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REPRESENTATIVE SAMPLING GUIDANCE

VOLUME 2: AIR (SHORT-TERM MONITORING)

Interim Final

Environmental Response Team
Office of Emergency and Remedial Response
Office of Solid Waste and Emergency Response

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This guidance is applicable throughout the Superfund Program for short-term air sampling and monitoring. It is a necessary component of Superfund guidance because of its focus on short-term air monitoring.

Though this document contains valid information for performing air impact assessments for long-term actions, it may be useful to consult air sampling guidance which focuses on long-term monitoring, if applicable to the given situation. The References section of this document contains a number of sources that focus on air sampling for long-term monitoring.

Questions, comments, and recommendations are welcomed regarding the *Superfund Program Representative Sampling Guidance, Volume 2: Air (Short-Term Monitoring)*. Send remarks to:

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1.0 INTRODUCTION

1.1 OBJECTIVE AND SCOPE

This document is the second volume of a series of guidance documents designed to assist site managers in obtaining representative samples at Superfund sites. While most of the information contained within this document is valid for any Superfund activity where air sampling is necessary, the specific focus is on short-term air monitoring (i.e., measuring for immediate effects or worst-case scenarios rather than trends).

Unlike soil and water, air is an extremely variable matrix. Contaminant concentrations in air can vary naturally by orders of magnitude because of changes in weather conditions on site. Thus, for air, representative sampling strives to reflect accurately the concentration of the contaminant(s) of concern at a given time, and to determine whether that period of time represents "typical" or "worst case" site conditions, both spatially and temporally. This guidance document aids in developing and implementing a sampling design which assesses the site's impact on ambient air while maintaining the objectives and scope of the Superfund Program. Impact assessments, when done properly, yield a comprehensive set of data that is very useful for site and risk characterization.

An **air impact assessment** (also referred to as air pathway assessment or analysis) is a systematic evaluation of the potential or actual effects of an emission source on air quality. The primary goals of an air impact or pathway assessment are:

- Characterization of air emission sources
- Determination of the effects of atmospheric processes such as transport and dilution
- Evaluation of the exposure potential at receptors of interest

1.2 TERMINOLOGY

In this document, the term **air monitoring** refers to the use of direct-reading instruments and other screening or monitoring equipment and techniques which provide real-time data on the levels of airborne contaminants. Examples of air monitoring equipment are hand-held photoionization detectors (PIDs), flame

ionization detectors (FIDs), and oxygen/combustible gas detectors.

Air sampling is defined as those sampling and analytical techniques which require either off-site or on-site laboratory analysis, and therefore do not provide immediate results. Air *sampling* techniques are used to gain more accurate information than most air *monitoring* technologies in detecting, identifying, and quantifying specific chemical compounds. Examples of air sampling equipment include sampling bags, sorbent tubes/cartridges, and impingers.

Both air monitoring and sampling under the Superfund program are conducted in the following four situations:

Site Assessments:

Site assessments are undertaken to determine if hazardous substances are being released and the extent of contamination at a site. This information is useful for determining the appropriate response to a release or threatened release. Site assessments may include a site inspection, multi-media sampling, and other data collection.

Emergency Responses:

Emergency responses are immediate responses to a release or threatened release of hazardous substances presenting an imminent danger to public health or welfare or the environment (e.g. chemical spills, fires, or chemical process failures resulting in an uncontrolled release of hazardous substances).

Early Actions:

Early actions are initiated to eliminate non-ubiquitous hazardous substances from locations where problems have developed or are likely to develop as a result of the presence of these contaminants. Early actions are generally limited to mitigating surface and shallow subsurface contamination, access control, and addressing other threats that can be dealt with relatively quickly. The responses may include any activity conducted to abate, prevent, minimize, stabilize, or eliminate a threat to public health or welfare and the environment.

Long-Term Actions:

Long-term actions are undertaken to address situations that are (or have the potential to be)

chronic in nature (e.g., ground water remediation, wetland restoration). These actions often include the use of treatment technologies to reduce threats. In long-term actions, trends in contaminant concentrations and mobility often are studied to develop a cleanup strategy.

