE SCREENING ASSESSMENT METHODOLOGY

# DRAFT FINAL (Revised)

# AIR RELEASE SCREENING ASSESSMENT METHODOLOGY

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### 1.0 INTRODUCTION

A screening method has been developed for evaluating which waste management units have air releases warranting further investigation under a RCRA Facility Investigation (RFI). This method can be used as an intermediate step between the general qualitative determination of the RCRA Facility Assessment (RFA) regarding identification of air emissions that warrant an RFI, and the actual performance of a complicated and costly RFI. Specifically, this screening methodology provides a basis for identifying air releases with the potential to have resulted in off-site exposures that meet or exceed health-based criteria in the RFI Guidance.

This screening methodology has been developed as a technical aid for routine use by EPA Regional and State staff who may not be familiar with air release assessments. However, it should also be considered a resource available to prioritize waste management units which may warrant the conduct of an RFI for the air media. Alternative resources (e. g., available air monitoring data, more sophisticated modeling analyses, judgmental factors) may also provide important input to the RFI decision-making process.

The screening methodology itself is explained in Section 2 and example applications of it are presented in Section 3. A discussion of background information that addresses the technical basis for the air release screening methodology is presented in Appendix A.

### 2.0 SCREENING METHODOLOGY

This section presents the air release screening assessment methodology. This methodology can be used as a transition between the general qualitative determination made in the RFA regarding air emissions that warrant an RFI, and the actual performance of an RFI.

The primary (recommended) screening approach involves the application of available emission rate models and dispersion models. An alternative approach involves the use of technical aids based on scaling modeling results for a limited set of source scenarios.

The screening methodology for releases of organics is based on using the CHEMDAT6 air emission models, available from EPA's Office of Air Quality Planning and Standards (OAQPS), (U.S. EPA, December 1987). Specifically, the following unit categories are directly addressed in this section:

- Disposal impoundments
- Storage impoundments
- Oil Films on Storage Impoundments
- Mechanically Aerated Impoundments
- Diffused Air Systems
- Land treatment (emissions after tilling)
- Oil Film Surfaces on Land Treatment Units
- Closed landfills
- Open landfills
- Wastepiles

The alternative approach presented in this section involves scaling the emission rate results from numerous source scenarios that have been modeled using CHEMDAT6. These scaling computations can become tedious if numerous source scenarios are evaluated. In addition, the direct use of CHEMDAT6 models will provide more representative unit-specific emission estimates. Therefore, it is strongly recommended that EPA Regional and State agency staff develop a capability to use CHEMDAT6 directly to model unit-specific and facility-specific scenarios.

CHEMDAT6 has been developed for *use* on a microcomputer using LOTUS spreadsheet software; therefore, these models can easily be used by staff familiar with LOTUS applications. However, the basic strategy described in this section to estimate ambient concentrations can still be successfully used even without using LOTUS.

The screening methodology for organic emissions from storage tanks is based on emission factors in EPA's AP-42, "Compilation of Air Pollutant Emission Factors" (U.S. EPA, September 1985). The following categories of tanks are addressed:

- Fixed roof tanks
- Floating roof tanks
- Variable vapor space tanks.

Open tanks should be assessed using the methodology for storage impoundments.

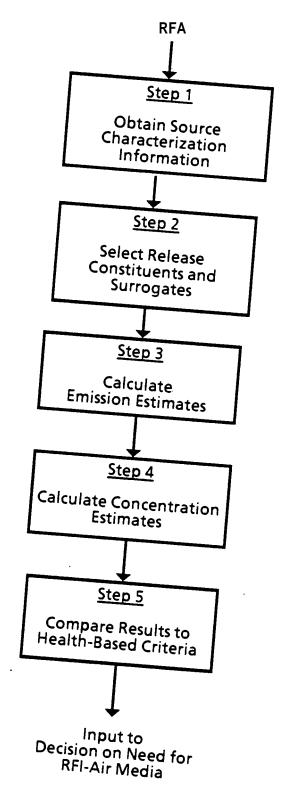
The screening methodology for particulate matter releases from wind erosion of storage piles and batch dumping and loader activity on the pile is based on emission factors in EPA's AP-42 (U.S. EPA, September 1985). The screening methodology for particulate matter releases from wind erosion of flat, exposed, contaminated surface areas is based on emission factors in EPA's "Fugitive Emissions from Integrated Iron and Steel Plants" (U.S. EPA, March 1978). The EPA-OAQPS is currently developing guidance regarding particulate emissions for treatment, storage, and disposal facilities.

# 2.1 <u>Overview</u>

The air release screening assessment methodology involves applying emission rate and dispersion results to estimate long-term ambient concentrations at receptor locations for comparison to health-based criteria. The methodology consists of five steps as follows (see Figure 2-1):

Step 1 - Obtain Source Characterization Information: This information (e.g., unit size, operational schedule) is needed to define the emission potential of the specific unit.

FIGURE 2-1
SCREENING METHODOLOGY OVERVIEW



- Step 2- Select Release Constituents and Surrogates: The primary approach involves using the actual physical/chemical properties for all unit-specific constituents for emission modeling purposes. The alternative (scaling) screening approach uses a limited set of constituents or surrogates to represent a wide range of potential release constituents. This surrogate approach significantly simplifies the screening assessment process.
- Step 3- Calculate Emission Estimates: The primary approach involves the use of emission rate models based on unit-specific source conditions. Modeling results of emission rates for a wide range of source conditions are also presented in Appendices C through Q. As an alternative approach, these modeling results can be interpolated to estimate an emission rate specific to the unit.
- Step 4- Calculate Concentration Estimates: Emission rates from Step 3 are used to calculate concentration estimates at receptor locations of interest. The primary approach involves the application of dispersion models based on site-specific meteorological conditions. As an alternative approach, dispersion conditions are accounted for by use of modeling results available in Appendix R for typical annual meteorological conditions.
- Step 5 Compare Concentration Results to Health-Based Criteria:
   Concentration results from Step 4 can be compared to constituent-specific health-based criteria provided in the RFI Guidance.

For some applications, Step 4 (Calculate Concentration Estimates) will not warrant the use of emission models because it can be assumed that all the volatile wastes handled will eventually be emitted to the air. This assumption is generally appropriate for highly volatile organic compounds placed in a disposal unit like a surface impoundment. In these cases, the air emission rate can be assumed to be equivalent to the disposal rate, so that an emission rate model may not be required. This assumption is valid because of the long-term residence time of wastes in the disposal units. In open units like surface impoundments, a substantial portion of the volatile constituents will frequently be released to the atmosphere within

several days. However, for more complex situations (e.g., storage or treatment units where total volatilization of the constituents is not expected), air emission models can be used to obtain a more refined long-term release rate.

Results from the air release screening assessment, using the above steps, will provide input to decisions on the need for an RFI for the air media. They can also be used to prioritize air emission sources at a facility (i.e., by identification of the major onsite air emission sources) as well as to prioritize the total release potential at candidate facilities.

# 2.2 <u>Step 1- Source Characterization Information</u>

Implementation of the air release screening assessment methodology involves collecting source characterization information, as illustrated in Figure 2-2. Specifically, this involves completion of Column 2 of unit-specific Emission Rate Estimation Worksheets (included in Appendix S) as specified in Figure 2-2. Parameters in Column 2 of the worksheet represent standard input used by the CHEMDAT6 air emission models or input to the AP-42 emission equations. Source characterization information should be available from the RFA but it may be necessary to request additional information from the facility owner or operator on an ad hoc basis.

Additional worksheets should be completed for each unit to be evaluated. Similar units can be grouped together and considered as one area source to simplify the assessment process. For example, several contiguous landfills of similar design could be evaluated efficiently **as** one (combined) source.

Completeness and quality of the source characterization information are very important and, as previously stated, directly affect the usefulness of the screening assessment results. Certain source characterization parameters are considered critical inputs to the screening assessment. These critical input parameters are needed to define the total mass of constituents in the waste input to the unit being evaluated or the potential for release of particles less than 10 microns. These parameters have been identified in the unit-specific worksheet (Tables S-1 through S-13 for VO sources and Tables S-14 and 15 for particulate sources).

# FIGURE 2-2 STEP 1 - OBTAIN SOURCE CHARACTERIZATION INFORMATION

**RFA** Complete Column 2 of Unit-Specific Emission Rate Estimation Worksheet: Closed landfill - Table S-8 Disposal impoundment - Table S-1 Open landfill - Table S-9 Storage impoundment/open tank-Table S-2 Wastepile - Table S-10 Oil film on storage impoundment - Fixed roof tank - Table S-11 Table S-3 Floating roof tank - Table S-12 Mechanically aerated impoundment - Variable vapor space tank -Table S-4 Table S-13 Diffused air system - Table S-5 Storage pile (particulates) -Table S-14 Land treatment (emissions after tilling - Table S-6 Exposed, flat, contaminated area Oil film surface on land treatment (particulates) Table S-15 unit - Table S-7 Complete Column 2 of additional worksheets for each unit to be evaluated (similar units can be grouped as one area source). Select typical and/or reasonable worst-case values specified in Appendices C-M if values or input parameters are not available. Disposal impoundment - Table C-1 ● Closed landfill - Table J-1 • Storage impoundment/open tank- • Open landfill - Table K-1 Table D-1 Wastepile - Table L-1 Oil film on storage impoundment - • Fixed roof tank - Table M-1 Table E-1 Floating roof tank - Table N-1 Mechanically aerated impoundment - • Variable vapor space tank -Table O-1 Table F-1 Diffused air system - Table G-1 Storage pile (particulates)-Table P-1 Land treatment (emissions after tilling) - Table H-1 Exposed, flat, contaminated area Oil film surface on land treatment (particulates)- Table Q-1

Step 2-

unit-Table I-I

Select Release Constituents and Surrogates

Unit-specific values for some of the source characterization parameters may be difficult to determine. For example, air porosity values of the fixed waste are needed for evaluating emissions from open landfills, closed landfills, and wastepiles, and total porosity values of the fixed waste are needed to evaluate emissions from open landfills and wastepiles. However, unit-specific data are typically not available for these parameters. If unit-specific values for input parameters are not available, typical and/or reasonable worst-case values should be selected from the range of values specified in Appendices C through Q.

Selection of source scenario input data should be based on realistic physical and chemical limitations. For example, the waste concentration value for a constituent should not exceed the constituent-specific volubility in water.

# 2.3 Step 2- Release Constituent Surrogates

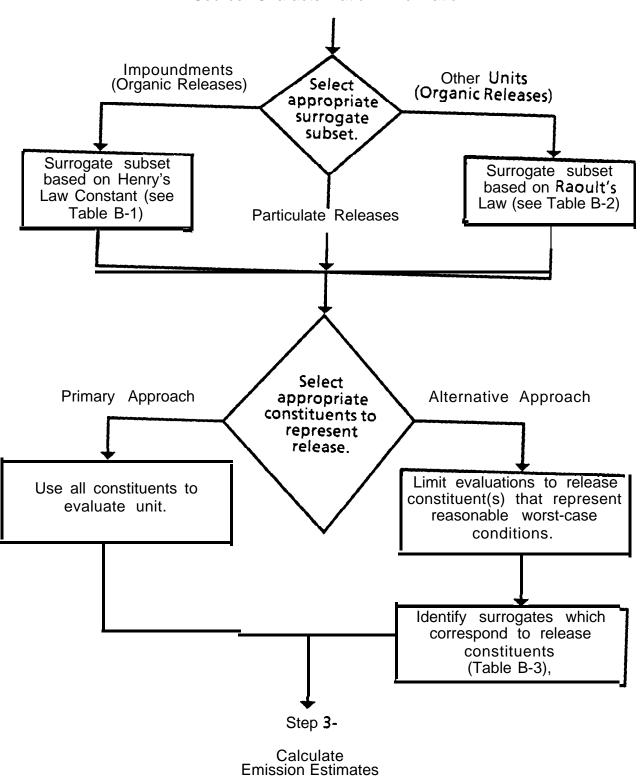
The primary approach involves using the actual physical/chemical properties for ail unit-specific constituents for emission modeling purposes. The alternative screening approach (scaling) uses a limited set of constituents or surrogates.

A limited set of surrogates is used to represent the constituents of concern in this alternative screening method to represent a wide range of potential release constituents. This significantly simplifies the screening assessment process since the list of potential air release constituents included in the <a href="RFI Guidance">RFI Guidance</a> is extensive. Selection of appropriate source release constituent surrogates is illustrated in Figure 2-3. Table B-3 presents the appropriate surrogate to be used for each constituent of concern. This step is not used in screening for particle emissions from storage piles and exposed areas.

Table B-3 of Appendix B, presents the appropriate surrogate to be used for each constituent of concern. Two subsets of surrogates are presented in Appendix B. The first subset is applicable to emissions that can be estimated based on Henry's Law Constant (i.e., applicable for low concentrations, less than 10 percent, of wastes in aqueous solution). Surrogates based on Henry's Law Constant are appropriate for units like storage and disposal impoundments. Henry's Law Constant surrogates are presented in Table B-1.

STEP 2- SELECT RELEASE CONSTITUENTS AND SURROGATES

Source Characterization information



The second subset is applicable to emissions that can be estimated based on Raoult's Law. Raoult's Law predicts the behavior of most concentrated mixtures of water and organic solvents (i.e., solution with over 10 percent solute). Surrogates based on Raoult's Law are appropriate for units like landfills, wastepiles, land treatment units and storage tanks. Raoult's Law surrogates are listed in Table B-2.

It is also necessary to select surrogates from the appropriate subset (i.e., from the Henry's Law Constant or Raoult's Law subset selected) to represent release constituents of interest. The primary approach is to use all surrogates from the appropriate subset to evaluate the unit. This approach will provide a comprehensive data base for the screening assessment. An alternative approach is to select release constituent(s) /surrogate(s) that represent reasonable worst-case conditions. Release constituents having the most restrictive health-based criteria and those having high volatility are frequently associated with these reasonable worst-case (long-term) release conditions.

# 2.4 <u>Step 3- Emission Estimates</u>

Two approaches for calculating emission estimates are identified in Figure 2-4. The primary approach involves the calculation of unit-specific emission rates based on available models (e.g., CHEMDAT6, et cetera). This approach is recommended for most applications.

The alternative approach involves the calculation of emissions by applying scaling factors to emission modeling results presented in Appendices C through Q for a limited set of source scenarios. This approach is appropriate when a rapid preliminary estimate is needed and modeling resources are not available. However, the primary approach will provide more representative unit-specific emission estimates.

Specific instructions for implementing the alternative emission estimation approach are presented in Figure 2-5.

Emission rate modeling results for a wide range of source scenario conditions are presented in Appendices C through Q to facilitate implementation of the alternative emission estimation approach. These available modeling results can be

# Appendix A

**Background Information** 

# FIGURE 2-5 STEP 3- CALCULATE EMISSION ESTIMATES (ALTERNATIVE APPROACH)

# Source Characterization Information/Constituent Surrogates

# Obtain Emission Rate Estimation Worksheets (as selected in Step 1):

Disposal impoundment - Table S -1 •

Storage impoundment/open tank - • Table 5-2

Oil film-on storage impoundment Table S-3

Mechanically aerated impoundment -Table S-4

Diffused air system - Table S-5

Land treatment - Table S-6

Oil film surface on land treatment unit -Table S-7

Closed landfill - Table S-8 Open landfill - Table S-9

Open landfill - Table S - 9

Fixed roof tank -Table S -11

Floating roof tank -Table S -12 Variable vapor space tank -Table S - 13

Storage pile (particulates)-Table S -1 4

Exposed, flat, contaminated area (particulates) - Table S -15

Select the source scenario for each modeling parameter (identified in Col. 1 of worksheets) that best represents unit-specif conditions from available cases (appropriate alternative case numbers are Identified in Col. 3 of the worksheet and case specifications are presented in Appendices C-Q):

Disposal-impoundment - Table C-1

Storage impoundment/open Table D-1 tank-

Oil film on storage impoundment Table E-1

Mechanically aerated impoundment --

Dffused-air system - Table G-1

Land treatment -Table H-1

Oil film surface on land treatment unit -Table I-2

Closed landfill - Table J -1 O en landfill - Table K-1

Wastepile - Table L-1
Eixed roof tank - Table M-1

Floating roof tank -Table N-1 Variable vapor space tank - Table 0-1 **Table Q-1** 

Storage pile (particulates) -Table P-1

Exposed, flat contamianted area (particulates) Table Q-1

Compute parameter-specific scaling factors by completing Cols. 4-11 (12 for Raoult's Law surrogates) of the worksheet or Col. 4 for particulate worksheets based on modeling results presented in Appendicess C-Q (computational instructions are presented with each worksheet):

Disposal-impoundment - Table C-2 ●

Storage impoundment/open tank Table D-2

Oil film on storage impoundment - Table E-2

Mechanically aerated impoundment - • Table F-2

Diffused air system - Table G-2

Land treatment - Table H-2 Oil film surface on land treatment unit -Table I-2

Closed landfill - Table J-2

Open landfill - Table K-2 Open landfill - Table K-2

Fixed roof tank -Table M-2 Floating roof tank - Table N-2 Variable vapor space tank -Table O-2

Storage pile (particulates) -Table P-2

Exposed, flat, contaminated area (particluates) Table Q-2

Complete unit-specific emission, rate, which accounts for unitspecific scaling factors (last line item on each worksheet based on instructions presented with each worksheet).

Step 4-

Calculate Concentration Estimates

interpolated to estimate a unit-specific emission rate. The process for calculating emission rate estimates for application to a specific unit (i. e., unit-specific application) is summarized in Figure 2-5.

Calculating emission rate estimates is accomplished by completing an Emission Rate Estimation Worksheet, included in Appendix S. A separate worksheet is provided in Appendix S for each unit category. Column 2 (unit-specific values for each modeling parameter) of the worksheet should already have been completed during Step 1.

The alternative emission estimation approach presented in Figure 2-5 also involves scaling the emission rate modeling results available in Appendices C through Q to represent unit-specific conditions. This is accomplished by first computing individual parameter-specific factors and then combining the results to calculate a unit-specific emission rate for each surrogate of interest. Therefore, it is necessary to select the appropriate source scenario that best represents unit-specific conditions for each modeling parameter (identified in Column 1 of the worksheet). Column 3 of the worksheet identifies the appropriate candidate scenario cases for each parameter. The source scenario case specifications (i.e., values of the modeling parameters for each case) are presented in Table C -1 (disposal impoundment), D-1 (storage impoundment), E-1 (oil film on storage impoundment), F-1 (mechanically aerated impoundment), G-1 (diffused air system), H-1 (land treatment), I-1 (oil film surface on land treatment unit), J-1 (closed landfill), K-1 (open landfill), L-1 (wastepile), M-1 (fixed roof tank), N-1 (floating roof tank), O-1 (variable vapor space tank), P-1 (storage piles), and Q-1 (exposed, flat, contaminated areas).

It is also recommended that a second scenario case be selected for each parameter in order to bracket source conditions. The selection of a second scenario is appropriate if unit-specific source conditions are different than those presented in the source scenario case specifications (Appendices C-Q).

Parameter-specific scaling factors are computed by following instructions in each worksheet and by completing Columns 4-11 (12). (Column 12 is needed for Raoult's Law surrogates.) Information needed to complete Columns 4-11 (12) is available in Appendices C through Q. Information needed to complete worksheets for particulate emissions are available in Appendices P and Q. Instructions for

computing unit-specific emission rates based on applying scaling factors are included in each **worksheet**.

The **last** set of three source scenario cases for unit-category modeling results presented in Appendices C through Q represents the **following**:

- Reasonable best-case emission rate for unit category (for a typical source surface area or tank size)
- Typical emission rate for unit category (for a typical source surface area or tank size)
- Reasonable worst-case emission rate for unit category (for a typical source surface area or tank size)

Frequently these cases can be used to rapidly estimate typical and extreme emission rates. However, they should not be considered as absolute values. These scenarios generally represent the range of source conditions identified in the <u>Hazardous Waste Treatment</u>, Storage and Disposal Facilities (TSDF) Air Emission Models (U.S. EPA, December 1987). But frequently this information was incomplete, and subjective estimates were postulated instead. Therefore, the emission rates for best, typical and worst case source scenarios should only be used as a preliminary basis to compare and prioritize sources.

At times one of the source scenario cases presented in the Appendices may be representative of the modeling parameters for the unit scenario being **evaluated**. For these **situations**, it is not necessary to implement all of the intermediate computational steps otherwise needed to complete the **worksheet**. **Instead**, the modeling results presented in Appendices C through Q can be used to directly represent unit-specific emission **rates**. **However**, it may be necessary to scale these results to account for the unit-specific surface area and waste constituent **concentrations**. (**Scaling** can be accomplished by the approach specified in each **worksheet**).

# 2.5 Step 4- Concentration Estimates

Emission rate values from Step 3 are used as input to calculate concentration estimates at receptor locations of interest. Dispersion conditions are accounted for by use of available modeling results for typical annual meteorological conditions. A summary of this process is included in Figure 2-6. Dispersion models can be applied to directly estimate concentration. This primary approach is recommended for most applications. The EPA-industrial Source Complex (ISC) model is generally appropriate for a wide range of sources in flat or rolling terrain. Alternative models are identified in the Guideline On Air Quality Models (Revised) (U.S. EPA, July 1988).

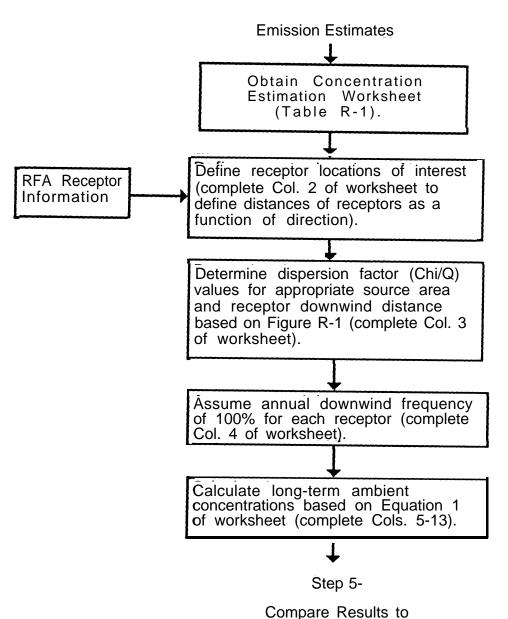
An alternative approach to obtain concentration estimates (for flat terrain sites) involves the application of dispersion factors presented in Appendix R. A Concentration Estimation Worksheet (Table R-1) is used as the basis for concentration calculations. This approach is appropriate when a rapid preliminary estimate is needed and modeling resources are not available. However, the primary approach will provide more representative site-specific concentration estimates.

Specific instructions for implementing the alternative concentration estimation approach are presented in Figure 2-7.

Concentrations should be estimated at locations corresponding to receptors of concern (pursuant to <u>RFI Guidance</u>). Receptor information may also be available from the RFA. Column 2 of the worksheet should be completed to define distances to receptors as a function of direction.

Ambient concentrations are influenced by atmospheric dispersion conditions in addition to emission rates. Atmospheric dispersion conditions for ground-level non-buoyant releases (as is the case for surface impoundment, landfill, land treatment unit, and wastepile applications) can be accounted for by the use of dispersion factors. Appropriate dispersion factors based on Figure R-1 should be used to complete Column 3 of the worksheet. The dispersion factors presented in Figure R-1 include individual plots for a range of unit-surface-area sizes. Instruction regarding the use of these plots to determine unit- and receptor-specific dispersion factors is included with Figure R-1.

# FIGURE 2-7 STEP 4 - CALCULATE CONCENTRATION ESTIMATES (ALTERNATIVE APPROACH)



Health-Based Criteria

The dispersion factors presented in Figure R-1 are based on the assumption that winds are flowing in one direction (i.e., toward the receptor of interest) 100 percent of the time on an annual basis. This conservative assumption of a wind direction frequency of 100% for each receptor of interest should be used if Figure R-1 is used. as the basis to estimate dispersion conditions for Column 4 of the worksheets.

The information entered into Column 3 and 4 of the worksheet, plus the emission rate results calculated during Step 3, provides the required input to calculate ambient concentrations. Specifically, Equation 1 presented in the worksheet should be used to obtain ambient concentrations for each surrogate and receptor location. Equation 1 of Table R-1 includes a safety factor of 10 which is applied to all concentration estimates based on the scaling approach. This factor accounts for the inherent uncertainty involved in the scaling approach. This safety factor is applicable to all concentration estimates based on emission rates obtained via the scaling approach. These results should be entered into Columns 5 through 13 of the worksheet.

# 2.6 Step 5 - Health Criteria Comparisons

Concentration results from Step 4 can be compared to constituent-specific health-based criteria provided in the <u>RFI Guidance</u> (see Figure 2-8). To facilitate this comparison, it is recommended that the appropriate reference toxic and carcinogenic criteria be entered in the space allocated in the Concentration Estimation Worksheet.

Interpretation of the ambient concentration estimates should also account for the uncertainties associated with the following components of the assessment:

- Inaccuracies in input source characterization data will directly affect concentration results.
- Emission rate models have not been extensively verified. However, OAQPS states, "In general, considering the uncertainty of field emission measurements, agreement between measured and predicted emissions generally agree within an order of magnitude." (U.S. EPA, April 1987). These verifications have been for short-term emission conditions. Model

performance is expected to be better for long-term emission rate estimation (as used for this screening assessment).

• inaccuracies associated with use of the alternative emission estimation approach presented in Figure 2-5.

Source conditions for the unit of interest may not be the same as those for the source scenarios presented in Appendices C-Q. Therefore, scenarios should be selected to bracket the unit-specific conditions in order to obtain a range of emission rate estimates.

The use of scaling factors for each source parameter may yield somewhat different emission rate values compared to those based on direct use of a model with unit-specific **inputs**. These differences are attributed to the interrelationships of source parameters which may not be **linear**. A comparison of direct modeling results versus scaling estimates is presented in Exhibit 2-1.

Atmospheric dispersion models for long-term applications (as used for this screening assessment) typically are accurate within a factor of  $\pm 2$  to 3 for flat terrain (inaccuracy can be a factor of 10 in complex terrain.

**Therefore, "safety factors"** commensurate with these uncertainties should be applied to concentration estimates for health criteria **comparisons**.

The calculations of emission rate and concentration estimates obtained have been for a I-year period. Some units, such as closed landfills, will have different average emission rates for longer exposure periods for certain constituents. The air pathway health-based criteria included in the RFI Guidance are based on a 70-year exposure period. Appendices C through Q each contain a set of scenario cases for 1-,5-,10-, and 70-year exposures for information purposes. However, only inactive units are expected to have an average 70-year emission rate that is significantly different from the I-year rate. All of the emission results presented in Appendices C through Q are assumed to be active with the exception of closed landfills (Appendix J). Air concentrations for each one-year period within the reference 70 year exposure period should be less than those associated with constituent-specific health criteria.

EXHIBIT 2-1

RATIO OF SCALING ESTIMATES TO CHEMDAT6
EMISSION RATE MODELING RESULTS (FIGURE 2-5)

	Reasonable Best Case/Worst Case Emission Rate Scenarios									
Unit Type	Henry's Law Surrogates: Raoult's Law Surrogates: Particle Case:	MHLB HVHB Particle	HHLB HVMB	LHMB HVLB 	MHMB MVHB 	HHMB M∨ <u>M</u> B	LHHB MVLB 	MHHB LVMB 	HHHB VHVHB 	 VHVLB
Disposal Impoundment		<u>0.81</u> 1.00	<u>0.81</u> 1.00	<u>0.86</u> 1.04	<u>0.81</u> 1.00	<u>0.81</u> 1.00	0.68 1.03	<u>0.81</u> 1.00	<u>0.81</u> 1.00	
Storage Impoundment		1.10 1.51	1.00 1.43	1.10 1.50	1.00 1.52	1.10 1.43	0.97 0.79	1.00 1.51	1.00 1.43	
Oil Film on Storage Impoundment		1.10 1.06	1.10 1.05	1.10 1.04	1.10 4.10	1.08 3.25	1.10 4.12	1.24 1.25	1.10 1.00	1.10 1.00
Mechanically Aerated Impoundment		1.00 0.84	1.00 1.00	1.00 0.76	1.00 0.91	1.00 0.99	1.00 0.81	1.00 0.93	1.00 1.00	
Diffused Air System		<u>1.00</u> 1.00	1.00 1.00	1.00 1.00	1.00 0.99	1.00 1.00	<u>1.00</u> 0.99	1.01 1.00	1.00 0.99	
Land Treatment (after tilling)		1.20 0.91	1.06 0.98	1.00 1.00	3.67 0.74	2.83 0.75	1.27 0.91	<u>5.28</u> 1.40	1.06 0.99	1.00 1.00
Oil Film Surface on Land Treatment Unit		<u>0.92</u> 1.31	0.92 1.28	0.92 1.25	3.93 1.09	<u>5.68</u> 1.06	3.98 1.09	1.08 0.77	<u>0.92</u> 1.00	0.92 1.03
Closed Landfill		<u>1.20</u> 1.01	1.18 1.01	1.16 1.00	1.14 1.01	1.11 1.01	1.14 1.02	1.18 1.02	1.18 0.99	1.20 1.00
Open Landfill		1.29 1.02	1.16 1.19	1.23 1.05	0.94 0.73	1.23 0.90	0.91 0.70	<u>0.40</u> 0.72	<u>0.98</u> 0.94	<u>0.98</u> 0.94
Wastepile		<u>0.99</u> 1.00	<u>0.98</u> 1.02	<u>0.98</u> 1.00	0.99 1.00	<u>0.98</u> 1.00	0.99 1.01	1.25 0.79	1.02 1.00	1.02 1.00
Fixed Roof Tank		*	*	*	0.82 0.53	0.81 0.53	0.82 0.50	0.90 0.89	*	*
Floating Roof Tank		*	*	*	1.00 1.01	<u>0.96</u> 1.01	0.98 1.00	<u>0.95</u> 1.01	*	*
Variable Vapor Space Tank		1.00 0.92	1.00 1.00	1.00 0.96	1.00 1.00	1.00 0.91	1.00 0. <b>9</b> 5	1.00 1.00	1.00 0.92	1.00 1.02
Storage Pile (Particulates)		<u>0.88</u> 1.00			•					
Contaminated Area (Particulates)		0.98 0.98								

<sup>\*</sup>This type of tank is not typically used for materials with this high vapor pressure.

### 3.0 EXAMPLE APPLICATIONS

Two case studies have been selected to demonstrate the application of the alternative (scaling) air assessment screening methodology based on the technical aids presented in Appendices B through S. The first example involves a storage impoundment and the second a closed landfill.

### 3.1 Case Study A

Case Study A involves a storage impoundment located close to a small community. The closest resident lives 0.2 mile south of the unit. The impoundment has a surface area of 1 acre, a depth of 0.9 meter, and a typical storage time cycle of 1.2 days. Wind data from the nearest National Weather Service station indicate that northerly winds occur 10 percent of the time annually. Waste records for the unit indicate the frequent appearance of carbon tetrachloride. Limited waste analyses indicate that a 1,000-ppm concentration of this constituent in the impoundment is a reasonable assumption. The object of this example screening assessment is to estimate the ambient concentrations at the nearest residence. Following is a summary of this example application.

# Step 1- Obtain Source Characterization Information

The appropriate Emission Rate Estimation Worksheet for this case study is Table S-2 for storage impoundment units. The unit information provided above is sufficient to complete Column 2 for Lines 1-4 of the worksheet (see Exhibit 3-1) pursuant to Instruction A of the Worksheet (Table S-2).

### Step 2- Select Release Constituent Surrogates

Based on Figure 2-3, it is apparent that the Henry's Law Constant surrogate subset (Table B-1) is appropriate for a storage impoundment unit. Evaluation of Table B-3 indicates that the following surrogate inapplicable to Case Study A:

EXHIBIT 3-1 TABLE S-2
EMISSION RATE ESTIMATION WORKSHEET - STORAGE IMPOUNDMENT EXAMPLE

Line	col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Instruction A: Instruction B: Input Unit- Select a Representative		Instruction C:  Determine Surrogate-Specific Scaling Factors**								
	Modeling Parameters	Specific Values	Case from Appendix D - Table D-1 (underline selected case)	нунв	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VНVНВ
1	Area*	1 acres				-					
2	Depth*	<u>0.9m</u>	1,2,3,or4		0.57						
3 R	Retention time*	<u>1.2</u> days	5,6,7or8		4.1						_
4	Constituent concentration*	1000 ppm	-								
	Coi	INSTRUCTION [ mplete Lines 5-6				SURRO	OGATE-SP	ECIFIC V	ALUES		
5 <sub>[u</sub>	Account for Area nit-specific area/(C	Case 18 area =	0.4 acres)		2.5						
6 A	account for Unit-Sp [unit-specific conc				1.0				******		
7	Typical Surrogate- (Case 18), 10° g/yr	Specific Emission	n Rate	34.0	39.24	3.25	38.10	38.40	1.97	38.74	39.24
<b>8</b> C	calculate Unit-Spe (multiply lines #2	cific Emission Ra 2x #3x #5x #6x	te, 10°g/yr <b>#7)</b>		229.0			_			

\* Critical input values

\*\* Scaling Factor determined for Lines 2 and 3 from Appendix D - Emission Rate Estimate from Table D-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

<u>Constituent</u>	Surrogate No.	Surrogate Code

• Carbon tetrachloride 3 HHLB

# Step 3- Calculate Emission Estimates

\*Line 2:

This step involves implementing Instructions B-D of the Worksheet (Table S-2). Instruction B involves selection of representative cases from Table D-1 which best match actual unit values in Column 2. A review of Table D-1 indicates that Case 1 (based on a depth of 0.9 meter) best estimates the depth of the example case (also a depth of 0.9 meters has been specified for Case Study A). Table D-1 also indicates that Case 5 (based on a retention cycle of 1 day) best represents the example case (a retention cycle of 1.2 days has been specified for Case Study A).

Implementation of Instruction C involves determination of surrogate-specific scaling factors. For this example this involved completion of Column 5 for lines 2 and 3 of the Worksheet (Table S-2). Emission rates for Cases 1 and 5, and a typical emission rate (Case 18) were obtained from Table D-2 as follows:

Case	Emission Rate (I O <sup>6</sup> g/yr)
Case	Carbon Tetrachloride
Case 1	22.5
Case 5	161.5
Case 18	39.2

Column 5 of the worksheet (for carbon tetrachloride) was completed via the following computations (Case 18 represents a typical emission rate for the source category of storage impoundment):

Case 1 Emission Rate (from Table D-2)

Case 18 Emission Rate (from Line 7 of the Worksheet)

= 22.5

39.2

\*Line 3:

Implementation of Instruction D of the Worksheet (Table S-2) involves completion of Lines 5-6 and 8 as follows:

\*Line 5:

\*Line 8:

Emission Rate = Line 2 x Line 3 x Line 5 x Line 6 x Line7  
= 
$$0.57 \times 4.1 \times 2.5 \times 1.0 \times 39.2$$
  
=  $229.0 \times 10^6 \text{g/yr}$   
=  $229.0 \times 10^9 \text{g/y}$ 

Step 4- Calculate Concentration Estimates

This step involves use of the Concentration Estimation Worksheet (Table R-I). Application of the Worksheet involves implementation of Instructions A-D included in Table R-1. The example Concentration Estimation Worksheet for Case Study A is presented in Exhibit 3-2. Implementation of Instruction A involves input of the distance of the receptor from the downwind unit boundary for sectors of interest. Notice that the receptor distance of 0.2 mile (Column 2) corresponds with the south (downwind) sector. This is because the frequency of northerly winds obtained from the National Weather Service (as stated at the beginning of 3.1) represents the

# EXHIBIT 3-2 TABLE R-1 CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13	
	Instruction A:		Instruction D:   Instruction D:   Compute Long-Term Concentration Estimates (μg/m³) Based on Equator Assume (select and circle appropriate surrogate subset, Henry's Law Constant or Raoult's L	Equation 1 * It's Law or particle case)									
Downwind Sector	Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB MVLB	MHHB or LVMB	HHHB or vнvнв	 VHVLB	= Henry's Law Constant Surrogate = Raoult's Law Surrogate
N													
NNE													
NE													
ENE													
E													
ESE													
SE													
SSE													
S	0.2	6.4 x 10 <sup>-5</sup>	100		4600								
SSW	<u> </u>												
SW	<u> </u>												
WSW	<u> </u>												
W													
WNW													
NW													
	eria (µg/m³) Fl Guidance	Toxic Criteria Carcinogenic			NA 0.03***	:							

Equation 1 Long-Term Concentration Est. (µg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17 x 10°) x

NA Not available

 $Mg/yr = 10^{6}g/yr$ 

<sup>(</sup>Safety Factor = 10) Distance from downward unit boundary

<sup>\*\*\*</sup> Criterion for carbon tetrachloride

direction **"from** which the wind is flowing. " This is standard meteorological **terminology**. **Therefore**, northerly winds affect receptors south of the **unit**.

Implementation of Instruction B involves determination of the appropriate dispersion factor for the downwind distance **selected**. The dispersion factor obtained from Figure R-1 for this example is **6.4 x** 10-5 sec/m3 (**entered** in Column **3** of the Concentration Estimation **Worksheet**). This value is applicable to a receptor **0.2** mile downwind from a l-acre area **source**.

Implementation of Instruction C involves entering the downwind frequency for the sector of interest in Column 4 of the Worksheet. The downwind frequency (conservatively assumed to be 100 percent if Table R-1 dispersion factors are used) for a receptor located south of the unit is entered in Column 4 of the Worksheet.

implementation of Instruction D involves computation of air concentrations based on Equation 1 of the Worksheet (Table R-1). The concentration estimate for carbon tetrachloride was calculated using Equation 1 of the Worksheet as follows:

#### • Worksheet estimate:

```
Concentration (\mug/m3) = Col. 3 x Col. 4x Emission Rate x (unit conversion = 3.17x 10<sup>2</sup>) (Safety factor = 10) = (6.4x 10<sup>-5</sup>)X (100)x(229.0)x(3.17x102)x(10) = 4600 \mug/m 3
```

#### <u>Step5 - Compare Results to Health Criteria</u>

Available health-based criteria from the <u>RFI Guidance</u> were entered into the Concentration Estimation Worksheet (see Exhibit 3-2). These results indicate that carbon tetrachloride concentrations at the nearest receptor significantly exceed the carcinogenic health-based criteria. Based on the expected carbon tetrachloride concentrations, this unit is a prime candidate for unit-specific emission rate and dispersion modeling to confirm the need for an RFI for the air media.

#### 3.2 Case Study B

Case Study B involves a closed landfill of 7 acres with a waste-bed thickness of 25 feet and a cap thickness of 6 feet. Benzene is believed to be a primary constituent of the waste (approximately 10 percent). The closest resident lives 1 mile east of the unit. The prevailing winds (which occur 20 percent of the time annually, based on available facility data) are from the west (i.e., these winds will affect the downwind sector east of the unit). Following is a summary of the screening assessment for Case Study B.

#### Step 1- Obtain Source Characterization Information

The appropriate Emission Rate Estimation Worksheet for Case Study B is Table S-8 for closed landfill units: The unit information provided is sufficient to complete Column 2 of the worksheet, with one exception (see Exhibit 3-3): the air porosity of the fixed waste is not known. Therefore, typical conditions [i.e., 25 percent as represented by Cases 14 and 22 (see Table J-1) will be assumed for this assessment].

#### Step 2- Select Release Constituent Surrogates

Based on Figure 2-3, it is apparent that the Raoult's Law surrogate subset (Table B-2) is appropriate for a closed landfill unit. Evaluation of Table B-3 indicates that the following surrogate is applied to Case Study B:

<u>Constituent</u>	Surrogate No.	Surrogate Code
Benzene	1	HVHB

#### Step 3- Calculate Emission Estimates

The calculational inputs for the Emission Rate Estimations Worksheets for Case Study B are presented in Exhibit 3-3 and 3-4. Scenario Case 1 (Exhibit 3-3) and Scenario Case 2 (Exhibit 3-4) were selected to bracket the actual waste-bed thickness for the example unit. Scenario Case 1 is associated with a waste-bed thickness of 15-feet and Case 2 with a 30-foot bed thickness. The actual waste-bed thickness is 25 feet. The resulting benzene emission rate estimates range from 46.4 x 10<sup>6</sup>g/yr to 83.4 x 10<sup>6</sup>g/yr.