1.3 AIR IMPACT ASSESSMENT STRATEGIES

Two basic approaches can be used to conduct air impact assessments: either 1) modeling or 2) monitoring (measurement). The modeling approach forecasts the overall site emission rate(s) and pattern(s). Data from preliminary air monitoring (e.g., wind direction, wind speed) are entered into an appropriate air dispersion model which predicts either the maximum or the average air concentrations at selected locations or distances during the time period of concern. This overall modeling strategy is presented in Volume 4 of the Air/Superfund National Technical Guidance Series on Air Pathway Assessments. Specific applications of this strategy are presented in various Air/Superfund technical guidance documents (see References Section).

Note: Issues covered in this guidance document apply only to monitoring (data gathering).

The second basic assessment strategy involves monitoring actual air impacts during specific time intervals (e.g., during clean-up operations). This documented impact can be used to confirm or refute modeling results, or to extrapolate the probable "worst case" concentrations (i.e., when a combination of meteorological and site conditions is expected to cause the highest concentration of contaminants). This extrapolation is important because worst-case conditions may exist at a site over a longer time period than the duration of sampling.

A strong technical background in air emissions modeling, monitoring, and risk assessment is required in order to make appropriate assumptions and judgments when performing an air impact assessment. The Air/Superfund National Technical Guidance Series on Air Pathway Assessments should serve as a guide to On-Scene Coordinators, Remedial Project Managers, Site Assessment Managers, and Regional air program staff when establishing data quality objectives and appropriate approaches for an air impact assessment. This series allows flexibility in tailoring the air assessment to the specific conditions at a site, the relative risk posed by air and other pathways of exposure, and the resource constraints of

the program. The Air Methods Database, which contains information on chemical analysis methods can be a useful resource. Air impact assessments are not simple, concrete procedures; the Air/Superfund National Technical Guidance Series is designed for flexibility and the use of professional judgment.

Because of the uniqueness of the air medium, this representative sampling guidance document is **not** a "how-to" manual for developing an air sampling plan; rather, it presents factors that should be considered in conjunction with other EPA guidance when developing a site-specific sampling plan. These considerations include:

- The selection of sampling and analytical methods
- The location and number of sampling points
- The time, duration, and frequency of sampling events
- Meteorological data
- The impact of topographic, meteorologic, and physical/chemical parameters on the sampling plan design

This guidance document also presents an overview of the sampling and analytical techniques used when implementing the sampling plan, and the quality assurance/quality control (QA/QC) requirements which must be incorporated into sampling activities. The Air/Superfund National Technical Guidance Series on Air Pathway Assessments should be referred to for more specific applications and guidance on air monitoring and modeling.

1.4 REPRESENTATIVE SAMPLING

Representative air sampling ensures that a sample or group of samples accurately reflects the concentration of the contaminant(s) of concern at a given time and that the selected time period is truly representative of either "typical" or "worst case" conditions. The site-specific sampling plan should be designed to identify sources of contaminant emissions, to establish either natural background or upwind conditions, to establish baseline concentrations of contaminants (i.e., prior to intrusive activities), and to identify contaminants of concern and the ranges of their concentration on site and downwind of the site. Each site's sampling plan should be designed to answer the following questions:

- What objective will the sampling achieve?
- What sampling design approach is appropriate to accurately characterize the on-site and upwind emissions of contaminants and their downwind transport?

- How many samples need to be collected to adequately depict site conditions, the impact of upwind sources, and/or the variability of the downwind transport of contaminants?
- During what time period should samples be collected?
- What equipment should be used to collect and analyze samples?
- What precautions should be taken when shipping samples from the field to the laboratory?
- Which QA/QC samples are applicable?

The following factors affect the representativeness of samples and measurements collected at a site:

- Meteorology, suspected upwind sources, and topography of sampling locations
- Number of distinct sampling events
- Duration of sampling activities sufficient for the period of exposure
- Timing of sampling activities with respect to expected "ambient" or "worst case" emissions (time of sampling also depends on downwind transport of contaminants)
- Distinction between meteorology during the sampling period(s) and the typical meteorology during the entire period of concern
- Analytes of concern
- Type of release (e.g., sampling during a drum rupture or instantaneous release, versus a continuous release from contaminated soil)

1.5 CONCEPTUAL SITE MODEL

A conceptual site model is a useful tool for selecting sampling locations. It helps ensure that sources, pathways, and receptors throughout the site have been considered before sampling locations are chosen. The conceptual model assists the Site Manager in evaluating the interaction of different site features. Risk assessors use conceptual models to help plan for risk assessment activities. Frequently, a conceptual model is created as a site map (see Figure 1) or it may be developed as a flow diagram which describes potential migration of contaminants to site receptors (see Appendix C).

A conceptual model follows contaminants from their sources, to pathways (e.g., air, surface water), and eventually to the assessment endpoints. Consider the following when creating a conceptual model:

- The state(s) of each contaminant and its potential mobility
- Site topographical features
- Meteorological conditions (e.g., wind direction/speed, average precipitation, temperature, humidity)
- Human/wildlife activities on or near the site

The conceptual site model on the next page is an example created for this document. The model assists in identifying the following site characteristics:

Potential Sources:

Site (waste pile, lagoon, factory emissions); drum dump (or associated soil gas); cropland (e.g., pesticide application)

Potential Migration Pathway (Air):

Gases/vapors released from the waste pile, lagoon, factory (emissions), drum dump (or associated soil gas), or cropland

Potential Migration Routes:

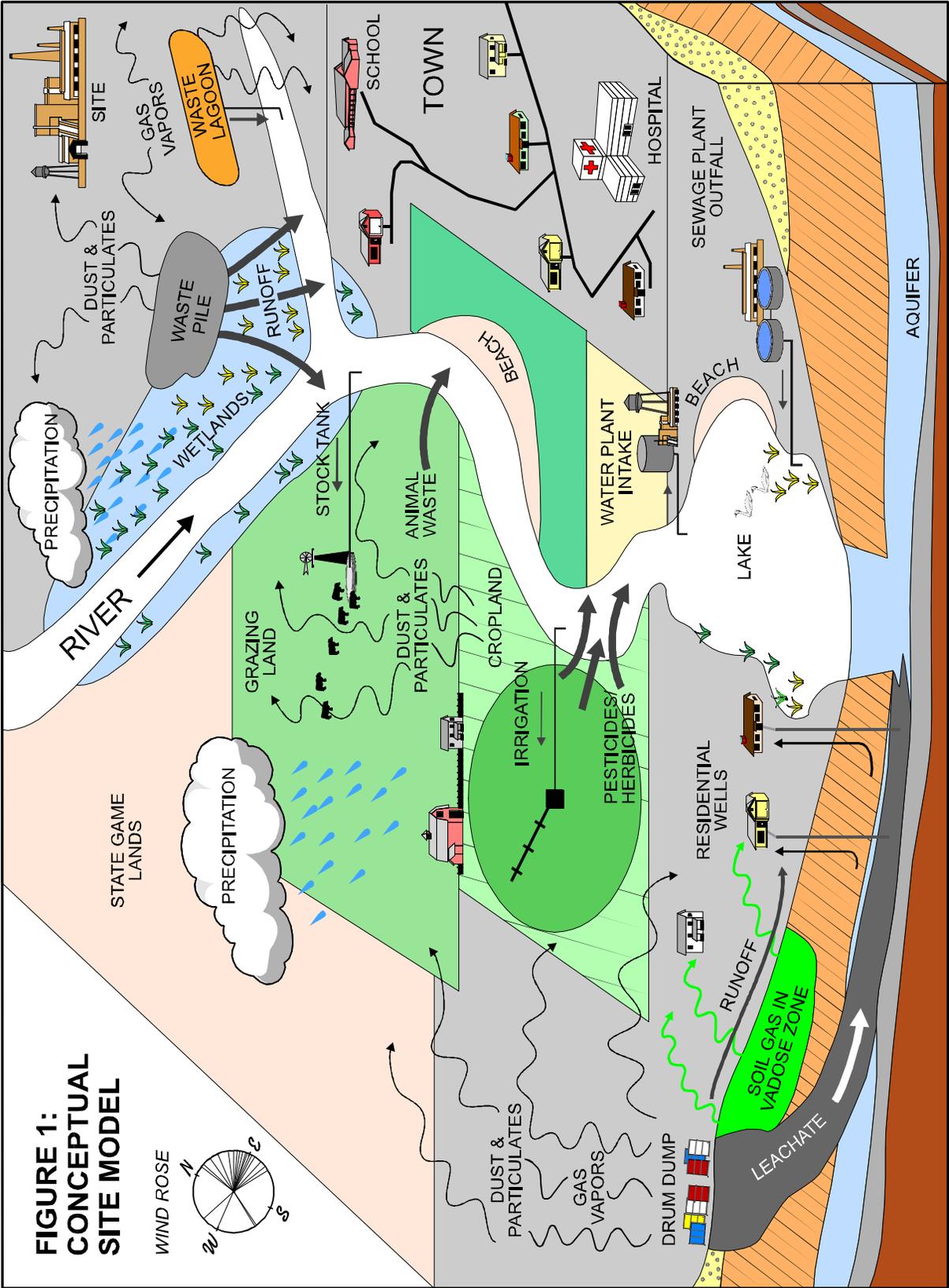
Inhalation, Absorption/Direct Contact -- Gases/vapors released from the waste pile, lagoon, factory (emissions), drum dump (or associated soil gas), or cropland