EXHIBIT 3-4
TABLE S-8
EMISSION RATE ESTIMATION WORKSHEET - CLOSED LANDFILL EXAMPLE

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col6	Col 7	Col 8	Col9	Col10	Col11	Col 12	
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix F -	Instruction C:  Determine Surrogate-Specific Scaling Factors**									
	Parameters	Values	Table F-1 (underline selected case)	нунв	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVНВ	VHVL8	
1	Area*	7acres											
2 \	Waste-bed thickness*	<u>25</u> ft	l, <u>2</u> ,3 or 4	1.8		*************************		<del></del>					
3 C	Cap thickness	<u>6</u> ft	5, 6, <u>7</u> or8	0.95	<del></del>				*****************				
4 (	Constituent content of waste*	10 percent	<u>9,</u> 10, 11 or 12	<u>1.0</u>	*******	***************************************					<del></del>		
5 A	Air porosity (fixed waste)	25 percent	13, <u>14</u> , 15 or16	<u>1.0</u>			<del></del>			<del></del>			
	Co	INSTRUCTION E				<u>s</u>	URROGAT	E-SPECIF	IC VALUE	<u>:S</u>			
်[ur	Account for Area nit-specific area/(Ca	se 22 area = 3	s.5 acres)]	2.0	_	_	_						
7	Typical Surrogate-Specific Emission Rate (Case 22), 10° g/yr				22.4	47.0	0.445	0.398	0.808	1.55E- 05	119	264	
8	Calculate Unit-Spe (multiply lines#2 x		83.4					****************			****		

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-5 from Appendix J - Emission Rate Estimate from Table J-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

#### Step 4- Calculate Concentration Estimates

The example Concentration Estimation Worksheets for Case Study Bare presented in Exhibits 3-5 (Scenario Case 1) and 3-6 (Scenario Case 2). The resulting benzene concentration at the nearest receptor is estimated to range from 69  $\mu g/m^3$  to 124  $\mu g/m^3$ .

#### Step 5- Compare Results to Health Criteria

A review of results presented in Exhibits 3-5 and 3-6 indicates that the estimated benzene concentrations of 69  $\mu g/m^3$  to 124  $\mu g/m^3$  are approximately 1000 times the carcinogenic criterion of 0.1  $\mu g/m^3$ . A toxic criterion is not available for benzene. Based on the results presented in Exhibits 3-5 and 3-6, this unit is a prime candidate for an air release RFI.

EXHIBIT 3-5
TABLE R-1
CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE (Scenario Case 1)

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13	
	Instruction A:	<del></del> )	Instruction C: Assume		(sel	C ect and cir	ompute Lo cle approp	ng-Term C riate surro	oncentrat	nstruction ion Estima et, Henry's	tes (µg/m³)	) Based on ant or Raou	Equation 1" ult's Law or particle case)
Downwind Sector	Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	or VHVLB	= Henry's Law Constant Surrogate = Raoult's Law Surrogate
N				1	*********		<del></del>			<del></del>			
NNE			<u> </u>	<del>                                     </del>			<del></del>						
NE				<del> </del>									
ENE				1									
E	1.0	4.7 x 10-6	100	69									
ESE				<del>                                     </del>				<del></del>					
SE			1						*******				
SSE				<b> </b>						<del></del>	<del></del>		
S													
SSW				1					···			· · · · · · · · · · · · · · · · · · ·	
SW				1									<del></del>
wsw											<del></del>		
W									~	·····			
WNW				<u> </u>			<del>~~~~~~~</del>				<del></del>		
NW				I			<del></del>	<del></del>	<del></del>				
WWW			I	1									

Equation 1 Long-Term Concentration Est. (µg/m²) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17x 10) x (Safety Factor = 10)
\*\* Distance from downward unit boundary

NA Not available

 $Mg/yr = 10^{\circ}g/yr$ 

<sup>\*\*\*</sup> Criterion for benzene

# EXHIBIT 3-6 TABLE R-1 CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE (Scenario Case 2)

Col 1	Çol 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13			
	Instruction A:		Instruction C: Assume		(sele				oncentrat		tes (µg/m³)		Equation 1* ilt's Law or particle case)		
Distance to Downwind Receptors** Sector (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Annual Downwind Frequency of 100% (percent)	Downwind Frequency of 100%	Downwind Frequency of 100%	Downwind Frequency of 100%	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	or VHVLB	= Henry's Law Constant Surrogate = Raoult's Law Surrogate
N							<del></del>								
NNE															
NE															
ENE															
E	1.0	4.7 x 10 <sup>-6</sup>	100	124											
ESE												,,			
SE															
SSE															
5															
SSW															
SW															
wsw				<u> </u>											
N				<b></b>											
WNW				<b></b>							·				
NW				<b> </b>											
WNV										~		erena de la composición dela composición de la composición de la composición de la composición de la composición dela composición de la composición de la composición dela composición dela composición de la composición dela composición de la composición dela composición dela composi			
	ealth Criteria (µg/m³) Toxic Criteria ased on RFI Guidance Carcinogenic Criteria			NA 0.1***								,			

<sup>\*</sup> Equation 1 Long-Term Concentration Est. (μg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17 x 10²) x (Safety Factor = 10)

NA Not available

 $Mg/yr = 10^6 g/yr$ 

<sup>\*\*</sup> Distance from downward unit boundary

<sup>\*\*\*</sup> Criterion for benzene

#### 4.0 REFERENCES

- U.S. EPA, September 1985 (and subsequent supplements): <u>Compilation of Air</u> Pollutant Emission Factors, Vol. I, Washington, DC 20460.
- U.S. EPA, June 1974. <u>Development of Emission Factors for Fugitive Dust Sources.</u> Research Triangle Park NC, 27711.
- U.S. EPA, March 1978. <u>Fugitive Emissions from Integrated Iron and Steel Plants.</u> EPA 600/2-78-050, Washington, D.C.
- U.S. EPA, July 1988. <u>Guidelines on Air Quality Models (Revised).</u> EPA-450/2 -78-027R,. Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711.
- U.S. EPA. December 1987. <u>Hazardous Waste Treatment Storage and Disposal Facilities (TSDF) Air Emission Models.</u> Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711 (CHEMDAT6).
- U.S. EPA, 1989. <u>RCRA Facility Investigation (RFI) Guidance.</u> Office of Solid Waste, Washington, D.C. 20460.
- Turner, D.B. 1969. Workbook of Atmospheric Dispersion Estimates. Public Health Service, Cincinnati, OH.

#### A.O BACKGROUND INFORMATION

The air release screening assessment methodology has been developed based on use of available air emissions models applicable to facilities for treatment, storage, and disposal of hazardous waste, and on results of atmospheric dispersion modeling. The emission models were used to calculate emission rates for a wide range of source scenarios. (An emission rate is defined as the source release rate for the air pathway in terms of mass per unit of time.) These modeling results have been summarized in this document so that they can be easily used by Environmental Protection Agency (EPA) Regional and State Agency staff to estimate emission rates for facility-specific and unit-specific applications. These source-specific emission rates can be used in conjunction with dispersion modeling results, representative of typical annual conditions, to estimate long-term ambient concentrations at locations of interest. (Ambient concentrations are defined as the concentrations of the released constituent downwind from the source. ) The emission rate and atmospheric dispersion modeling approaches used to develop the screening methodology are discussed in the subsections that follow.

#### A.1 Emission Rate Models

The air release screening assessment methodology has been based primarily on application of air emission models (available on a diskette for use on a microcomputer) developed by EPA's Office of Air Quality Planning and Standards (OAQPS) to estimate organic releases for hazardous waste treatment, storage, and disposal facilities (TSDFs) (U.S. EPA, December 1987). Computer-compatible air emission models (referred to as CHEMDAT6 models) are available for the following sources:

- Surface impoundments, which for modeling purposes include quiescent impoundments, aerated impoundments, and open -top tanks
  - Disposal impoundments
  - Storage impoundments
  - Oil films on storage impoundments
  - Aerated impoundments

- Land treatment
  - Soil emissions subsequent to waste tilling
  - Oil film surfaces
- Closed landfills
- Open landfills
- Waste piles

Since the results presented in this document are based on the December 1987 version of CHEMDAT6, subsequent modifications to any of these models may require revisions to this screening methodology

The available models for CHEMDAT6 provide a basis to estimate emissions for numerous unit categories (e.g., surface impoundments, landfills) as previously listed. Therefore, the CHEMDAT6 models will be applicable to a wide range of air release screening assessments. CHEMDAT6 (December 1987 versions) does not, however, include models for the following sources:

- Land treatment waste application
- Fixation pits
- Container loading
- Container storage
- Container cleaning
- Stationary tank loading
- Stationary tank storage
- Fugitive emissions
- Vacuum truck loading

However, guidance for estimating organic emissions from these sources is available from OAQPS (U.S. EPA, December 1987).

In addition to the CHEMDAT6 model, emission equations from EPA's AP-42, "Compilation of Air Pollutant Emission Factors" and "Fugitive Emissions from Integrated Iron and Steel Plants" have been used for estimating organic emissions from storage tanks and particulate matter emissions that are less than 10 microns in diameter from storage piles and exposed areas which result from wind erosion and activities on storage piles.

#### A.2 Source Scenarios

A wide range of source scenarios were evaluated as a basis for developing the air release assessment methodology. This involved identification of a limited set of surrogates to represent the numerous individual potential air release constituents of concern. This also involved evaluating of the sensitivity of the input parameters used by the CHEMDAT6 air emission models and the AP-42 emission equation input parameters.

#### A.2.1 Release Constituent Surrogates

A limited set of surrogates was required to simplify the air release assessment methodology since the list of potential air release constituents included in the RFI <u>Guidance</u> (U.S. EPA, 1988) is extensive. The set of surrogates selected for this application was the same list developed by OAQPS for assessment of organic emissions from TSDFs (see Appendix B).

Two subsets of surrogates are presented in Appendix B. The first subset is applicable to air emission modeling applications based on the *use* of the Henry's Law Constant (Table B-1) and the second subset is based on use of Raoult's Law (Table B-2). Raoult's Law accurately predicts the behavior of most concentrated mixtures of water and organic solvents (i. e., solutions over 10 percent solute). According to Raoult's Law, the rate of volatilization of each chemical in a mixture is proportional to the product of its concentration in the mixture and its vapor pressure. Therefore, Raoult's Law can be used to characterize potential for volatilization. This is especially useful when the unit of concern entails container storage, tank storage, or treatment of concentrated waste streams.

The Henry's Law Constant is the ratio of the vapor pressure of a constituent to its aqueous volubility (at equilibrium). This constant can be used to assess the relative ease with which the compound may vaporize from the aqueous solution and will be most useful when the unit being assessed is a surface impoundment or tank containing dilute wastewaters. The potential for significant vaporization increases as the value for the Henry's Law Constant increases; when it is greater than 1OE-3, rapid volatilization will generally occur.

The surrogates presented in Appendix B span the range from very high volatility to low volatility (frequently classified as semi-volatiles). Biodegradation potential has also been accounted for in the surrogate specifications. Therefore, a cross-reference of constituents has also been provided in Appendix B (Table B-3). This listing provides the basis for the identification of the appropriate surrogate for individual air release constituents of interest. Instructions for use of Appendix B data are provided in Section 2.

#### A.2.2 Sensitivity Analyses

Sensitivity analyses of the input parameters used by the CHEMDAT6 air emission models emission rate relative to output were evaluated to determine the feasibility of developing a source characterization index. The object of the source characterization index was to define a simple relationship between the primary source description parameters and the emission rate of the release. This evaluation was accomplished by modeling a series of source scenario cases for each unit category (i. e., categories such as surface impoundments and landfills). Each of these source scenario cases represents long-term (i. e., annual) emission conditions. A base case representative of typical source conditions was defined for each unit category. These typical conditions were specified based on TSDF survey results and on guidance presented in the OAQPS air emissions modeling report (U.S. EPA, December 1987). This base case provided a standard for comparison to results of parametric analyses. The parametric analyses consisted of varying (one at a time) the input values for the most sensitive modeling parameters. These input parameter values were varied over a range of expected source conditions. In addition to the parametric analyses and the typical (base-case) scenario, a reasonable best-case (minimum emission rate) and a reasonable worst-case (maximum emission rate) source scenario were also modeled. The most sensitive modeling parameters and their associated range of values were determined by considering model sensitivity results and TSDF source survey information presented in the OAQPS air emission modeling report (U.S. EPA, December 1987), as well as other judgmental factors. A similar sensitivity analysis was performed for the three tank types.

A summary of the air emissions modeling parameters, input values, and modeling results (emission rates) is presented in Appendices C through Q. Evaluation of these results indicates that emission rates are highly dependent on numerous sensitive source parameters. Therefore, these complex relationships are not conducive to development of a source characterization index (i.e., defining a simple relationship between the primary source description parameters and the emission rate of the release). However, the modeling results presented in Appendices C through Q provide data which can be interpolated to estimate unit-specific emission rates with minimal guidance. The methodology for application of these data is discussed in Section 2.

#### A.3 Atmospheric Dispersion Conditions

Atmospheric dispersion conditions affect the downwind dilution of emissions from a source. Available EPA dispersion models can be used to account for site specific meteorological and source conditions. For this screening assessment, modeling results are presented which represent typical dispersion conditions (neutral stability and 10-mph winds) in the United States.

Dispersion modeling results to be used for the screening assessment (assuming flat terrain) are presented in Appendix R (Figure R-1) and are applicable to ground-level sources with non-buoyant releases (this assumption is valid for surface impoundments, land treatment units, landfills, waste piles, tanks, and exposed areas). These results are presented in terms of dispersion factors. Dispersion factors can be considered as the ratio of the ambient concentration to the source emission rate. Therefore, dispersion factors facilitate the calculation of ambient concentrations if emission rate estimates are available.

The dispersion factors presented in Figure R-1 were developed from similar dispersion graphs presented in a standard technical reference (Turner, 1969). These dispersion factors are applicable to long-term (e.g., annual) conditions. It has been assumed that dispersion factors (and, thus also ambient concentrations) decrease as a function of downwind distance but are uniform in the crosswind direction within a 22.5 degree sector (22.5 degree sectors correspond with major compass directions such as N, NNW, NW, etc.). The dispersion factors presented in Figure R-1 also account for the initial plume size, which corresponds to the surface area of the

resource (Turner, 1969). Results presented in Figure R-1 are expected to be similar to results from the EPA-approved Industrial Source Complex dispersion model.

Appendix B

Release Constituent Surrogate Data

TABLE B-1
SURROGATE PROPERTIES - HENRY'S LAW CONSTANT SUBSET

Code	No.	Characteristics	Henry's Law* Constant 298°K
MHLB	6	medium Henry's Law, low biodegradation	2.22E-05
HHLB	3	high Henry's Law, low biodegradation	3.00E-02
LHMB	8, 9	low Henry's Law, medium biodegradation	1.58E-07
МНМВ	5	medium Henry's Law, medium biodegradation	4.08E-05
ннмв	2	high Henry's Law, medium biodegradation	1.18E-03
LHHB	7	low Henry's Law, high biodegradation	1.58E-07
МННВ	4	medium Henry's Law, high biodegradation	6.80E-05
НННВ	1	high Henry's Law, high biodegradation	5.38E-03

\*Key: low Henry's Law Constant < 1.0E-05 atm-m<sup>3</sup>/g mol medium Henry's Law Constant 1.0E-05 - 1.0E-3 high Henry's Law Constant > 1.0E-03

TABLE B-2
SURROGATE PROPERTIES - RAOULT'S LAW SUBSET

Code	No.	Characteristics	Vapor Pressure (25°C)
HVHB	1	high volatility, high biodegradation	206
HVMB	2	high volatility, medium biodegradation	182
HVLB	3	high volatility, low biodegradation	256
MVHB	4	medium volatility, high biodegradation	2.62
MVMB	5	medium volatility, medium biodegradation	2.02
MVLB	6	medium volatility, low biodegradation	2.91
LVMB	7, 8, 9	low volatility, medium biodegradation	0.0001
VHVHB	10, 11	very high volatility, high biodegradation	1890
VHVLB	12	very high volatility, low biodegradation	2030

\*Key: low volatility, < 1.0E-05 atm medium volatility, 1.0E-05 - 1.0E-3 high volatility, 1.0E-03 - 1.0 very high volatility, > 1.0

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
Acrylamide	79-06-1	7	4
Acrylonitrile	107-13-1	4	1
Aldicarb	116-06-3	8	9
Aldrin	309-00-2	3	7
Aniline	62-53-3	8	5
Arsenic	7440-38-2	0	0
Benz(a)anthracene	56-55-3	9	7
Benzene	71-43-2	1	1
Benzo(a)pyrene	50-32-8	9	8
Beryllium	7440-41-7	0	0
Bis(2-chloroethyl)ether	111-44-4	5	5
Bromodichloromethane	75-27-4	3	7
Cadmium	7440-43-9	0	0
Carbon tetrachloride	56-23-5	3	3
Chlordane	57-74-9	6	7
1 -Chloro-2, 3- epoxy propane (Epichlorohydrin)	106-89-8	6	3
Chloroform	67-66-3	3	3
Chromium (hexavalent)	7440-47-3	0	0
DDT	50-29-3	3	7
Dibenz(a,h) anthracene	53-70-3	9	7
1,2-Dibromo-3- Chloropropane (DBCP)	96-12-8	6	6
1,2-Dibromoethane	106-93-4	3	3
1,2-Dichloroethane	107-06-2	3	3
1,1-Dichloroethylene	75-35-4	3	3
Dichloromethane (Methylene chloride)	75-09-2	1	1

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES (Continued)

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
2,4-Dichlorophenol	120-83-2	8	5
2,4-Dinitrophenol	51-28-5	9	3
2,4-Dinitrotoluene	121-14-2	9	6
1,4-Dioxane	123-91-1	6	3
1,2-Diphenylhydrazine	122-66-7	9	7
Endosulfan	115-29-7	9	7
Ethylene oxide	75-21-8	4	10
Heptachlor	76-44-8	3	7
Hexachlorobenzene	118-74-1	6	7
Hexachlorobutadiene	87-68-3	3	6
Hexachloroethane	67-72-1	9	6
Hydrazine	302-01-2	9	3
Isobutyl alcohol	78-83-1	7	4
Lindane (gamma- Hexachlorocyclohexane)	58-89-9	9	7
3-Methyl-cholanthrene	56-49-5	6	7
4,4-Methylene-bis-(2- chloroaniline)	101-14-4	3	6
Methyl parathion	298-00-0	6	6
Nickel	1440-02-0	0	0
Nickel (refinery dust)	7440-02-0	0	0
Nickel subsulfide	12035-72-2	0	0
2-Nitropropane	79-46-9	6	3
N-Nitroso-N-methyl urea	684-93-5	5	9
N-Nitroso-pyrrolidine	930-55-2	2	2
Pentachlorobenzene	608-93-5	3	6
Pentachlorophenol	87-86-5	9	7

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES (Continued)

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
Perchloroethylene (Tetrachloroethylene)	127-18-4	3	3
Styrene	100-42-5	3	6
1,2,4,5- Tetrachlorobenzene	95-94-3	3	6
1,1,2,2-Tetrachloroethane	79-34-5	6	6
2,3,4,6-Tetrachlorophenol	58-90-2	9	6
Tetraethyl lead	78-00-2	3	6
Thiourea	62-56-6	6	3
Toxaphene	8001 -35-2	3	6
1,1,2-Trichloroethane	79-00-5	6	3
Trichloroethylene	79-01-6	3	3
2,4,5-Trichlorophenol	95-95-4	6	6
2,4,6-Trichlorophenol	88-06-2	6	6

## Appendix C

Emission Rate Estimates Disposal Impoundments (Quiescent Surfaces)

TABLE C-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - DISPOSAL IMPOUNDMENT\*

Modeling		CASE NUMBERS																	
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	3.6
Turnovers (per yr)	2	2	2	2	0.5	1	2	3	2	2	2	2	2	2	2	2	1	2	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	10	1000	4000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

- Input assumptions:
   Active biomass = 0.0 g/l
   Biomass solids in = 0.0 m³/sec
   Submerged air flow = 0.0 m³/sec
  Reasonable Best Case (minimum) Emissions (assuming typical source area)

  \* \* \* Typical Emission Conditions (assuming typical source area)

  \* \* \* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAt6 be used to calculate emission estimates directly.