Potential Receptors of Concern:

Human Population

Residents/Workers/Trespassers:

Inhalation or absorption/direct contact with gases/vapors released from the waste pile, lagoon, factory (emissions), drum dump (or associated soil gas)



Biota

Endangered/threatened species or human food chain organisms which are suspected to be inhaling or in direct contact with contaminated air

Preliminary site information may provide the identification of the contaminant(s) of concern and the level(s) of the contamination. A sampling plan should be developed based upon the selected receptors of concern and the suspected sources and pathways. The model may assist in the selection of on-site and off-site sampling locations.

1.6 UNIQUENESS OF AIR AS A SAMPLING MEDIUM

Because of its variability, air is a unique medium when compared to soil and water. When proper representative sampling procedures are used, soil and water samples collected at the same location but at different times should produce similar results. Results from air samples collected at the same location but at different times can differ by orders of magnitude because of changes in predominant wind direction and

on-site conditions. When air measurements are used to represent the average air impact due specifically to a hazardous waste site (versus the overall ambient air quality), error most often arises in extrapolating the data from a limited time period to a much longer time period. Because of the variability of contaminants existing and dispersing in air, interval calculations, such as those used with soil and water, do not apply.

1.7 EXAMPLE SITES

Two example sites are presented in Appendix B. The examples, a wood preserving facility and a train derailment site, have been included to illustrate the development of a site-specific representative air sampling plan for two different situations.

2.0 SAMPLING DESIGN

2.1 INTRODUCTION

In the Superfund Program, site managers conduct air monitoring and sampling during site assessments, emergency responses, early actions, and remedial actions. Each of the activities has a related air monitoring/sampling objective which is used to determine the potential hazards to workers and/or the community. This chapter discusses air monitoring/sampling situations. It is important to remember that the general sampling decisions presented here should also be considered during a more extensive air impact assessment, which might be performed for remedial investigations.

The goal of an air sampling plan is to accurately assess a site's effect on air quality. This effect is expressed in terms of overall average and/or maximum air concentrations. Unlike soil concentrations, air concentrations at points of interest can vary by orders of magnitude throughout the period of concern. This variability is a major consideration in designing an air sampling plan. Determining the location of potential sources is essential to the selection of sampling locations.

Downwind air concentration is determined by the amount of material being released from the site into the air (the emission rate) and by the degree that the contamination dilutes as it is transported. On-site activities and site meteorology greatly influence contaminant emission rates, while local meteorology and topography govern downwind dilution. Besides the wind direction, the other meteorological condition of major concern is the atmospheric stability class. (See Section 1.3 of Appendix A for a discussion of stability classes.) Incorporate all of these considerations into an air sampling plan.

The complexity of a sampling strategy depends on its objectives. Characterization studies of the pollutant contribution from a single point source tend to be simple. Characterization studies of the fate and transport of components of multiple sources require a more complex sampling strategy. Resource constraints may also affect the complexity of the sampling design.