TABLE C-2
EMISSION RATE ESTIMATES (106 g/yr) - DISPOSAL IMPOUNDMENT

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	16.2	32.4	64.8	89.9	8.1	16.2	32.4	48.6
HHLB	16.2	32.4	64.8	90.0	8.1	16.2	32.4	48.6
LHMB	11.0	14.1	16.1	16.7	7.3	11.0	14.1	15.4
мнмв	16.2	32.4	64.8	90.0	8.1	16.2	32.4	48.6
ННМВ	16.2	32.4	64.8	90.0	8.1	16.2	32.4	48.6
LHHB	8.0	9.4	10.1	10.4	6.0	8.0	9.4	9.9
мннв	16.2	32.4	64.8	90.0	8.1	16.2	32.4	48.6
нннв	16.2	32.4	64.8	90.0	8.1	16.2	32.4	48.6
Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	1 Year (Case 13)	5 Years (Case 14)	10 Years (Case 15)	70 Years (Case 16)
MHLB	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
ННГВ	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
LHMB	0.1	14.1	28.2	56.4	14.1	14.1	14.1	14.1
мнмв	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
ННМА	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
LHH8	0.1	9.4	18.7	37.5	9.4	9.4	9.4	9.4
Мннв	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
нннв	0.3	32.4	64.8	129.6	32.4	32.4	32.4	32.4
Henry's Law Constant Surrogate	(Case 17)	(Case 18)	(Case 19)					
MHLB	0.1	32.4	388.4		<b></b>			<u> </u>
ннів	0.1	32.4	388.8				<del> </del>	ļ
LHMB	0.1	14.,1	67.5		1		1	<del> </del>
мнмв	0.1	32.4	388.8		1		<b> </b>	1
ннмв	0.1	32.4	388.8	1	1	l	<u> </u>	1
LHHB	0.1	9.4	41.6		1		l	<b></b>
мннв	0.1	32.4	388.8	1			<del>                                     </del>	1
нннв	0.1	32.4	388.8	<del> </del>	<del> </del>	<del></del>	<del> </del>	<del> </del>

## Appendix D

Emission Rate Estimates
Storage Impoundments/Open Tanks
(Quiescent Surfaces)

TABLE D-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - STORAGE IMPOUNDMENT\*

Modeling									CASE	NUMBE	ERS								
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	5.0
Retention time (days)	20	20	20	20	1	20	50	550	20	20	20	20	20	20	20	20	550	20	1
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	10	1000	4000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

- Input assumptions:
   Active biomass = 0.0 g/l
   Biomass solids in = 0.0 m³/sec
  Reasonable Best Case (minimum) Emissions (assuming typical source area)
  Typical Emission Conditions (assuming typical source area)
  Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

# Appendix E

Emission Rate Estimates
Oil Films on Storage Impoundments

TABLE E-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OIL FILM ON STORAGE IMPOUNDMENT\*

Modeling									CAS	E NUMBE	RS								
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth of oil film (m)	7.2E-04	7.2E-03	7.2E-02	7.2E-01	7.2E-02	7.2E-04	7.2E-02	7.2E-01											
Retention time (days)	20	20	20	20	1	20	50	365	20	20	20	20	20	20	20	20	365	20	1
constituent concentration in oil (ppm)	200	200	200	200	200	200	200	200	100	200	1000	5000	200	200	200	200	100	200	5000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	to	10	to
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

- Input assumptions:
   Oil (fraction of waste) = 1.0
   Molecular weight of oil = 282
   Density of oil = 1.0
  Reasonable Best Case (minimum) Emissions (assuming typical source area)

  \*\* Typical Emission Conditions (assuming typical source area)

  \*\*\* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual Input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly.

F-2

TABLE E-2
EMISSION RATE ESTIMATES (106 g/yr) - OIL FILMS ON STORAGE IMPOUNDMENTS

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
HVMB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
HVLB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
MVHB	3.94E-03	0.039	0.394	1.851	2.115	0.394	0.158	0.022
MVMB	3.94E-03	0.039	0.389	1.388	1.517	0.389	0.158	0.02
MVLB	3.94E-03	0.039	0.394	1.868	2.137	0.394	0.158	0.02
LVMB	1.08E-04	1.10E-04	1.10E-04	1.06E-04	1.02E-04	1.10E-04	1.10E-04	1 08E-(
VHVHB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.02
VHVLB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0 02
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	1 Year	5 Years	10 Years	70 Yea
_		•			(Case 13)	(Case 14)	(Case 15)	(Case 1
HVHB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.39
HVMB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.39
HVLB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.39
нунв	0.197	0.394	1.968	9.838	0.394	0.394	0.394	0.39
MVMB	0.195	0.389	1.945	9.727	0.389	0.389	0.389	0 38
MVLB	0.197	0.394	1.968	9.839	0.394	0.394	0.394	0.39
LVMB	5.50E-05	1.10E-04	5.50E-04	2.75E-03	1.10E-04	1.10E-04	1.10E-04	1.10E-
VHVHB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.39
VHVLB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.39
Raoult's Law Surrogate	(Case 17)	(Case 18)	(Case 19)					
HVHB	1.08E-04	0.394	1863.51					
HVMB	1.08E-04	0.394	1886.53					
HVLB	1.08E-04	0.394	1904.63					
MVHB .	1.08E-04	0.394	60.60					
MVMB	1.08E-04	0.394	41.68					
MVLB	1.08E-04	0.394	61.35					
LVMB	4.25E-05	1.10E-04	1.97E-03					
VHVHB	1.08E-04	0.394	1971.00					
VHVLB	1.08E-04	0.394	1971.00					

## Appendix F

**Emission Rate Estimates Mechanically Aerated Impoundments** 

TABLE F-1 EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - MECHANICALLY AERATED IMPOUNDMENT\*

Modeling											CASE	NUME	ERS										
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	5.0
Retention time (days)	10	10	10	10	3	10	15	20	10	10	10	10	10	10	10	10	10	10	10	10	20	10	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	4000
Fraction agitated	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.17	0.24	0.52	0.87	0.24	0.24	0.24	0.24	0.17	0.24	0.87
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	5	10	70	1	1	1

Oxygen transfer correction factor = 0.83 Impeller diameter = 61 cm Impeller speed = 126 rad/sec

Note: If actual input values, vary significantly from the above scenarios it is recommended that CHEMBAT6 be used to calculateemission estimates directly.

Input assumptions:
- Active biomass = 0.0 g/l
- Biomass solids in = 0.0 m³/sec
- Submerged air flow = 0.0 m³/sec

Number of impellers = 1
Reasonable Best Case (minimum) Emissions (assuming typical source area)

\*\*\*\* Typical Emission Conditions (assuming typical source area)

\*\*\*\*\* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

TABLE F-2
EMISSION RATE ESTIMATES (106 g/yr) - MECHANICALLY AERATED IMPOUNDMENTS

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	47.2	90.6	168.1	220.8	253.9	90.6	62.1	47.2
HHLB	49.2	98.4	196.5	272.6	326.9	98.4	65.6	49.2
LHMB	11.0	12.3	13.2	13.4	13.5	12.3	11.6	11.0
MHMB	48.3	94.7	182.6	246.5	289.4	94.7	64.0	48.3
ННМВ	49.2	98.3	195.8	271.2	324.9	98.3	65.6	49.2
LHHB	7.9	8.5	8.9	9.0	9.1	8.5	8.2	7.9
MHHB	48.6	95.9	187.0	254.6	300.9	95.9	64.5	48.6
НННВ	49.2	98.4	186.4	272.3	326.6	98.4	65.6	49.2
Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
MHLB	0.91	90.6	181.2	362.4	86.6	90.6	95.4	97.0
HHLB	0.98	98.4	196.9	393.8	98.4	98.4	98.5	98.6
LHMB	0.12	12.3	24.7	49.4	8.9	12.3	25.5	40.2
MHMB	0.95	94.7	189.5	379.0	92.6	94.7	97.1	97.9
HHMB	0.98	98.3	196.5	393.0	98.0	98.3	98.5	98.5
LHHB	0.085	8.5	17.1	34.2	6.0	8.5	18.8	31.3
MHHB	0.96	95.9	191.9	383.8	94.4	95.9	97.6	98.1
НННВ	0.98	98.4	196.8	393.6	98.3	98.4	98.5	98.6
Henry's Law Constant Surrogate	1 Year (Case 17)	5 Years (Case 18)	10 Years (Case 19)	70 Years (Case 20)	(Case 21)	(Case 22)	(Case 23)	
MHLB	90.6	90.6	90.6	90.6	0.24	90.6	3,169.2	
HHLB	98.4	98.4	98.4	98.4	0.25	98.4	3,635.2	
LHMB	12.3	12.3	12.3	12.3	0.070	12.3	252.4	
MHMB	94.7	94.7	94.7	94.7	0.24	94.7	3,414.6	
HHMB	98.3	98.3	98.3	98.3	0.25	98.3	3,624.2	
LHHB	8.5	8.5	8.5	8.5	0.050	8.5	174.9	
MHHB	95.9	95.9	95.9	95.9	0.24	95.9	3,487.5	
НННВ	98.4	98.4	98.4	98.4	0.25	98.4	3,633.5	

## Appendix G

Emission Rate Estimates Diffused Air Systems

**TABLE G-1** EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - DIFFUSED AIR SYSTEM\*

Modeling	CASE NUMBERS																						
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23***
Area (acres)	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-0
Depth (m)	2	4	5	6	4	4	4	4	4	4	4 .	4	4	4	4	4	4	4	4	4	2	4	6
Retention time (hours)	4	4	4	4	3	4	5	6	4	4	4	4	4	4	4	4	4	4	4	4	6	4	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	4000
Submerged air flow (m³/sec)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.04	0.045	0.05	0.04	0.04	0.04	0.04	0.03	0.04	0.05
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

Input assumptions:

Active biomass = 0.0 g/l Biomass solids in = 0.0 m³/sec

Fraction agitated = 0.0

Number of impellers = 1

Oxygen transfer corr

Impeller diameter = 1

Oxygen transfer rating = 3 lb O₂/h-hp

Reasonable Best Case (minimum) Emissions (assuming typical source area)

Typical Emission Conditions (assuming typical source area)

Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Power (total) = 75 hp Oxygen transfer correction factor = 0.83 Impeller diameter = 61 cm Impeller speed = 126 rad/sec

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly.

## Appendix H

Emission Rate Estimates Land Treatment (Emissions After Tilling)

**TABLE H-1** EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - LAND TREATMENT (EMISSIONS AFTER TILLING)\*

Modeling		CASE NUMBERS																					
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Annual waste (oil & water) throughput ( 10°g/yr)	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
Oil content of waste(%)	2	10	20	50	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	2	10	50
Constituent of interest content of oil (ppm)	2000	2000	2000	2000	500	2000	5000	10,000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	500	2000	10000
Soil porosity (%)	50	50	50	50	50	50	50	50	43	50	50	65	50	50	50	50	50	50	50	50	43	50	65
Tilling depth (cm)	20	20	20	20	20	20	20	20	20	20	20	20	15	20	40	65	20	20	20	20	65	20	15
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	I	1	1	1	5	10	70	1	1	1

Input assumptions:

- Molecular weight of oil = 282
- Organics (VO) dissolved in water = 0.0 Biodegradation considered = yes
- - Reasonable Best Case (minimum) Emissions (assuming typical source area)
- \* \* \* Typical Emission Conditions (assuming typical source area)
- \* \* \* \* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly.

7-1

TABLE H-2 EMISSION RATE ESTIMATES (10°g/yr) - LAND TREATMENT (EMISSION AFTER TILLING)

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	0.071	0.341	0.650	1.431	0.085	0.341	0853	1.706
HVMB	0.072	0.357	0.708	1.730	0.089	0.357	0.892	1.784
HVLB	0.072	0.359	0.719	1.793	0.090	0.359	0.898	1.796
MVHB	0.044	0.108	0.153	0.243	0.027	0.108	0.271	0.542
MVMB	0.063	0.219	0.338	0.533	0.055	0.219	0.548	1.096
MVLB	0.071	0.338	0.639	1.382	0.085	0.338	0.845	1.690
LVMB	7.92E-04	1.80E-03	2.16E-03	3.60E-03	4.50E-04	1.BOE-03	4.50E-03	9.00E-03
VHVHB	0.072	0.356	0.708	1.728	0.089	0.356	0.891	1.782
VHVLB	0.072	0.359	0.719	1.796	0.090	0.359	0.898	1.796
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
HVHB	0.334	0.341	0.345	0.349	0.346	0341	0.325	0.308
HVMB	0.355	0.357	0.357	0.358	0.357	0.357	0.354	0.351
HVLB	0.359	0.359	0.359	0.359	0.359	0.359	0.359	0.359
HVHB	0.091	0.108	0.121	0.147	0.125	0.108	0.077	0.060
MVMB	0.194	0.219	0.235	0.262	0.240	0.219	0.169	0.133
MVLB	0.330	0.338	0.342	0.347	0.343	0.338	0.319	0.300
LVMB	1.44E-03	1.80E-03	1.80E-03	2.52E-03	2.16E-03	1.80E-03	1.08E-03	1.08E-03
VHVHB	0.355	0.356	0.357	0.358	0.357	0.356	0.354	0.350
VHVLB	0.359	0.359	0.359	0.359	0.359	0.359	0.359	0.359
Raoult's Law Surrogate	(Case 17)	(Case 18)	(Case 19)	(Case 20)	(Case 21)	(Case 22)	(Case 23)	
HVHB	0.341	0.341	0.341	0.341	0.017	0.341	8.118	
HVMB	0.357	0.357	0.357	0.357	0.018	0.357	8.847	
HVLB	0.359	0.359	0.359	0.359	0.018	0.359	8.982	
MVHB	0.108	0.108	0.108	0.108	0.006	0.108	1.908	
MVM8	0.219	0.219	0.219	0.219	0.011	0.219	4.194	
MVLB	0.338	0.338	0.338	0.338	0.017	0.338	7.974	
LVMB	1.80E-03	1.80E-03	1.80E-03	1.80E-03	9.00E-05	1.80E-03	2.70E-02	
VHVHB	0.356	0.356	0.356	0.356	0.018	0.356	8.838	
VHVLB	0.359	0.359	0.359	0.359	0.018	0.359	8.982	

#### Appendix I

Emission Rate Estimates
Oil Film Surface on Land Treatment Units

TABLE I-1 EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OIL FILM SURFACE ON LAND TREATMENT UNITS\*

Modeling									CASI	NUMBI	ERS								
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19***
Area (acres)	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Depth of oil film (m)	7.2E-04	7.2E-03	7.2E-02	7.2E-01	7.2E-02	7.2E-04	7.2E-02	7.2E-0											
Number of Applications per year	365	365	365	365	20	50	365	730	365	365	365	365	365	365	365	365	20	365	730
Constituent concentration in oil (ppm)	200	200	200	200	200	200	200	200	100	200	1000	5000	200	200	200	200	100	200	5000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

- Input assumptions:
  - Flow =  $0.0 \,\mathrm{m}^3/\mathrm{sec}$
  - Oil (fraction of waste) = 1.0
  - Molecular weight of oil = 282
  - Density of oil = 1.0 g/cc
- Reasonable Best Case (minimum) Emissions (assuming typical source area)
- \*\*\* Typical Emission Conditions (assuming typical source area)

  \*\*\*\* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly.

TABLE I-2
EMISSION RATE ESTIMATES (106 g/yr) - OIL FILM SURFACE ON LAND TREATMENT UNIT

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	' (Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	1.3	13.1	131.4	1,205.2	7.2	18.0	131.4	262.8
HVMB	1.3	13.1	131.4	1,225.5	7.2	18.0	131.4	262.8
HVLB	1,3	13.1	131.4	1,242.0	7.2	18.0	131.4	262.8
MVHB	1.3	12.2	30.8	34.7	7.1	15.4	30.8	32.7
MVMB	1.3	11.0	22.0	23.8	6.9	13.2	22.0	22.8
MVLB	1.3	12.3	31.2	35.1	7.1	15.5	31.2	33.1
LVMB	1.55E-03	1.54E-03	1.45E-03	1.31E-03	1.54E-03	1.53E-03	1.45E-03	1.31E-
VHVHB	1.3	13.1	131.4	1,314.0	7.2	18.0	131.4	262.8
VHVLB	1.3	13.1	131.4	1,314.0	7.2	18.0	131.4	262.8
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	1 Year (Case 13)	5 Years (Case 14)	10 Years (Case 15)	70 Yea (Case 1
HVHB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVMB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVLB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVHB	15.4	30.8	154.2	771.1	30.8	30.8	30.8	30.8
MVMB	11.0	22.0	109.9	549.7	22.0	22.0	22.0	22.0
MVLB	15.6	31.2	155.9	779.5	31.2	31.2	31.2	31.2
LVMB	7.23E-04	1.45E-03	7.23E-03	0.036	1.45E-03	1.45E-03	1.45E-03	1.45E-
VHVHB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
VHVLB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
Raoult's Law Surrogate	(Case 17)	(Case 18)	(Case 19)					
HVHB	0.036	131.4	46,072.4					·
HVMB	0.036	131.4	47,942.7				*	<del></del>
HVLB	0.036	131.4	49,634.6					
MVHB	0.036	30.8	846.7					
MVMB	0.036	22.0	580.7					
MVLB	0.036	31.2	857.3					
LVMB	7.62E-04	1.45E-03	.038			<del></del>		
VHVHB	0.036	131.4	65,699.1					
VHVLB	0.036	131.4	65,699.7					<del></del>

#### Appendix J

#### Emission Rate Estimates Closed Landfills

TABLE J-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - CLOSED LANDFILL (VENTED)\*

Modeling											CASE	NUMBE	RS										
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Waste-bed thickness (ft)	15	30	60	120	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	120
Cap thickness (ft)	3.5	3.5	3.5	3.5	2	3.5	5	6	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	6	3.5	2
Weight percent organics (VO) in waste	40	40	40	40	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	25	25	25	25	5	25	50	75	25	25	25	25	5	25	75
Waste liquid density (g/cm³)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Cap air porosity (%)	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Cap total porosity (%)	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41
Temperature beneath cap (°C)	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Typical barometric pressure (mb)	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013
Typical barometric pressure drop (mb)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

#### \* Input assumptions:

- 100% of the organics in waste is the constituent of interest
- Weight percent oil in waste = 0.0% (fraction = 0.0)
- Weight percent water in waste = 100%-organics (fraction = 1.0-organics)
   Barometric pumping time = 86,400 sec
   Molecular weight oil = 147

\*\*

- Reasonable Best Case (minimum) Emissions (assuming typical source area)
- Typical Emission Conditions (assuming typical source area)
  - Reasonable Worst Case (maximum) Emissions (assuming typical source area)

- CHEMDAT6 CC/GVOC conversion factor = 1750

- Active biomass = 0.0 g/cc

- Organics dissolved in water = 0 (i.e., use Raoult's Law)

R ho-liquid density = 1.0 g/cm<sup>3</sup>

- Molecular weight of liquid = 18

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE J-2
EMISSION RATE ESTIMATES (10°g/yr) - CLOSED LANDFILL (VENTED)