An optimal sampling strategy accounts for the following site parameters:

- Location of stationary as well as mobile sources
- Analytes of concern

- Analytical detection limit needed
- Rate of release and transport of pollutants from sources
- Sufficient numbers of samples in terms of location and time to meet sampling objectives
- Availability of space and utilities for operating sampling equipment
- Meteorological monitoring data
- Meteorological conditions in which sampling is to be conducted

The U.S. EPA's *Quality Assurance Sampling Plan for Environmental Response (QASPER)*, OSWER Directive 9360.4-01, was designed to develop sampling plans for response actions. QASPER is menu-driven software which prompts the user to input background information and to select prescribed parameters for development of a site-specific sampling plan. It also gives the user access to any previously developed site-specific sampling plans. QASPER is a useful resource that should be consulted when developing a sampling plan.

2.2 OBJECTIVES

Air sampling is conducted to demonstrate the presence or absence of airborne contaminants. Sampling objectives determine sample quantities, sampling program length, sample locations, detection limits, and analytical response time. Detection limits depend on the contaminants being investigated and the particular site situation. It is important to know why air sampling data are needed and how the data will be used. Ensure that the sampling detection limits are adequate for the intended use of the results. Legal and liability objectives also need to be fulfilled.

2.2.1 Data Quality Objectives

Data Quality Objectives (DQOs) must be considered when designing an air sampling plan. DQOs are used to develop a scientific and resource-effective sampling plan. The DQO process is a seven part planning tool based on the scientific method, to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application. Figure 2 describes the steps in the DQO process.

Air samples are collected to address the following specific objectives in the Superfund Program:

- On-Site Health and Safety Assessment -- to determine proper levels of protection for on-site personnel.
- Off-Site Acute Exposure Assessment -- to evaluate the potential of airborne contaminants from the site to cause acute exposure to nearby populations.
- Off-Site Chronic Exposure Assessment -- to evaluate the potential of airborne contaminants from the site to cause chronic exposure to nearby populations.
- Environmental Impacts -- to evaluate potential acute or chronic effects on environmental receptors (e.g., fisheries or wetlands) from airborne contaminants.
- Confirmatory Sampling -- to confirm air monitoring data.
- Odor Complaint Assessment -- to investigate odor sources.
- Source Evaluation -- to identify potential sources of airborne contaminants on site and off site as well as the specific contaminants associated with those sources.

Table 1 illustrates which of the above objectives apply to the four air sampling site situations listed in Section 2.1. When developing the sampling plan, consider the following site and meteorological conditions:

- Worst case -- sampling conducted under meteorological and/or site conditions which result in elevated or "worst" ambient concentrations.
- Typical -- routine daily sampling or routine scheduled sampling at pre-established locations.
- One-Time -- only one chance is available to collect a sample without regard to time or conditions (e.g., during a fire). (Qualitative data acquired under these conditions usually are applicable only to the time period during which the data were collected. They may not be accurate enough to be used in estimating the magnitude of an air impact during other periods or over a long time interval.)

2.2.2 On-Site Health and Safety Assessment

Data collection is necessary for selecting the proper levels of personal protection for site workers. After the level of protective equipment is selected, subsequent air monitoring ensures that new releases do not warrant either elevating the level of protection or moving the support zone. Appropriate real-time monitoring equipment can determine:

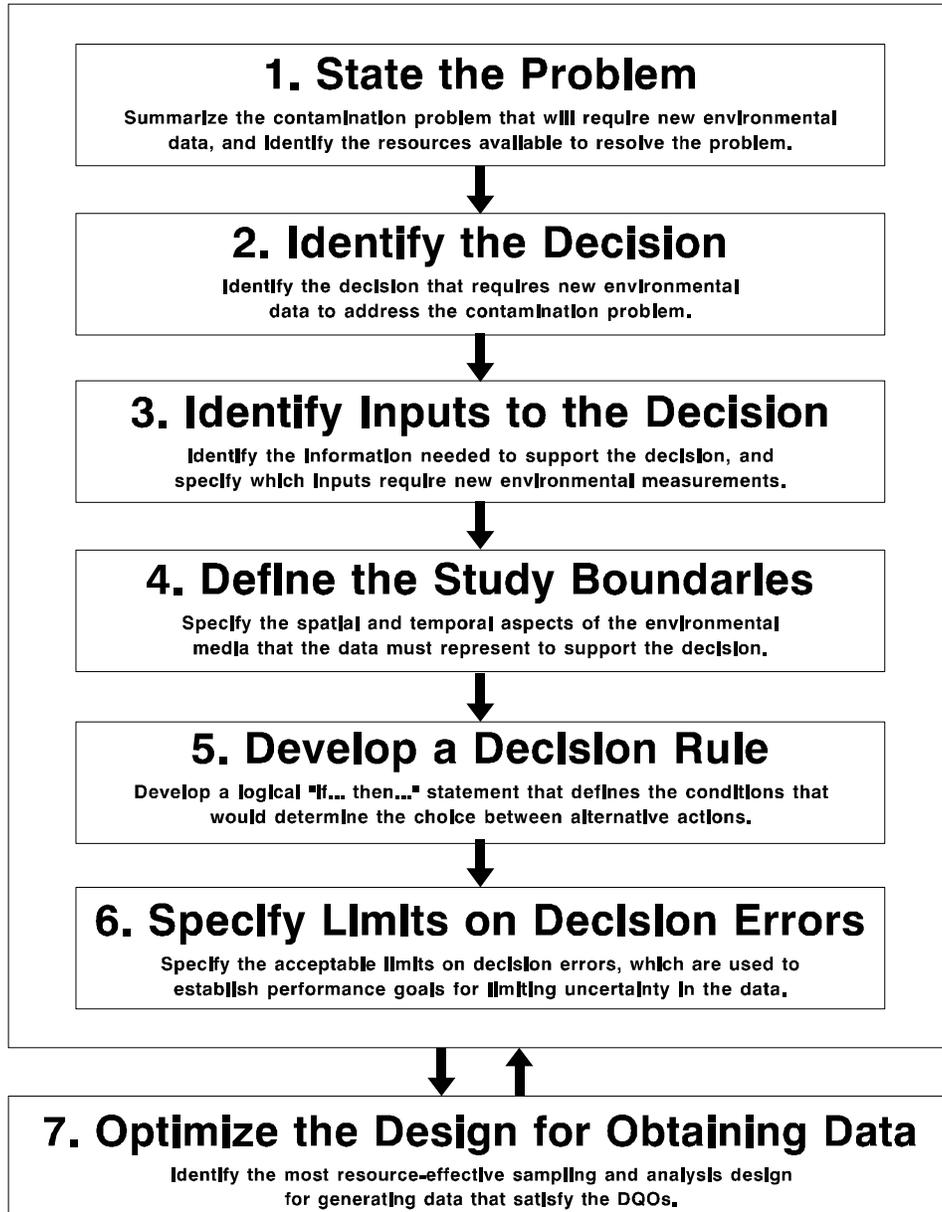
- Oxygen content (percent oxygen)
- Percent lower explosive limit (LEL)
- Total suspended particulates and aerosols
- Organic compound concentrations
- Radiation levels
- Toxic gases (e.g., HCN, H₂S)

2.2.3 Off-Site Acute Exposure Assessment

The exposure of off-site receptors is typically evaluated at several steps of the Superfund process. Both modeling and monitoring approaches may be employed as part of an overall air impact assessment. The potential of airborne contaminants from the site to cause acute exposure (by inhalation, absorption, or irritation) in nearby populations must be considered.

Acute exposure is defined as one or more short-term chemical exposures that cause adverse health effects in an individual. Acute health effects are generally observed immediately or within the first few days following exposure; however, there may be a longer period of latency before effects appear.

Figure 2
The Data Quality Objectives Process



Adapted from Data Quality Objectives for Superfund

TABLE 1: Air Sampling Objectives/Situations

OBJECTIVES	SITUATIONS			
	Emergency Response	Site Assessment	Early Action	Long-Term Action
On-Site Health and Safety Assessment	X	X	X	X
Off-Site Acute Exposure Assessment	X	X	X	X
Off-Site Chronic Exposure Assessment		X	X	X
Environmental Impact	X	X	X	X
Confirmatory Sampling	X		X	X
Odor Complaint Assessment	X	X	X	
Source Evaluation	X	X	X	X
Air Pathway Assessment		X		X
Modeling	X		X	X

Note: Removal actions can occur during an Emergency Response, Early Action, or Long-Term Action.