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	2.44E +01	4.44E +01	8.44E +01	1.64E + 02	2.78E +01	2.44E +01	2.31 E+01	2.26E +01
HVMB	2.24E +01	3.96E +01	7.40E +01	1.43E +02	2.63E +01	2.24E +01	2.08E +01	2.02E +01
HVLB	4.69E +01	8.60E +01	1.64E +02	3.20E +02	5.29E +01	4.70E +01	4.46E +01	4.37E +01
MVHB	4.45E -01	8.24E-01	1.58E +00	3.10E +00	4.94E-01	4.45E-01	4.25E-01	4.18E-01
MVMB	3.98E-01	7.46E-01	1.44E+00	2.83E +00	4.36E-01	3.98E-01	3.83E-01	3.77E-01
MVLB	8.08E-01	1.51 E+00	2.92E+00	5.73E +00	8.88E-01	8.08E-01	7.77E-01	7.64E-01
LVMB	1.55E-05	2.83E-05	5.39E-05	1.05E-04	1.76E-05	1.55E -05	1.47E-05	1.44E-05
VHVHB	1.19E +02	2.15E +02	4.09E +02	7.96E +02	1.35E +02	1.19E +02	1.12E +02	1.0E +02
VHVLB	2.64E +02		9.03E +02	1.76E +03	3.02E +02	2.64E +02	2.49E + 02	2.43E +02
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
HVHB	2.44E +01	2.44E +01	2.44E +01	2.44E +01	8.45E +00	2.44E +01	4.44E +01	6.44E +01
HVMB	2.24E +01	2.24E +01	2.24E +01	2.24E +01	8.63E +00	2.24E+01	3.96E +01	5.68E +01
HVLB	4.68E +01	4.70E +01	4.70E +01	4.70E +01	1.57E +01	4.70E +01	8.60E +01	1.25E +02
MVHB	4.45E-01	4.45E-01	4.45E-01	4.45E-01	1.41E-01	4.45E-01	8.25E-01	1.20E+O0
MVMB	3.98E-01	3.98E-01	3.98E-01	3.98E-01	1.20E-01	3.98E-01	7.46E-01	1.09E +00
MVLB	8.08E-01	8.08E-01	8.08E-01	8.08 E-O1	2.46E-01	8.08E-01	1.51E +00	2.21E+O0
LVMB	1.55E-05	1.55E-05	1.55E-05	1.55E-05	5.29E-06	1.55E-05	2.83E-05	4.11E-05
VHVHB	1.18E +02	1.19E +02	1.19E +02	1.19E +02	4.14E +01	1.19E +02	2.15E +02	3.11E +02
VHVLB	2.61E+02	2.64E +02	2.64E +02	2.65E + 02	9.40E+01	2.64E +02	4.75E +02	6.85E +02
Raoult's Law Surrogate	1 Year (Case 17)	5 Years (Case 18)	10 Years (Case 19)	70 Years (Case 20)	(Case 21)	(Case 22)	(Case 23)	
HVHB	2.44E +01	2.44E +01	2.44E +01	2.38 +01	6.59E +00	2.44E +01	4.88E +02	
HVMB	2.24E +01	2.24E+01	2.23E +01	2.18E +01	6.47E +00	2.24E +01	4.22E +02	
HVLB	4.70E+01	4.68E +01	4.66E+01	4.45E +01	1.24E +01	4.70E +01	9.51E+02	· · · · · · · · · · · · · · · · · · ·
MVHB	4.45E-01	4.45E-01	4.45E-01	4.45E-01	1.14E-01	4.45E-01	9.22E+00	
м∨мВ	3.98E-01	3.98E-01	3.98E -01	3.98E -01	9.89E 02	3.98E-01	8.44E +00	
MVLB	8.08E-01	8.08E-01	8.08E -01	8.08E-01	2.02E-01	8.08E-01	1.70E + 01	
LVMB	1 55E-05	1.55E-05	1.55E-05	1.55E-05	4 15E-06	1.55E-05	3 12E-04	
VHVHB	1.19E + 02	1.18E + 02	1.17E + 02	1 04E + 02	3.22E + 01	1 19E + 02	2.36E + 03	
VHVLB	2.64E + 02	2 60E + 02	2.54E + 02	1.98[ + 02	7 24E + 01	2.64E + 02	5.20E + 03	

## AppendixK

Emission Rate Estimates
Open Landfills

TABLE K-1 EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OPEN LANDFILL\*

Modeling											CASE	NUMBE	RS										
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Waste-bed thickness (ft)	3	7.5	15	30	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	3	7.5	30
Constituent content of waste (%)	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	5	25	35	50	25	25	25	25	25	25	25	25	5	25	50
Total porosity of fixed waste (%)	50	50	50	50	50	50	50	50	50	50	50	50	10	25	50	75	50	50	50	50	75	50	10
Waste liquid density (g/cm³)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

Note: If actual values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly.

Input assumptions
Organic (VO) concentration of waste = 1,000,000 ppmw
Molecular weight of oil = 147
Organics dissolved in water = O (i.e., no)
Biodegradation = O (i.e., no)

\*\*\*
\*\*\*
Reasonable Best Case (minimum) Emissions (assuming typical source area)
Typical Emission Conditions (assuming typical source area)

\*\*\*\*
Reasonable Worst Case (maximum) Emissions (assuming typical source area)

TABLE K-2
EMISSION RATE ESTIMATES (106 g/yr) OPEN LANDFILL

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6) _	(Case 7)	(Case 8)
HVHB	769.2	766.2	781.2	781.2	386.9	766.2	946.5	1149.3
HVMB	841.3	841.3	B41.3	841.3	420.7	841.3	1036.6	1250.7
HVLB	817.3	811.3	811.3	841.3	409.4	811.3	991.6	1216.9
MVHB	78.1	75.1	90.1	60.1	37.6	75.1	90.1	101.4
MVMB	60.1	60.1	60.1	60.1	30.0	60.1	67.6	101.4
MVLB	78.1	75.1	90.1	60.1	37.6	75.1	90.1	101.4
LVMB	0.5	0.6	0.6	0.6	0.3	0.6	0.7	0.7
VHVHB	2361.7	2358.7	2373.8	2343.7	1179.4	2358.7	2884.6	3549.4
VHVLB	2518.0	2509.0	2524.0	2524.0	1258.2	2509.0	3087.4	3786.0
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
HVHB	30.0	766.2	1592.5	3455.5	3846.1	1547.5	766.2	510 8
HVMB	30.0	841.3	1742.8	3786.0	4206.7	1682.7	841.3	555.9
HVLB	30.0	811.3	1697.7	3680.8	4086.5	1637.6	811.3	540.9
MVHB	2.4	75.1	165.3	345.5	375.6	150.2	75.1	45.1
MVMB	2.0	<b>`6</b> 0.1	120.2	270.4	300.5	120.2	60.1	45.1
MVLB	2.3	75.1	150.2	330.5	375.6	150.2	75.1	45.1
LVMB	0.02	0.6	1.1	2.4	2.7	1.1	0.6	0.3
VHVHB	75.1	2358.7	4882.7	10336.4	11297.9	4717.5	2358.7	1577.5
VHVLB	75.1	2509.0	5213.3	10907.3	11853.8	5033.0	2509.0	1682.7
Raoult's Law Surrogate	1 year (Case 17)	5 years (Case 18)	10 years (Case 19)	70 years (Case 20)	(Case 21)	(Case 22)	(Case 23)	
HVHB	766.2	1727.7	2433.9	6445.2	7.9	766.2	25961.1	
HVMB	841.3	1878.0	2659.2	7046.2	8.6	841.3	28395.0	
HVLB	811.3	1832.9	2584.1	6850.9	8.4	811.3	27583.7	
MVHB	75.1	165.3	240.4	646.0	0.8	75.1	2569.1	
MVMB	60.1	135.2	195.3	510.8	0.6	60.1	2028.2	Î
MVLB	75.1	165.3	240.4	631.0	0.8	75.1	2569.1	
LVMB	0.6	1.2	1.7	4.4	0.01	0.6	17.6	1
VHVHB	2358.7	5273.4	7451.8	14558.1	24.1	2358.7	78829.9	
VHVLB	2509.0	5618.9	7917.5	14723.3	25.7	2509.0	83697.6	

## Appendix L

Emission Rate Estimates Wastepiles

TABLE L-1 EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - WASTEPILES\*

Modeling											CASE	NUMBE	RS										
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Turnover rate (per year)	730	365	140	52	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	52	140	730
Constituent content of waste (%)	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	5	25	35	50	25	25	25	25	25	25	25	25	5	25	50
Total porosity of fixed waste (%)	50	50	50	50	50	50	50	50	50	50	50	50	10	25	50	75	50	50	50	50	75	50	10
Pile height(m)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Waste liquid density (g/cm³)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	I	1	1	1	1	1	1	5	10	70	1	1	1

- Input assumptions:
  - Organic (VO) concentration of waste = 1,000,000 ppmw
  - Molecular weight of oil = 147
  - Organics dissolved in water = O (i.e., no)
- Biodegradation = O (i.e., no)

  \*\* Reasonable Best Case (minimum) Emissions (assuming typical source area)

  \*\*\* Typical Emission Conditions (assuming typical source area)
- \* \*\*\* Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual Input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE L-2 EMISSION RATE ESTIMATES (106 g/yr) - WASTEPILE

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	595.3	421.1	261.4	159.7	130.6	261.4	320.1	391.7
HVMB	651.6	460.9	284.9	174.4	143.1	284.9	350.2	429 1
HVLB	633.7	447.9	277.0	169.5	139.2	277.0	340.3	416.7
MVHB	59.3	41.9	26.0	15.9	13.0	26.0	31.8	38.9
MVMB	47.6	33.6	20.9	12.7	10.4	20.9	25.6	31.3
MVLB	58.3	41.2	25.5	15.6	12.8	25.5	31.3	38.3
LVM8	0.4	0.3	0.2	0.1	0.1	0.2	0.2	0.3
VHVHB	1824.4	1289.4	799.3	487.9	399.7	799.3	981.3	1199.0
VHVLB	1947.9	1378.6	852.1	520.3	426.7	852.1	1044.6	1282.0
Raoult's Law Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
HVHB	8.0	261.4	540.8	1173.9	1305.8	522.3	261.4	174.1
HVMB	8.8	284.9	593.5	1284.7	1429.8	572.4	284.9	190.7
HVLB	8.5	277.0	575.1	1247.8	1387.6	556.6	277.0	185.2
MVHB	0.8	26.0	53.8	116.6	129.8	52.0	26.0	17 3
MVMB	0.6	20.9	43.3	93.6	104.2	41.7	20.9	13.9
MVLB	0.8	25.5	53.0	114.8	127.7	51.2	25.5	17.0
LVMB	0.01	0.2	0.4	0.8	0.9	0.4	0.2	0.1
VHVHB	24.5	799.3	659.3	3,587.6	4,009.7	1,598.6	799.3	532.9
VHVLB	26.1	852.1	767.4	3,825.0	4,273.5	1,706.8	852.1	569.8
Raoult's Law Surrogate	(Case 17)	(Case 18)	(Case 19)	(Case 20)	(Case 21)	(Case 22)	(Case 23)	
HVHB	261.4	261.4	261.4	261.4	1.6	261.4	20,061.7	
НУМВ	284.9	284.9	284.9	284.9	1.8	284.9	21,944.4	
HVLB	277.0	277.0	277.0	277.0	1.7	277.0	21,327.1	
MVHB	26.0	26.0	26.0	26.0	0.2	26.0	1,993.8	
MVMB	20.9	20.9	20.9	20.9	0.1	20.9	1,601.8	
MVLB	25.5	25.5	25.5	25.5	0.2	25.5	1,959.9	
LVMB	0.2	0.2	0.2	0.2	0.001	0.2	13.7	<del> </del>
VHVHB	799.3	799.3	799.3	799.3	5.0	799.3	61,419.6	
VHVLB	852.1	852.1	852.1	852.1	5.3	852.1	65,431.9	<del>                                     </del>

Appendix M

Emission Rate Estimates
Fixed Roof Tanks

TABLE M-1 EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - FIXED ROOF TANK

Modeling											С	ASE <b>N</b> U	JMBER!	5										
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22*	23**	24***
Tank diameter (ft)	10	20	40	60	100	200	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	20	100	200
Tank height (ft)	40	40	40	40	40	40	10	20	30	40	50	40	40	40	40	40	40	40	40	40	40	40	40	50
Turnovers (per yr)	2674	668	167	74	27	7	107	53	36	27	21	4	21	42	127	212	297	27	27	27	27	668	27	59
throughput (10°gal/yr)	63	63	63	63	63	63	63	63	63	63	63	10	50	100	300	500	700	63	63	63	63	63	63	700
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1		1	I		1	1	I	5	10	70	1	1	1

- Reasonable Best Case (minimum) Emissions (assuming typical tank size)
  Typical Emission Conditions (assuming typical tank size)
  Reasonable Worst Case (maximum) Emission (assuming typical tank size)

Note: If actual input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly.

TABLE M-2
EMISSION RATE ESTIMATES (106 g/yr) - FIXED ROOF TANK

Raoult's Law	(Ca	se 1)	(Cas	e 2)	(Cas	e 3)	(Cas	e 4)	(Cas	se 5)	(Cas	e 6)	(Cas	ie 7)	(Cas	se 8)
Surrogate	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
HVHB*																
HVMB*												· · · · · · · · · · · · · · · · · · ·				
HVLB*	<u> </u>												<u> </u>			
MVHB	1.6E-02	9.3E-01	9.8E-02	9.3E-01	3.6E-01	1.4E + 00	7.3E-01	2.7E + 00	1.8E + 00	3.9E + 00	5.9E + 00	3.9E + 00	8.7E-01	1.8E + 00	1.2E + 00	2.7E + 00
MVMB	1.6E-02	8.5E-01	9.8E-02	8.5E-01	3.6E-01	1.2E + 00	7.3E-01	2.5E + 00	1.8E + 00		5.8E + 00		8.7E-01	1.6E + 00	1.2E + 00	2.5E + 00
MVLB	2.9E-02	1.7E + 00	1.8E-01	1.7E + 00	6.5E-01	2.5E + 00	1,3E + 00		3.2E + 00	7.1E + 00	1.0E + 01	7.1E + 00	1.6E + 00	3.3E + 00		5.0E + 00
LVMB	1.4E-05	3.1E-05	8.5E-05	3.1E-05	3.2E-04	4.5E-05	6.4E-04	9.1E-05	1.5E-03	1.3E-04	5.1E-03	1.3E-04	7.6E-04	6.0E-05	1.1E-03	9.1E-05
VHVHB*															*****	3114 03
VHVLB*		<del> </del>						<del></del>		<del>                                     </del>			<del> </del>			
Raoult's Law	(Ca	se 9)	(Case	e 10)	(Cas	e 11)	(Cas	e 12)	(Case	e 13)	(Cas	e 14)	(Cas	e 15)	(Cas	e 16)
Surrogate	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
HVHB*													<del></del>	<b></b>		
HVMB*										<u> </u>			<del></del>			
HVLB*																
MVHB	1.5E + 00	3.9E + 00	1.8E + 00	3.9E + 00	2.0E + 00	3.9E + 00	1.8E + 00	6.1E-01	1.8E + 00	3.1E + 00	1.8E + 00	4.9E + 00	1.8E + 00	8.4E + 00	1.8E + 00	9.2E + 00
MVMB	1.5E + 00	3.5E + 00	1.8E + 00	3.5E + 00	2.0E + 00	3.5E + 00	1.8E + 00	5.6£-01	1.8E + 00	2.8E + 00	1.8E + 00	4.5E + 00	1.8E + 00	7.7E + 00	1.8E + 00	8.4E + 00
MVLB	2.7E + 00	7.1E + 00	3.2E + 00	7.1E + 00	3.5E + 00	7.1E + 00	3.2E + 00	1.1E+00	3.2E + 00	5.7E + 00	3.2E + 00	9.1E + 00	3.2E + 00	5.9E + 01	3.2E + 00	1.7E + 01
LVMB	1.3E-03	1.3E-04	1.5E-03	1.3E-04	1.7E-03	1.3E-04	1.5E-03	2.1E-05	1.5E-03	1.0E-04	1.5E-03	1.7E-04	1.5E-03	2.8E-04	1.5E-03	3.1E-04
VHVHB*																
VHVLB*								•		-			<del></del>			
Raoult's Law	(Cas	e 17)	(Case	e 18)	(Cas	e 19)	(Cas	e 20)	(Case	e 21)	(Cas	e 22)	(Cas	e 23)	(Cas	e 24)
Surrogate	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
H∨HB*															·······	
HVMB													<del></del>		<u> </u>	
HVLB*											<del> </del>		<del> </del>		<del></del>	
MVHB	1.8E + 00	1.3E + 01	1.8E + 00	3.9E + 00	1.8E + 00	3.9E + 00	1.8E + 00	3.9E + 00	1.8E + 00	3.9E + 00	9.8E-02	9.3E-01	1.8E + 00	3.9E + 00	6 6E + 00	3.0E + 01
MVMB	1.8E + 00	1.2E + 01	1.8E + 00	3.5E + 00	1.8E + 00	3.5E + 00			1.8E + 00		9.8E-02	8.5E-01	1.8E + 00	3.5E + 00		2.8E + 01
MVLB	3.2E + 00	2.4E + 01	3.2E + 00	7.1E + 00	3.2E + 00	7.1E + 00			3.2E + 00		1.8E-01	1.7E + 00	3.2E + 00	7.1E + 00	1.2E + 01	5.6E + 01
LVMB	1.5E-03	4.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	8.5E-05	3.1E-05	1.5E-03	1.3E-04	5.7E-03	1.0E-03
VHVHB*	<b> </b>	<u> </u>			<del>                                     </del>								<del></del>			
VHVLB*													<del></del>	<u> </u>		<b> </b>
This tune of to		٠	لسسب				L		L	<u></u>	L		L	L	L	<u> </u>

<sup>\*</sup>This type of tank is not typically used for materials with this high vapor pressure.

#### Appendix N

Emission Rate Estimates Floating Roof Tanks

TABLE N-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATION - FLOATING ROOF TANK

Modeling													C	ASE N	IUMBE	RS												
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26*	27**	28***
Rim seal class (see Table J-3)	Α	8	С	D	E	F	G	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н	Н
Shell condition (see Table J-4)	Α	Α	Α	Α	Α	Α	Α	Α	Α	В	С	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	С
Average liquid density (lb/gal)	6.1	6.1	6.1	6.1	6.1	61	6.1	6.1	6.1	6.1	6.1	5.6	7.6	9.6	116	13.4	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	5.6	6.1	13.4
Tank diameter (ft)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	30	60	100	140	180	100	100	100	100	30	100	180
Tank throughput (10° gal/yr)	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	15	10	70	1	1	1	1

- Estimated Best Case (minimum) Emissions (assuming typical tank size)
  Typical Emission Conditions (assuming typical tank size)
  Estimated Worst Case (maximum) Emissions (assuming typical tank size)

Note: If actual input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly

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TABLE N-2
EMISSION RATE ESTIMATES (106 g/yr) - FLOATING ROOF TANK

Raoult's Law		Case 1			Case 2			Case 3			Case 4			Case 5			Case 6	
Surrogates	Rim	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rım	Withdrawal	Fitting
н∨нв*																		
HVMB*																		
HVLB*														<b>†</b>			<b> </b>	
M∨HB	1.3E-02	6.2E-02	3.0E-02	3.5E-02	6.2E-02	3.0E-02	5.5E-02	6.2E-02	3.0E-02	9.6E-02	6.2E-02	3 0E-02	1 8E-01	6.2E-02	3.0E-02	3.3E-01	6.2E-02	3 0E-02
MVMB	1.2E-02	6.2E-02	2.8E-02	3.2E-02	6.2E-02	2.8E-02	5.1E-02	6.2E-02	2.8E-02	8.8E-02	6.2E-02	2.8E-02	1.6E-01	6.2E-02	2.8E-02	3.1E-01	6.2E-02	2.8E-02
MVLB	2.4E-02	6.2E-02	5.6E-02	6.4E-02	6.2E-02	5.6E-02	1.0E-01	6.2E-02	5.6E-02	1.8E-01	6.2E-02	5.6E-02	3.3E-01	6.2E-02	5.6E-02	6.2E-01	6.2E-02	5.6E-02
LVMB	4.4E-07	6.2E-02	1.0E-06	1.2E-06	6.2E-02	1.0E-06	1.9E-06	6.2E-02	1.0E-06	3.2E-06	6.2E-02	1.0E-06	6.0E-06	6.2E-02	1.0E-06	1.1E-05	6.2E-02	1.0E-06
VHVHB*																<del></del>		
VHVLB*																		
Raoult's Law		Case 7			Case 8			Case 9			Case 10			Case 11			Case 12	
Surrogates	Rım	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rım	Withdrawal	Fitting	Rım	Withdrawai	Fitting
HVHB*																		
HVMB*												-					<u> </u>	
HVLB*																		
MVHB	6 2E-01	6 2E-02	3.0E-02	1.0E+00	6.2E-02	3 0E-02	1.0E + 00	6.2E-02	3.0E-02	1.0E + 00	3.1E-01	3.0E-02	1.0E - 00	6.2E+00	3.0E-02	1.0E + 00	5.7E-02	3.0E-02
MVMB	5.7E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	3.1E-01	2.8E-02	9.5E-01	6.2E+00	2.8E-02	9.5E-01	5.7E-02	2.8E-02
	1.1E+00	6.2E-02	5.6E-02	1.9E + 00	6.2E-02	5.6E-02	¹ 9E + 00	6 2E-02	5.6E-02	1.9E + 00	3.1E-01	5.6E-02	1.9E + 00	6.2E+00	5.6E-02	1.9E + 00	5.7E-02	5.6E-02
MVLB		1			6 35 03	1.05.06	3.5E-05	6 2E-02	1 0E-06	3.5E-05	3.1E-01	1.0E-06	3.5E-05	6.2E+00	1.0E-06	3.5E-05	5.7E-02	1.0E-06
LVMB	2.1E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3 36 03	0 21.02	I OF OO I	3.36.03	1 3.16.01	1.02.00		0.261001	1.06-00	3.36,03	1 3.7E-UZ I	I.OL-OU
	2.1E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3.56.05	0 21-02	1 02-00	3.32.03	3.12-01	1.02 00	3.52.03	0.22.100	1.02-00	3.36-03	3.7E-02	1.02-00

<sup>\*</sup> This type of tank is not typically used for materials with this high vapor pressure.

TABLE N-2
EMISSION RATE ESTIMATES (10°g/yr) - FLOATING ROOF TANK (CONTINUED)

Raoult's Law		Case 13			Case 14		Case 15			Case 16				Case 17		Case 18		
Surrogates	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*																		
HVMB*																		
HVLB*																		
MVHB	1.0E + 00	7.8E-02	3.0E-02	1.0E+00	9.8E-02	3.0E-02	1.0E + 00	1.2E-01	3.0E-02	1.0E + 00	1.4E-01	3.0E-02	3.1E-01	2.3E-01	3.0E-02	6.2E-01	1.1E-01	3.0E-02
MVMB	9.5E-01	7.8E-02	2.8E-02	9.5E-01	9.8E-02	2.8E-02	9.5E-01	1.2E-01	2.8E-02	9.5E-01	1.4E-01	2.8E-02	2.9E-01	2.3E-01	2.8E-02	5.7E-01	1.1E-01	2.8E-02
MVLB	1.9E+00	7.8E-02	5.6E-02	1.9E+00	9.8E-02	5.6E-02	1.9E+00	1.2E-01	5.6E-02	1.9E+00	1.4E-01	5.6E-02	5.8E-01	2.3E-01	5.6E-02	1.2E+00	1.1E-01	5.6E-02
LVMB	3.5E-05	7.8E-02	1.OE-06	3.5E-05	9.8E-02	1.0E-06	3.5E-05	1.2E-01	1.0E-06	3.5E-05	1.4E-01	1.0E-06	1.1E-05	2.3E-01	1.0E-06	2.1E-05	1.1E-01	1.0E-06
VHVHB*																		
VHVLB*																		
Daguille		Case 19			0 00													
Raoult's		Case 19			Case 20			Case 21			Case 22			Case 23			Case 24	
Law Surrogates	Rim	Withdrawal	Fitting	Rim	Withdrawal	F1ttlng	Rim	Case 21 Withdrawal	Fitting	Rim	Case 22 Withdrawal	Fitting	Rim	Case 23 Withdrawal	Fitting	Rim	Case 24 Withdrawal	Fitting
Law	Rim	1	Fitting	Rim		F1ttlng	Rim	1	Fitting	Rim	1	Fitting	Rim	I	Fitting	Rim		Fitting
Law Surrogates	Rim	1	Fitting	Rim		F1ttlng	Rim	1	Fitting	Rim	1	Fitting	Rim	I	Fitting	Rim		Fitting
Law Surrogates HVH8*	Rim	1	Fitting	Rim		F1ttIng	Rim	1	Fitting	Rim	1	Fitting	Rim	I	Fitting	Rim		Fitting
Law Surrogates HVH8* HVMB*	Rim	1	Fitting 3.0E-02	Rim		F1tting  3.0E-02	Rim	1	Fitting 3.0E-02	Rim	1	Fitting 3.0E-02	Rim	I	Fitting 3.0E.02	Rim		Fitting 3.0E-02
Law Surrogates  HVH8*  HVMB*		Withdrawal			Withdrawal			Withdrawal			Withdrawal			Withdrawal			Withdrawal	
Law Surrogates  HVH8*  HVMB*  HVLB*	1.0E+00	Withdrawal	3.0E-02	1.5E+00	Withdrawal	3.0E-02	1.9E+00	Withdrawal	3.0E-02	1.0E+00	Withdrawal	3.0E-02	1.0E+00	Withdrawal	3.0E.02	1.0E+00	Withdrawal	3.0E-02
Law Surrogates  HVH8*  HVMB*  HVLB*  MVHB	1.0E+00 9.5E-01	6.2E-02	3.0E-02 2.8E-02	1.5E+00 1.3E+00	4.4E-02	3.0E-02 2.8E-02	1.9E+00 1.7E+00	3.4E-02	3.0E-02 2.8E-02	1.0E+00 9.5E-01	6.2E-02	3.0E-02 2.8E-02	1.0E+00 9.5E01	6.2E-02	3.0E.02 2.8E-02	1.0E+00 9.5E-01	6.2E-02	3.0E-02 2.8E-02
Law Surrogates  HVH8*  HVMB*  HVLB*  MVHB  MVMB	1.0E+00 9.5E-01 1.9E+00	6.2E-02 6.2E-02 6.2E-02	3.0E-02 2.8E-02 5.6E-02	1.5E+00 1.3E+00 2.7E+00	4.4E-02 4.4E-02 4.4E-02	3.0E-02 2.8E-02 5.6E-02	1.9E+00 1.7E+00 3.5E+00	3.4E-02 3.4E-02 3.4E-02	3.0E-02 2.8E-02 5.6E-02	1.0E+00 9.5E-01 1.9E+00	6.2E-02 6.2E-02	3.0E-02 2.8E-02 5.6E-02	1.0E+00 9.5E01 1.9E+00	6.2E-02 6.2E-02 6.2E-02	3.0E.02 2.8E-02 5.6E-02	1.0E+00 9.5E-01 1.9E+00	6.2E-02 6.2E-02	3.0E-02 2.8E-02 5.6E-02

This type of tank is not typically used for materials with this high vapor pressure

TABLE N-2
EMISSION RATE ESTIMATES 10°g/yr) - FLOATING ROOF TANK (CONTINUED)

Raoult's Law								Case 27			Case 28	
Surrogates	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*										-		
HVMB*												
HVLB*			_									
MVHB	1.0E + 00	6.2E-02	3.0E-02	3.1E-01	2.2E-01	3.0E-02	1.0E + 00	6.2E-02	3.0E-02	1.9E + 00	7.4E+00	3.0E-02
1	9.5E-01	6.2E-02	2.8E-02	2.9E-01	2.2E-01	2.8E-02	9.5E-01	6 2E-02	2.8E-02	1.7E+00	7.4E+00	2.8E-02
MVLB	1.9E+00	6.2E-02	5.6E-02	5.8E-01	2.2E-01	5.6E-02	1.9E+00	6.2E-02	5.6E-02	3.5E + 00	7.4E+00	5.6E-02
LVMB	3.5E-05	6.2E-02	1.0E-06	1.0E-05	2.2E-01	1.0E-06	3.5E-05	6.2E-02	1.0E-06	6.3E-05	7.4E+00	1.0E-06
VHVHB*					1							
VHVLB*												

This type of tank is not typically used for materials with this high vapor pressure

# TABLE N-3 TANK RIM SEAL CLASSES

DESCRIPTION	CLASS
External Floating Roof Tank:	
Metallic shoe seal	
- primary seal only	E (E)*
with shoe mounted secondary seal	C (D)*
with rim mounted secondary seal	A (B)*
Liquid mounted resilient seal	
- primary seal only	С
with weather shield	В
with rim mounted secondary seal	Α
Vapor mounted resilient <b>seal</b>	
- primary seal only	Н
with weather shield	G
with rim mounted secondary seal	F
Internal Floating Roof Tank:	
Liquid mounted resilient seal	
- primary seal only	Α
with rim mounted secondary seal	Α
Vapor mounted resilient seal	
- primary seal only	В
with rim mounted secondary seal	А

<sup>\*</sup>For riveted tank

TABLE N-4
TANK SHELL CONDITIONS

CLASS	DESCRIPTION
А	Light rust
В	Dense rust
С	Gunite lined

#### Appendix O

Emission Rate Estimates Variable Vapor Space Tanks

TABLE 0-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - VARIABLE VAPOR SPACE TANK

Modeling							CA	SE NUM	BERS						
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13*	14**	15***
Throughput (10°gal/yr)	.5	10	24	42	10	10	10	10	10	10	10	10	10	10	40
Transfers into tank(#/yr)	60	60	60	60	3	60	120	250	60	60	60	60	60	60	250
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

- \* Reasonable Best Case (minimum) Emissions (assuming typical tank size)
- \*\* Typical Emission Conditions (assuming typical tank size)
- Reasonable Worst Case (maximum) Emissions (assuming typical tank size)

Note: If actual input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly.

TABLE 0-2 EMISSION RATE ESTIMATES (10°g/yr)-VARIABLE VAPOR SPACE TANK

Raoult's Law Surrogates	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8
HVHB	7.8E-01	3.0E+01	7.7E+01	1.3E+02	3.1E+01	3.0E+01	2.9E+01	2.8E+01
HVMB	6.7E-01	2.6E+01	6.6E+01	1.2E+02	2.7E+01	2.6E+01	2.5E+01	2.4E+01
HVLB	1.5E+00	5.9E+01	1.5E+02	2.6E+02	6.0E+01	5.9E+01	5.8E+01	5.4E+01
MVHB	1.5E-02	5.7E-01	1.5E+00	2.6E+00	5.9E-01	5.7E-01	5.6E-01	5.3E-01
MVMB	1.4E-02	5.3E-01	1.3E+00	2.3E+00	5.4E-01	5.3E-01	5.1E-01	4.8E-01
MVLB	2.7E-02	1.1E+00	2.7E+00	4.7E+00	1.1E+00	1.1E+00	1.0E+00	9.8E-01
LVMB	5.OE-07	1.9E-05	4.9E-05	8.6E-05	2.OE-05	1.9E-05	1.9E-05	1.8E-05
VHVHB	3.8E+00	1.5E+02	3.7E+02	6.5E+02	1.5E+02	1.5E+02	1.4E+02	1.3E+02
VHVLB	8.3E+00	3.2E+02	8.2E+02	1.4E+03	3.3E+02	3.2E+02	3.1E+02	3.0E+02
Raoult's Law Surrogates	Case 9	Case 10	Case 11	Case 12	Case 13	Case 14	Case 15	
HVHB	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	1.3E+02	
HVMB	2.6E+01	2.6E+01	2.6E+01	2.6E+01	2.6E+01	2.6E+01	1.1E+02	
HVLB	5.9E+01	5.9E+01	5.9E+01	5.9E+01	5.9E+01	5.9E+01	2.5E+02	
MVHB	5.7E-01	5.7E-01	5.7E-01	5.7E-01	5.7E-01	5.7E-01	2.4E+00	
MVMB	5.3E-01	5.3E-01	5.3E-01	5.3E-01	5.3E-01	5.3E-01	2.2E+00	
MVLB	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	4.4E+00	
LVMB	1.9E-05	1.9E-05	1.9E-05	1.9E-05	1.9E-05	1.9E-05	8.1 E-OS	
VHVHB	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	6.1E+02	
VHVLB	3.2E+02	3.2E+02	3.2E+02	3.2E+02	3.2E+02	3.2E+02	1.3E+03	I

#### Appendix P

Emission Rate Estimates Particles from Storage Piles

TABLE P-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - PARTICLES FROM STORAGE PILES

Modeling														CAS	SE NU	MBER	s												
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27*	28**	29***
Area of surface of pile [acres)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Silt content (%)	2	5	10	20	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	5	15	20
% of time windspeed exceeds 12 mph	10	10	10	10	5	10	15	25	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	5	10	25
Days of precipitation ≥ .01 inch per year (see Figure P-I)	60	60	60	60	60	60	60	60	20	60	100	120	60	60	60	60	60	60	60	60	60	60	60	60	60	60	100	60	20
Mean windspeed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	6	10	14	10	10	10	10	10	10	10	10	10	10	10	6	10	14
Moisture content (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	3	6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	0.5	0.5
Vehicle weight (tons) (assume front end loader)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	2	4	10	4	4	4	4	4	4	4
Number of wheels on loader	4	4	4	4	4	4	4	4	4	4	. 4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Throughput (102 tons/yr)	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500
Mass fraction of contaminant (ppm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1 .	1	1	1
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

Note: If actual unit specific parameters are significantly different from the cases provided above it is recommended that emission rates be calculated directly based on the methodology presented in AP-42 (4th Edition Volume I - Supplement B, September 1988)

<sup>\*</sup> Reasonable Best Case (minimum) Emissions (assuming typical surface area)

\*\* Typical Emission Condition (assuming typical surface area)

\*\*\* Reasonable Worst Case (maximum) Emissions (assuming typical surface area)

Table P-2. Emission Rate Estimates (IO g/yr) - Particles from Storage Piles\*

Case	Wind Erosion**	Batch Dump***	Vehicle Activity****
1	8.1E-07	1.1E-06	1.4E-07
2	2.0E-06	2.8E-06	3.6E-07
3	4.0E-06	5.6E-06	7.1E-07
4	8.1E-06	1.1E-05	1.4E-06
5	3.1E-06	8.7E-06	1.1E-06
6	6.2E-06	8.7E-06	1.1E-06
7	9.0E-06	8.7E-06	1.1E-06
8	1.5E-05	8.7E-06	1.1E-06
9	6.9E-06	8.7E-06	1.2E-06
10	6.2E-06	8.7E-06	1.1E-06
11	5.2E-06	8.7E-06	9.3E-07
12	5.0E-06	8.7E-06	8.6E-07
13	6.2E-06	5.1E-06	1.1E-06
14	6.2E-06	8.7E-06	1.1E-06
15	6.2E-06	1.2E-05	1.1E-06
16	6.2E-06	8.7E-06	1.1E-06
17	6.2E-06	2.1E-06	1.1E-06
18	6.2E-06	2.3E-07	1.1E-06
19	6.2E-06	5.9E-08	1.1E-06
20	6.2E-06	8.7E-06	6.5E-07
21	6.2E-06	8.7E-06	1.1E-06
22	6.2E-06	8.7E-06	2.1E-06
23	6.2E-06	8.7E-06	1.1E-06
24	6.2E-06	8.7E-06	1.1E-06
25	6.2E-06	8.7E-06	1.1E-06
26	6.2E-06	8.7E-06	1.1E-06
27	8.8E-07	4.2E-07	3.1E-07
28	6.2E-06	8.7E-06	1.1E-06
29	2.3E-05	1.6E-05	1.7E-06

\*Particle size of 10 microns assumed (emission rate particle multiplier of 0.5 used, based on pg. 4-7 of Control of Open Fugitive Dust Sources, U.S. EPA, September 1988). Constituent concentration of 1 ppm assumed.

\*\*Emission rate estimates for wind erosion based on Equation 3, p. 11.2.3-5 of Compilation of Air Pollutant Emission Factors, Vol.I, (U.S. EPA, September 1985).

\*\*\*Emission rate estimates for batch dump operations were calculated using Equation 1, p. 11.2.3-3 of Compilation of Air Pollutant Emission Factors, Vol. 1. (U.S. EPA, September 1985). Drop height of 21.9 feet and dumping device capacity of 6.375 yd³assumed.

\*\*\*\*Emission rate estimates for vehicle activity were calculated using Equation 1, p. 11.2.1-1 of Compilation of Air Pollutant Emission Factors, Vol. 1, (U.S. EPA, September, 1985) assuming one vehicle in continuous operation for 2,080 hours per year at speed of 3 mph (this low speed assumed to account for loading/unloading in immediate vicinity of the waste pile.) Minor adjustments in emission rates should be implemented if unit-specific vehicle speeds and/or total vehicle miles traveled per year are higher than these assumptions.

## MEAN NUMBER OF DAYS WITH 0.01 INCH OR MORE OF PRECIPITATION, ANNUAL

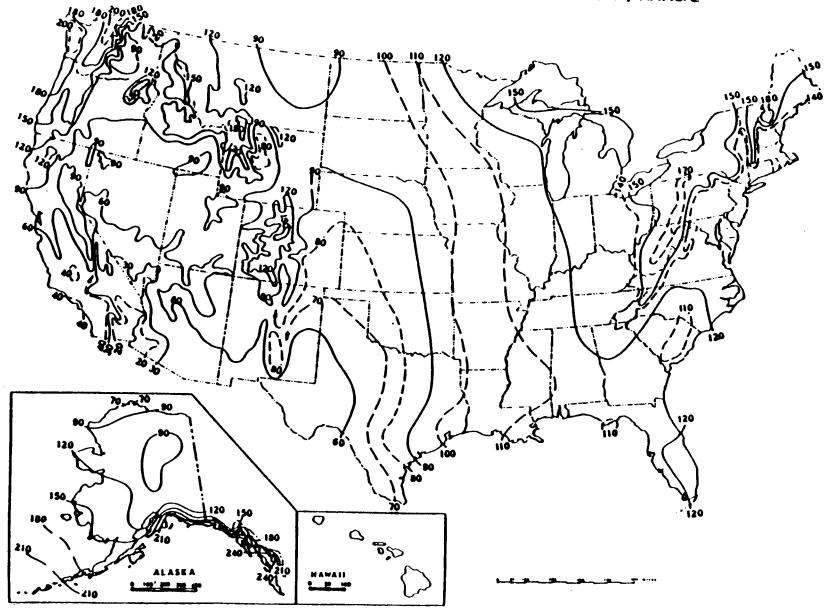


Figure P-1. Map of Precipitation Frequency (AP-42)

## Appendix Q

Emission Rate Estimates

Particles from Exposed, Flat, Contaminated Areas

#### EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - PARTICLES FROM EXPOSED, FLAT, CONTAMINATED AREAS

Modeling												CAS	E NUME	BERS											1
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23*	24**	25***
Area of exposed area (acres)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Silt content (%)	2	5	10	20	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	5	15	20
Surface erodibility (tons/acreyear)(see Table Q-3)	47	47	47	47	38	56	86	134	220	47	47	47	47	47	47	47	47	47	47	47	47	47	38	47	220
Precipitation- evaporation (PE) Index (see FigureQ-1)	100	100	100	100	100	100	100	100	100	20	60	100	200	300	100	100	100	100	100	100	100	100	120	100	20
% of time wind speed exceeds 12 mph	10	10	10	10	10	10	10	10	10	10	10	10	10	10	5	to	15	25	10	10	10	10	5	10	25
Mass fraction of contaminant (ppm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

If actual unit-specific parameters are significantly different from those provided above it is recommended that emission rates be calculated directly using the methodology provided in Control of Open Fugitive Dust Sources (U.S. EPA, September 1988).

Reasonable Best Case (minimum) Emissions (assuming typical surface area)
Typical Emission Conditions (assuming typical surface area)
Reasonable Worst Case (maximum) Emissions (assuming typical surface area)

TABLE Q-2
EMISSION RATE ESTIMATES (10° g/yr) PARTICLES FROM EXPOSED AREAS\*

Case	Estimated Emission Rates** (10 <sup>6</sup> g/yr)					
1	4.8E-08					
2	1.2E-07					
3	. 2.4E-07					
4	4.8E-07					
5	2.9E-07					
6	4.3E-07					
7	6.7E-05					
8	1.0E-06					
9	1.7E-06					
10	9.1E-06					
11	1.0E-06					
12	3.6E-07					
13	9.1E-06					
14	4.0E-08					
15	1.8E-07					
16	3.6E-07					
17	5.5E-07					
18	9.1E-07					
19	3.6E-07					
20	3.6E-07					
21	3.6E-07					
22	3.6E-07					
23	3.4E-08					
24	3.6E-07					
25	1.4E-04					

<sup>\*</sup> Particle size of 10 microns assumed (emission rate particle multiplier of 0.5 used, based on p. 6-9 of Control of Open Fugitive Dust Sources, U.S. EPA,

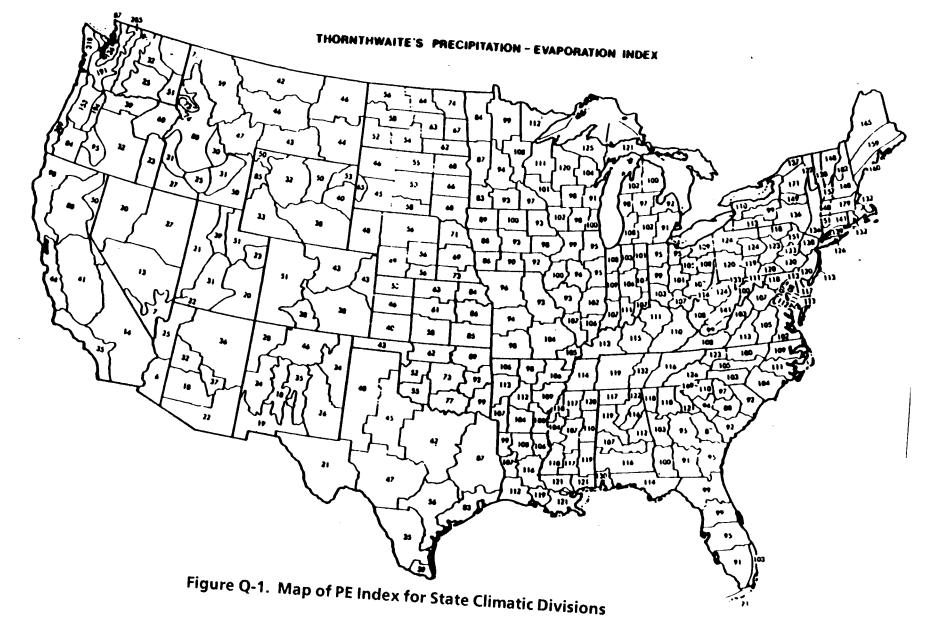
<sup>\*\*</sup> September 1988). Constituent concentration of 1 ppm assumed.

Emission rate estimates for particles from exposed areas were calculated using Equation 8, p. 4-2 of Fugitive Emissions from Integrated Iron and Steel Plants (U.S. EPA, March 1978).

TABLE Q-3
SOIL ERODIBILITY FOR VARIOUS SOIL TEXTURAL CLASSES\*

Predominant Soil Textural Class	Erodibility, tons/acre/year
Sand	220
Loamy sand	134
Sandy loam	86
Clay	86
Silty clay	86
Loam	56
Sandy clay loam	56
Sandy clay	56
Silt loam	47
Clay loam	47
Silty clay loam	38
Silt	38

<sup>\*</sup> U.S. Department of Agriculture. July 1964. Guide for Wind Erosion Control on Cropland in the Great Plains States, Soil Conservation Service.



U. S. EPA, March 1977. Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions, OAQPS, Research Triangle Park, NC 27711)

# Appendix R Dispersion Estimates

# TABLE R-1 CONCENTRATION ESTIMATION WORKSHEET

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11		Col 13	
	Instruction A:		Instruction C: Assume		(sele				oncentrat	ion Estima	_ tes (μg/m³)	Based on Equation int or Raoult's Law o	
Downwind Sector	Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	or	y's Law Constant Surrogate It's Law Surrogate
N													
NNE													
NE													
ENE													
E											,		
ESE													
SE		1								·			
SSE				· · · · · · · · · · · · · · · · · · ·				· · · · · · · · · · · · · · · · · · ·					
5								······ ·····					
SSW													
SW													
wsw													
W													
WNW													
NW													
NNW			1	1									

Equation 1 Long-Term Concentration Est. (µg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17 x 10²) x (Safety Factor = 10) Mg/yr = 10<sup>6</sup>g/yr Distance from downward unit boundary

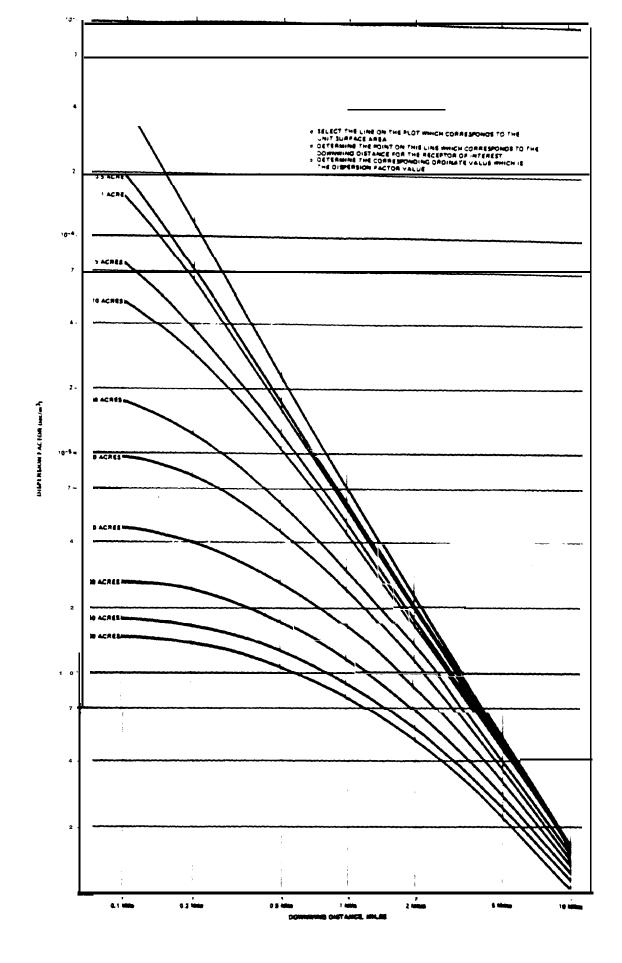


Figure R-1. Atmospheric Dispersion Factors for Typical U.S. Meteorological Conditions (Neutral Stability and IO-MPH Wind Speed)

# Appendix \$

Emission Rate Estimation
Worksheets

TABLE S-1 EMISSION RATE ESTIMATION WORKSHEET- DISPOSAL IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix C -		Dete	rmine Su		ction C: pecific So	caling Fa	ctors'*	
	Parameters	Values	Table C-1 (underline selected case)	MHLB	HHLB	LHMB	МНМВ	ННМВ	LHHB	MHHB	НННВ
1	Area*	acres									
2	Depth'	m	1,2,3or4	_	_	_	_	_	_	_	_
3	Turnovers*	/year	5,6,7or8	_	_	_		_	_		_
4 (	Constituent Concentration'	ppm		-							
	Cor	INSTRUCTION [ mplete Lines 5-6				SURR	OGATE-S	PECIFIC	<u>VALUE</u> S		
5 [ւ	Account for Area unit-specific area/(Ca	ase 18 area = 2	2.2 acres)]	_	_	_	_	_	_	_	_
6	Account for Conce [unit-specific cone./		= 1,000 ppm)]	_	_	_	_	_			_
7	Typical Surrogate-S (Case 18), 10 <sup>6</sup> g/yr	Specific Emission	n Rate	32.4	324	14.1	32.4	32.4	9.4	32.4	32.4
8	Calculate Unit-Spe (multiply lines #2 x					_	_	_		_	

<sup>\*</sup> Critical input values

\*\* Scaling Factor determined for Lines 2 and 3 from Appendix C - Emission Rate Estimate from Table C-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-2
EMISSION RATE ESTIMATION WORKSHEET- STORAGE IMPOUNDMENT

Line	e Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Madalina	Instruction A:	Instruction B: Select a Representative		Dete	rmine Su		ction C: pecific Sc	aling Fac	ctors**	
	Modeling Parameters	Specific Values	Case from Appendix D - Table D-1 (underline selected case)	MHLB	HHLB	LHMB	МНМВ	ННМВ	LHHB	МННВ	нннв
1	Area*	acres									
2	Depth'	m	1,2,3or4	_	_		_	_	_	_	
3	Retention time*	days	5,6,7,or8	_	_	_	_	_	_	_	
4 (	Constituent Concentration*	ppm									
	Cor	INSTRUCTION [mplete Lines 5-6				SURR	OGATE-SP	ECIFIC V	ALUES		
⁵[ur	Account for Area nit-specific area/(Cas	se 18 area = (	0.4 acres)]	_	_		_	_	_	_	
6	Account for Unit-S [unit-specific cone./	•		_			_	_	_	_	_
7	Typical Surrogate-S (Case 18), 10 <sup>s</sup> g/yr	n Rate	34.0	39.24	3.25	38.10	38.40	1.97	38.74	39.24	
8	Calculate Unit-Spe (multiply lines #2 x			_		_		_	_	_	

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2 and 3 from Appendix D - Emission Rate Estimate from Table D-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-3
EMISSION RATE ESTIMATION WORKSHEET - OIL FILM ON STORAGE IMPOUNDMENT

Line	e Col 1	Col 2	Col 3	Col 4	cot 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix E -			Determin	<u>Ir</u> e Surroga	nstruction ate-Speci		g Factor	s"	
	Parameters	Values	Table E-1 (underline selected case)	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	acres										
2	Depth of Oil Film*	m	I,2,3or4				_			_		
3	Retention Time*	days	5,6,7,or8				_					
4	Constituent Concentration*	<b></b>										
	Cor	INSTRUCTION [ mplete Lines 5-6				<u>s</u>	URROGAT	E-SPECIF	IC VALUE	: <u>S</u>		
⁵[ur	Account for Area nit-specific area/(Cas	se 18 area = 0	0.4 acres)]									
5	Account for Conce [unit-specific cone./	= 200 ppm)]										
7	Typical Surrogate-S (Case 18), 10 <sup>s</sup> g/yr	n Rate	0.394	0.394	0.394	0.394	0.389	0.394	1.IOE- 04	0.394	0.394	
8	Calculate Unit-Spe (multiply lines #2 x											

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2 and 3 from Appendix E - Emission Rate Estimate from Table E-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-4
EMISSION RATE ESTIMATION WORKSHEET- MECHANICALLY AERATED IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Madaliaa	Instruction A:	Instruction B: Select a Representative		Dete	rmine Su		ction C: pecific Sc	caling Fac	ctors**	
	Modeling Parameters	Specific Values	Case from Appendix F - Table F-1 (underline selected case)	MHLB	HHLB	LHMB	МНМВ	ННМВ	LHHB	МННВ	НННВ
1	Area*	acres									
2	Depth'	m	1,2,3 or 4								
3	Retention Time*	days	5,6,7 or 8								
4	Constituent Concentration*	ppm								·	
5	Fraction Agitated		13,14,15 or 16					<del></del>			
	Cor	INSTRUCTION Inplete Lines 6-7				SURR	OGATE-SF	ECIFIC V	<u>ALUES</u>		
<sup>6</sup> [ur	Account for Area nit-specific area/(Cas	se 22 area = (	0.4 acres)]								
7	Account for Conc. [unit-specific cone.		= 1,000 ppm)]								
8	Typical Surrogate-S (Case 22), 10°g/yr	Specific Emission	n Rate	90.6	984	12.3	94.7	98.3	8.5	95.9	98.4
9	Calculate Unit-Spe (multiply lines #2									_	

\* Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-3 and 5 from Appendix F - Emission Rate Estimate from Table F-2 divided by Typical Emission Rate defined in Case 22 (see line 8).

TABLE S-5
EMISSION RATE ESTIMATION WORKSHEET-

line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix G -		Dete	rmine Su		ction C: pecific Sc	aling Fac	tors**	
	Parameters	Values	Table G-1 (underline selected case)	MHLB	HHLB	LHMB	МНМВ	ННМВ	LHHB	МННВ	нннв
1	Area*	acres									
2	Depth'	m	1,2,3 or 4				<del></del>				
3	Retention Time*	hours	5,6,7 or 8								
4	Constituent Concentration*	ppm									
5 \$	Submerged Air Flow	m³/sec	13,14,15 or 16		<del></del>						
	Cor	INSTRUCTION [mplete Lines 6-7				SURRO	OGATE-SP	ECIFIC V	<u>ALUES</u>		
6	Account for Area [unit-specific area/(C	ase 22 area = 0	6.7 x 10³acres)]								
7	Account for Conce [unit-specific cone./		= 1,000 ppm)]								
8	Typical Surrogate-S (Case 22), 10 <sup>s</sup> g/yr	n Rate	3.9	205.4	0.086	6.4	51.5	0.055	8.1	128.9	
9	Calculate Unit-Spe (multiply lines #2x										

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-3 and 5 from Appendix G - Emission Rate Estimate from Table G-2 divided by Typical Emission Rate defined in Case 22 (see line 8)

TABLE S-6
EMISSION RATE ESTIMATION WORKSHEET - LAND TREATMENT EMISSIONS (AFTER TILLING)

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix H -			Determine		nstruction te-specif		g Factors	**	
	Parameters	Values	Table H-1 (underline selected case)	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Annual waste throughput* (water & oil)	106 g/yr										
2	Oil content of waste(%)*	percent	l,2,3 or 4						<del>,, , , , , , , , , , , , , , , , , , ,</del>			
3	Constituent concentration*	ррm	5,6,7 or 8						<del></del>			
4	Soil porosity	percent	9,10,11 or 12				<u></u>		<u></u>			
5	Tilling depth	c m	13,14, 15 or 16									
	Cor	INSTRUCTION D				<u>s</u>	URROGAT	E-SPECIF	IC VALUE	<u> </u>		
6 [	Account for Unit-S unit annual waste t	•	Waste Throughput 22 = 1,800 10°g/yr)]									
7	Typical Surrogate-S (Case 22), 10°g/yr	Rate	0.341	0357	0.359	0.108	0.219	0.338	0.0018	3 0.356	0.359	
8	Calculate Unit-Speci (multiply lines #2x		= :				·	<del></del>				

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-5 from Appendix H - Emission Rate Estimate from Table H-2 divided by Typical Emission Rate defined in Case 22 (see line 9).

TABLE S-7
EMISSION RATE ESTIMATION WORKSHEET- OIL FILM SURFACE ON LAND TREATMENT UNIT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Madalina	Instruction A: Input Unit-	Instruction B: Select a Representative			Determin		nstructior ate-Speci	<u>ı C:</u> fic Scalin	g Factors	**	
	Modeling Parameters	Specific Values	Case from Appendix I - Table I-1 (underline selected case)	нунв	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	acres						**	'			
2	Depth of Oil Film*	1,2,3 or 4						<del></del>				
3 /	Applications per Year	/year	5,6,7 or 8		**************************************					***		
4 (	Constituent Concentration'	ppm	-									
	Cor	INSTRUCTION During the Inplete Lines 5-6				<u>s</u>	URROGAT	E-SPECIF	FIC VALUE	<u>:S</u>		
⁵[ur	Account for Area	ase 18 area = 6	5.2 acres)]									
6	Account for Conce [unit-specific cone	= 200 ppm)]										
7	Typical Surrogate-Specific Emission Rate (Case 18), 10°g/yr				131.4	131.4	30.8	22.0	31.2	1.45E- 0 3	131.4	1314
8	Calculate Unit-Spe (multiply lines #2											

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2 and 3 from Appendix I - Emission Rate Estimate from Table 1-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-8
EMISSION RATE ESTIMATION WORKSHEET- CLOSED LANDFILL

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Madalin a	Instruction A:	Instruction B: Select a Representative			Determin	<u>Ir</u> e Surroga	nstruction ate-Speci		g Factors	**	
	Modeling Parameters	Specific Values	Case from Appendix J - Table J-1 (underline selected case)	нунв	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	acres	<b></b>									
2	Waste-bed thickness*	l,2,3 or 4		<del></del>				<del></del>	****			
3 (	Cap thickness	ft	5,6,7 or 8									
4	Constituent content of waste*	percent	9,10,11 or 12									
5 /	Air porosity	percent	13,14,15 or 16									
	Co	INSTRUCTION D				<u>s</u>	SURROGAT	E-SPECIF	IC VALUE	<u></u>		
<sup>6</sup> [uı	Account for Area nit-specific area/(Ca	ase 22 area = 3	3.5 acres)]					<del></del>				
7	Typical Surrogate-S (Case 22), 10°g/yr	n Rate	24.4	224	47.0	0.445	0.398	0.808	I.55E- 05	119	264	
8	Calculate Unit-Spe (multiply lines #2			***************************************		-						

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-5 from Appendix J - Emission Rate Estimate from Table J-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLE S-9
EMISSION RATE ESTIMATION WORKSHEET - OPEN LANDFILL

Line	e Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix K -			Determine		struction ite-Specif		g Factors	**	
	Parameters	Values	Table K-1 (underline selected case)	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	acres										
2	Waste-bed thickness*	ft	1,2,3 or 4				<del></del>					
3	Constituent content of waste*	percent	5,6,7 or 8									
4	Air porosity (fixed waste)	percent	9,10,11 or 12								<u> </u>	
5	Total porosity (fixed waste)	percent	13,14,15 or 16									
	Co	INSTRUCTION In Inplete Lines 6 a				<u>S</u>	URROGAT	E-SPECIF	IC VALUE	<u>S</u>		
6	Account for Area [unit-specific area/(C	3.5 acres)]										
7	Typical Surrogate-S (Case 22), 10°g/yr	n Rate	766.2	8413	811.3	75.1	60.1	75.1	0.6	2358.7	25090	
8	Calculate Unit-Spe (multiply lines #2x										***************************************	

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-5 from Appendix K - Emission Rate Estimate from Table K-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLE S-10 EMISSION RATE ESTIMATION WORKSHEET - WASTEPILES

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling	Instruction A: Input Unit- Specific	Instruction B: Select a Representative Case from Appendix L -			Determin	<u>Ir</u> e Surroga	nstruction ate-Specif		g Factors	**	
	Parameters	Values	Table L-1 (underline selected case)	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	acres										
2	Turnover rate *	per year	I,2,3 or 4				<del></del>					
3 (	Constituent content of waste*	percent	5,6,7 or 8									
4 /	Air porosity (fixed waste)	percent	9,10,11 or 12	***************************************							<del></del>	
5	Total porosity (fixed waste)	percent	13,14,15 or 16				****			<del></del>	***************************************	
	Co	INSTRUCTION D				<u>S</u>	URROGAT	E-SPECIF	IC VALUE	:S_		
6 [	Account for Area 6 [unit-specific area/(Case 22 area = 0.1 acres)]				***************************************						<u></u>	
7	Typical Surrogate-Specific Emission Rate (Case 22), 10°g/yr				284.9	277.0	26.0	20.9	25.5	0.2	799.3	852.1
8	Calculate Unit-Spec (multiply lines #2x								-		····	

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 2-5 from Appendix L- Emission Rate Estimate from Table L-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLES-11
EMISSION RATE ESTIMATION WORKSHEET - FIXED ROOF TANKS

_ine	e Col 1	Col 2	Col 3		Col 4	Col 5	Col 6	Col 7	Col <b>8</b>	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit- Specific Values	Instruction 8: Select a Representative Case from Appendix M - Table M-2 (underline		HVH8	HVM8	Determin HVLB	e Surroga	struction ite-Specif	fic Scaling		*, VHVHB	VUVI B
	rarameters		selected case)		пупо	LI A IAIO	ПУСЬ	INIAUD	IAI A IAI D	IVIVLD	LVIVID	VIIVIID	VHVLB
1	Diameter*	ft	1, 2, 3, 4, 5 or 6	Breathing Loss	_				-				<del></del>
2				Working Loss									
3	Height*	ft	<b>7,8</b> , 9, 10 or 11	Breathing Loss	_								
4				Working Loss	_					_	_		
5	Throughput*	x10 <sup>6</sup> gal/yr	<b>12,13</b> , <b>14,15</b> , 16 or 17	Working Loss		_	_				<del>-</del>	<del></del>	_
			RUCTION D: lete Lines 8-10				<u>s</u>	URROGAT	E-SPECIF	IC VALUE	: <u>S</u>		
6	Typical Surrog		orking Loss Emission					3.9	3.5	7.1	0.0001		
7	Typical Surrog		eathing Loss Emission					1.8	1.8	3.2	0.0015		
8		t-Specific Workir es #2x #4x #5>	ng Loss Emission Rate, 10 <sup>6</sup> g. c #6)	/yr	_						_		
9		t-Specific Breath es #1 x #3 x #7)	g/yr	_			_	•		<del></del>	e <del>rvienze</del> =		
10	Calculate Total	l Emission Rate 8 + #9)	e, 10 <sup>6</sup> g/yr						_				_

<sup>\*</sup> Critical input values

<sup>\*\*</sup> Scaling Factor determined for Lines 1-5 from Appendix M - Emission Rate Estimate from Table M-2 divided by Typical Emission Rate defined in Case 23 (see lines 7 and 8).

TABLE S-12
EMISSION RATE ESTIMATION WORKSHEET- FLOATING ROOF TANKS

			EMISSION RAIL	ESTIMATION WO	KKOIILLI	ILOAIII	NO ROC	ZI IANNO					
Line	cot 1	Col 2	Col 3		Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit- Specific Values	Instruction B: Select a Representative Case from Appendix N - Table N-1 (underline selected case)		нунв	HVMB		ine Surro	Instructic gate-Spec		ng Factors*		VHVLB
1	Rim seal class*		I,2,3,4,5,6,7 or 8	Rim Loss									
	Shell type* Average liquid density*	lb/gal	9,10 or II 12, 13, 14, 15 or 16	Withdrawał Loss Withdrawał Loss									
4 5 6	Diameter*	ft	17, 18, 19, 20 or 21	RIM Loss Withdrawal Loss									
7	Throughput	x10 <sup>6</sup> gal/yr		Fitting Loss							William Control of the Control of th		
8	Account for	Complete Throughput	RUCTION D: Lines 8 and 12-15	62v 10 <sup>6</sup> co	1/2001			SURROGA	ATE-SPECI	FIC VALU	IES		
9		ate-Specific Rim	t/(Case 27 throughpu Loss Emission Rate	n = 63x 10 ga				1.0	0.95	1.9	0.00004		
10		ate-Specific Wit	hdrawal Loss Emission Rat	e				0.062	0.062	0.062	0.062		
11		ate-Specific Fitti	ng Loss Emission Rate					0030	0.028	0.056	0.000001		
12	(multiply lines	#1 x #4 x #9)	ss Emission Rate, 10 <sup>6</sup> g/yr										
113	(multiply lines	#2 x #3 x #5 x	•										
114	(multiply lines	#6x #11)	Loss Emission Rate, 10 <sup>6</sup> g/y	r									· .
1.5		Emission Rate,  2 + #13 + #	• • •								***************************************		

<sup>&#</sup>x27; critical input values

<sup>&#</sup>x27;\* Scaling Factor determined for Lines 1-6 from Appendix N - Emission Rate Estimate from Table N-2 divided by Typical Emission Rate defined in Case 27 (see lines 9, 10 and 11).

TABLE S-13
EMISSION RATE ESTIMATION WORKSHEET - VARIABLE VAPOR SPACE TANKS

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling	Instruction A: Instruction 8: Input Unit-Specific Case from Appendix 0-	Instruction C: Determine Surrogate-Specific Scaling Factors**									
	Parameters	Values	Table O-1 (underline selected case)	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Throughput*	xI0 <sup>6</sup> gal/yr	I,2,3 or 4			-						
2	Transfers into tank*	#/yr	5,6,7 or 8						<del></del>			
	INSTRUCTION D: Complete Line 4					SI	JRROGAT	E-SPECIFI	C VALUE	<u>s</u>		
3	Typical Surrogate-Specific Emission Rate (Case 14) 10 <sup>66</sup> g/yr			30.	26	59	0.57	053	1.1	1.9E-05	150	320
4	4 Calculate Unit-Specific Emission Rate, 10°g/yr (multiply Lines #1 x #2 x #3)											

- \* Critical input values
- \* \* Scaling Factor determined for Lines 1 and 2 from Appendix 0- Emission Rate Estimate from Table O-2 divided by Typical Emission Rate defined in Case 14 (see line 3).

### **APPENDIX H**

# SOIL LOSS CALCULATION

## **EXCERPTED FROM**

U.S. EPA. Final Draft Superfund Exposure Assessment Manual. September, 1987. Office of Emergency and Remedial Response, Washington, D.C. 20460

#### APPENDIX H

#### SOIL LOSS CALCULATION

#### Introduction

Many of the organic substances of concern found at Superfund sites are relatively nonpolar, hydrophobic substances (Delos et al., 1984). Such substances can be expected to sorb to site soils and migrate from the site more slowly than will polar compounds. As discussed in Haith (1980) and Mills et al. (1982), estimates of the amount of hydrophobic compounds released in site runoff can be calculated using the Modified Universal Soil Loss Equation (MUSLE) and sorption partition coefficients derived from the compound's octanol-water partition coefficient. The MUSLE allows estimation of the amount of surface soil eroded in a storm event of given intensity, while sorption coefficients allow the projection of the amounts of contaminant carried along with the soil, and the amount carried in dissolved form.

#### Soil Loss Calculation

Equation 2-20 is the basic equation for estimating soil loss. Equations 2-21 through 2-24 are used to calculate certain input parameters required to apply Equation 2-20. The modified universal soil loss equation (Williams 1975), as presented in Mills et al. (1982), is:

$$Y(S)_{E} = a(V_{p}q_{p})^{0.56} KLSCP$$
 (2-20)

where

 $Y(s)_{E}$  = sediment yield (tons per event, metric tons per event).

a = conversion constant, (95 English, 11.8 metric). \*

V , = volume of runoff, (acre-feet,  $m^3$ ).

q peak flow rate, (cubic feet per second, ms/see).

Metric conversions presented in the following runoff contamination equations are from Mills et al. (1982).

K = the soil erodibility factor, (commonly expressed in tons per acre per dimensionless rainfall erodibility unit). K can be obtained from the local Soil Conservation Service office.

L = the slope-length factor, (dimensionless ratio).

S = the slope-steepness factor, (dimensionless ratio).

C = the cover factor, (dimensionless ratio: 1.0 for bare soil); see the following discussion for vegetated site "C" values).

P = the erosion control practice factor, (dimensionless ratio: 1.0 for uncontrolled hazardous waste sites).

Soil erodibility factors are indicators of the erosion potential of given soils types. As such, they are highly site-specific. K values for sites under study can be obtained from the local Soil Conservation Service office. The slope length factor, L, and the slope steepness factor, S, are generally entered into the MUSLE as a combined factor, LS, which is obtained from Figures 2-4 through 2-6. The cover management factor, C, is determined by the amount and type of vegetative cover present at the site. Its value is "1" (one) for bare soils. Consult Tables 2-4 through 2-5 to obtain C values for sites with vegetative covers. The factor, P, refers to any erosion control practices used on-site. Because these generally describe the type of agricultural plowing or planting practices, and because it is unlikely that any erosion control would be practiced at an abandoned hazardous waste site, use a worst-case (conservative) P value of 1 (one) for uncontrolled sites.

Storm runoff volume, V, is calculated as follows (Mills et al, 1982):

$$V_r = \alpha A Q_r \tag{2-21}$$

where

a = conversion constant, (0.083 English, 100 metric).

A = contaminated area, (acres, ha).

Q = depth of runoff, (in, cm).

Depth of runoff, Q, is determined by (Mockus 1972):

$$Q_{c} = (R_{c} - 0.2 S_{w})^{2} / (R_{c} + 0.8 S_{w})$$
 (2-22)

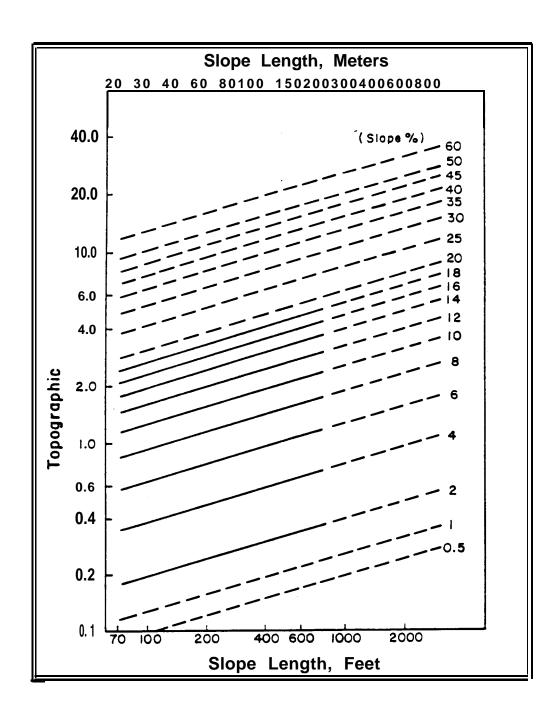


Figure 2-4. Slope Effect chart Applicable to Areas A-1 in Washington, Oregon, and Idaho, and All of A-3: See Figure 3-5 (USDA 1974 as Presented in Mills et al. 1982).

NOTE: Dashed lines are extension of LS formulae beyond values tested in studies.

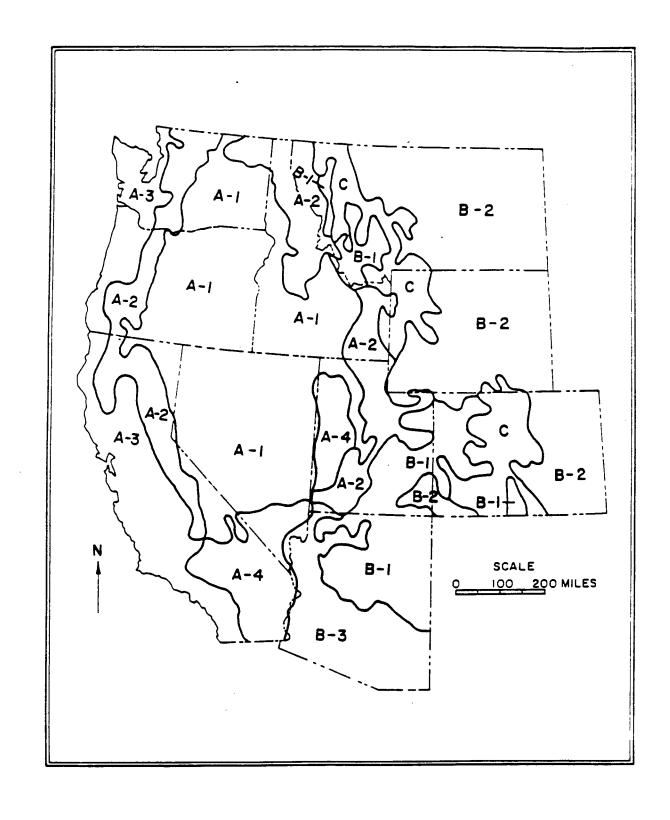


Figure 2-5. Soil Moisture-Soil Temperature Regimes of the Western United States (USDA 1974).

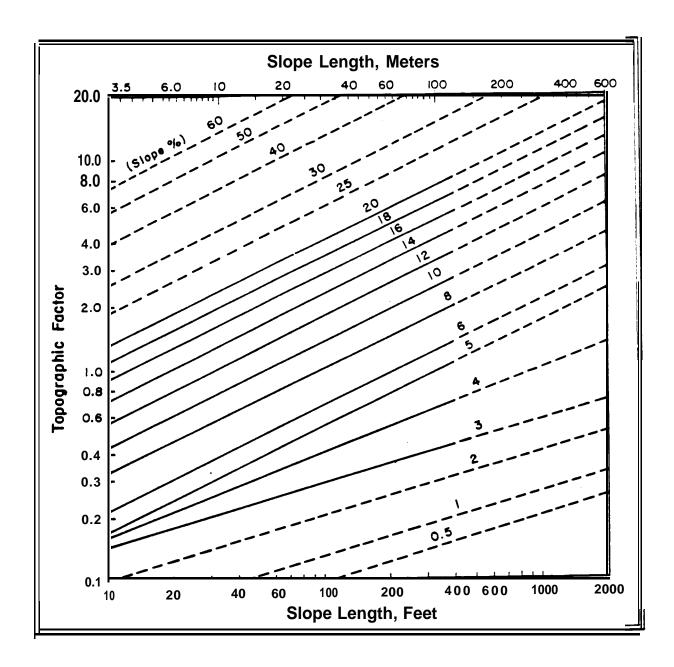


Figure 2-6. Slope Effect Chart for Areas Where Figure 3-5 Is Not Applicable (USDA 1974).

NOTE: The dashed lines represent estimates for slope dimensions beyond the range of lengths and steepnesses for which data are available.

TABLE 2-4

"C" VALUES FOR PERMANENT PASTURE,
RANGELAND, AND IDLE LAND

<u>Vegetal canopy</u> Type and height	Canopy cover° (%)	Cover that contacts the surface/Percent groundcover							
of raised canopy <sup>b</sup>		Type <sup>d</sup>	0	20	40	60	80	95-100	
No appreciable canopy		G <u>W</u>	0.45 0.45	0.20 0.24	0.10 0.15	0.042 0.090	0.013 0.043	0.003 0.011	
Canopy of tall weeds or short brush (0.5 m fall height)	25 50 75	O > O > O >	0.36 0.36 0.26 0.26 0.17 0.17	0.17 0.20 0.13 0.16 0.10 0.12	0.09 0.13 0.07 0.11 0.06 0.09	0.038 0.082 0.035 0.075 0.031 0.067	0,012 0.041 0.012 0.039 0.011 0.038	0.003 0.011 0.003 0.011 0.003 0.011	
Appreciable brush or brushes (2 m fall height)	25 50 75	0 3 0 3 0 3	0.40 0.40 0.34 0.34 0.28 0.28	0.18 0.22 0.16 0.19 0.14 0.17	0.09 0.14 0.085 0.13 0.08 0.12	0.040 0.085 0.038 0.081 0.036 0.077	0.013 0.042 0.012 0.041 0.012 0.040	0.003 0.011 0.003 0.011 0.003 0.011	
Trees but no appreciable low brush (4 m fall height)	25 50 75	G	0.42 0.42 0.39 0.39 0.36 0.36	0.19 0.23 0.18 0.21 0.17 0.20	0.10 0.14 0.09 0.14 0.09 0.13	0.041 0.087 0.040 0.085 0.039 0.083	0.013 0.042 0.013 0.042 0.012 0.041	0.003 0.011 0.003 0.011 0.003 0.011 I	

Source: Wischemier 1972.

a All values shown assume: (1) random distribution of mulch or vegetation and (2) mulch of appreciable depth where it exists.

- **b** Average fall height of waterdrops from canopy to soil surface: m = meters.
- Portion of total-area surface that would be hidden from view by canopy in a vertical projection (a bird's-eye view).
- d G: Cover at surface is grass, grasslike plants, decaying compacted duff, or litter at least 5 cm (2 in.) deep.
  - W: Cover at surface is mostly broadleaf herbaceous plants (as weeds) with little laterial-root network near the surface and/or undecayed residue.

TABLE 2-5

"C" VALUES FOR WOODLAND

Stand condition	Tree canopy percent of area	Forest litter percent of area	Undergrowth	"C" factor	
Well stocked	100-75	100-90	Managed <sup>d</sup> Unmanaged	0.001 0.003-0.011	
Mediurn stocked	70-40	85-75	Managed Unmanaged	0.002-0.004 0.01-0.04	
Poorly stocked	35-20	70-40	Managed Unmanaged	0.003-0.009 0.02-0.09°	

Source: Wischemier 1972.

- When tree canopy is less than 20 percent, the area will be considered as grass land or cropland for estimating soil loss.
- b Forest litter is assumed to be at least 2 in. deep over the percent ground surface area covered.
- Undergrowth is defined as shrubs, weeds, grasses, vines, etc., on the surface area not protected by forest litter, Usually found under canopy openings.
- d Managed grazing and fires are controlled.
  Unmanaged stands that are overgrazed or subjected to repeated burning.
- For unmanaged woodland with litter cover of less than 75 percent, C values should be derived by taking 0.7 of the appropriate values in Table 3-4. The factor of 0.7 adjusts for much higher soil organic matter on permanent woodland.

where

 $R_+ = the total storm rainfall, (in, cm).$ 

S =water retention factor, (in, cm).

The value of SW, the water retention factor, is obtained as follows (Mockus 1972):

$$S_{w} = \frac{1000}{CN} - 10 a$$
 (2-23)

where

 $S^{w} =$  water retention factor, (in, cm).

CN = the SCS Runoff Curve Number, (dimensionless, see Table 2-6).

a = conversion constant (1.0 English, 2.54 metric).

The CN factor is determined by the type of soil at the site, its condition, and other parameters that establish a value indicative of the tendency of the soil to absorb and hold precipitation or to allow precipitation to run off the surface. The analyst can obtain CN values of uncontrolled hazardous waste sites from Table 2-6.

The peak runoff rate,  $q_p$ , is determined as follows (Haith 1980):

$$q_{p} = \frac{aAR_{t}Q_{r}}{T_{r}(R_{t}-0.2 S_{w})}$$
 (2-24)

where

 $q_{\circ}$  = the peak runoff rate, (ft $^{3}$ /sec,  $m^{3}$ /sec).

a = conversion constant, (1 .01 English, 0.028 metric).

A = contaminated area, (acres, ha).

 $R_{+}$  = the total storm rainfall, (in, cm).

 $Q_r$  = the depth of runoff from the watershed area, (in, cm).

 $T_r = storm duration, (hr).$ 

TABLE 2-6
RUNOFF CURVE NUMBERS

		Site Type					
Soil Group	Description	Overall site <sup>a</sup>	Road/right of way	Meadow	Woods		
A	Lowest runoff potential: Includes deep sands with very little silt and clay, also deep, rapidly permeable loess (infiltration rate = 8-12 mm/h).	59	74	30	45		
В	Moderately low runoff potential: Mostly sandy soils less deep than A, and loess less deep or less aggregated than A, but the group as a whole has above-average infiltration after thorough wetting (infiltration rate = 4-8 mm/h).	74	84	58	66		
С	Moderately high runoff potential: Comprises shallow soils and soils containing considerable clay and colloids, though less than those of group D. The group has below-average infiltration after presaturation (infiltration rate = 1- 4 mm/h).	82	90	71	77		
D	Highest runoff potential: Includes mostly clays of high swelling percent, but the group also includes some shallow soils with nearly impermeable subhorizons near the surface (infiltration rate = 0-1 mm/h).	86	92	78	83		

Source: Adapted from Schwab et al. 1966.

a Values taken from farmstead category, which is a composite including buildings, farmyard, road, etc.

 $S_{w} =$  water retention factor, (in, cm).

#### **Dissolved/Sorbed Contaminant Release**

As discussed in Mills et al. (1985), the analyst can predict the degree of soil/water partitioning expected for given compounds once the storm event soil loss has been calculated with the following equations. First, the amounts of absorbed and dissolved substances are determined, using the equations presented below as adapted from Haith (1980):

$$S_s = [1/(1 + \Theta_c/K_d\beta)](C_i)(A)$$
 (2-25)  
and

$$D_{s} = [1/(1 + K_{d}\beta/\Theta_{c})] (C_{i}) (A)$$
 (2-26)

where

 $S_s$  = sorbed substance quantity, (kg, lb).

 $\theta_{c}$  = available water capacity of the top cm of soil (difference between wilting point and field capacity), (dimensionless).

 $K_d$  = sorption partition coefficient, (cm<sup>3</sup>/g).

 $\beta$  = soil bulk density, (g/cm<sup>3</sup>).

 $C_i$  = total substance concentration, (kg/ha-cm, lb/acre-cm).

A = contaminated area, (ha-cm, acre-cm). (Actually a volume; assumption is contamination in upper 1 cm is available for release).

 $D_s$  = dissolved substance quantity, (kg, lb).

This model assumes that only the contaminant in the top 1 cm of soil is available for release via runoff.

The soil sorption partition coefficient for a given chemical can be determined from known values of certain other physical/chemical parameters, primarily the chemical's octanol-water partition coefficient, volubility in water, or bioconcentration factor. Lyman et al. (1982) present regression equations that allow the analyst to determine sorption coefficients for specified groups of chemicals (e.g., herbicides, polynuclear aromatics). If parameter values required by the appropriate equations are not available in chemical reference literature, they

can be estimated according to procedures described in Lyman et al. (1982). Initially, the octanol-water partition coefficient can be estimated based on the substance's molecular structure. If necessary, this value can be used, in turn, to estimate either solubility in water or bioconcentration factor.

After calculating the amount of sorbed and dissolved contaminant, the total loading to the receiving waterbody is calculated as follows (adapted from Haith 1980):

$$PX_i = (Y(S)_{E}/100 B) S_s$$
 (2-27)

$$PQ_i = (Qr/Rt) D_s$$
 (2-28)

where

Px = sorbed substance loss per event, (kg, lb).

 $Y(S)_{E} =$  sediment yield, (tons per event, metric tons).

 $\beta$  = soil bulk density, (g/cm<sup>3</sup>).

 $S_s = sorbed$  substance quantity, (kg, lb).

PQ ;= dissolved substance loss per event, (kg, lb).

Q , = total storm runoff depth, (in, cm).

 $R_{+} = total storm rainfall, (in, cm).$ 

 $D_s = dissolved substance quantity, (kg, lb).$ 

 $Px_i$  and  $PQ_i$  can be converted to mass per volume terms for use in estimating contaminant concentration in the receiving waterbody by dividing by the site storm runoff volume ( $V_i$ , see Equation 2-21).

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