Monitoring for off-site acute exposure provides a basis for decisions to shelter-in-place or to evacuate the surrounding population. Evacuation and/or sheltering decisions are made by comparing the results of on-site and off-site monitoring with established health-based action levels. Real-time data are necessary since most action levels for acute exposure assessments are based on short-term average contaminant concentrations (e.g., 15-minute, 1-hour, 8-hour average concentrations), and the decision to evacuate must be made quickly. Off-site, real-time air monitoring for acute exposure assessment provides values for:

- Total organic compound concentrations
- Percent LELs
- Radiation levels
- Specific compound levels (or classes of compounds)

2.2.4 Off-Site Chronic Exposure Assessment

Long-term, average airborne contaminant data define the health risk to the surrounding population over time. Chronic health effects may appear after a period of continuous or repeated exposure to a contaminant, even at a low dosage. Off-site, long-term air sampling techniques detect specific compounds at lower concentration levels over longer periods than those detected by real-time air monitoring techniques.

Air sampling is performed at the site perimeter, at off-site locations (e.g., at selected receptor locations in the surrounding community, such as a nearby school), or on site, to determine:

- The presence of specific volatile and semi-volatile particulates, and inorganic compounds
- Concentrations of airborne contaminants for 24-hour and annual averages
- The rate of emissions from the site for subsequent air dispersion modeling

A modeling approach for the evaluation of off-site exposure generally involves atmospheric dispersion modeling using an EPA-approved model (e.g., Industrial Source Complex (ISC) model). Contact your Regional Air Program Coordinator for more information regarding specific models and their applications.

2.2.5 Environmental Impacts

For most sites, the evaluation of environmental impacts will be associated with the evaluation of off-site human exposures. The design of any air monitoring or sampling network for environmental impacts will focus primarily on determining exposure of human populations off site. In general, the same data used to evaluate the exposure of off-site populations also can be used to evaluate adverse effects on the environment. To address potential environmental impacts completely, it may be necessary to increase sampling locations (e.g., near surface waters) and to include in the target analyte list compounds that typically have a greater effect on nonhuman targets. Modeling and monitoring approaches may both be employed as part of the evaluation of environmental impacts.

2.2.6 Confirmatory Sampling

During clean-up activities, confirmatory sampling determines the accuracy of monitoring data and whether an immediate or long-term health threat still exists. Without confirmatory sampling, air releases of unknown origin and/or composition would not be detected. Air sampling is performed after real-time air monitoring equipment has narrowed the number of possible contaminants and has provided some measure of contaminant concentration.

During emergency responses, confirmatory air sampling is most often used to determine if an evacuation order can be lifted and/or to ensure that non-evacuated populations are not at risk. Confirmatory sampling is warranted when the site manager wishes to confirm that no airborne contaminants are present, that a site is not affecting air quality to a significant extent, or to verify real-time monitoring information.

2.2.7 Odor Complaint Assessment

A site manager will generally initiate an odor complaint assessment after local residents complain of unpleasant, irritating odors, or when irritating odors arise during a response action. Response to odor complaints requires both the identification of the contaminant(s) and its source (see Section 2.2.8). If the odor complaint is a repeated one, try to perform air sampling under the same meteorological conditions that existed when previous odors were reported.

2.2.8 Source Evaluation

Identification of potential sources of airborne contaminants and quantification of specific compounds emitted by these sources first require real-time air *monitoring* to locate the source, followed by air *sampling* to identify the compounds emitted. Sometimes, source evaluation is accomplished without sampling; it is possible to determine emissions of certain contaminants with mathematical formulas. During site assessment, source evaluation may be required to help differentiate site emissions from background air quality and off-site emissions from other nearby sources such as industries and highways.

Source emissions can then be used in an air quality dispersion modeling analysis to predict pollutant concentrations. Modeling results may provide the basis for locating off-site monitoring equipment and/or identifying potential evacuation areas. Air monitoring/sampling for source evaluation is performed to:

- Identify potential sources of air contaminants
- Identify specific compounds emitted by a source
- Quantify emissions for subsequent air dispersion modeling

2.3 AIR SAMPLING PLAN CHECKLIST

The following checklist consists of a series of questions to consider when developing the sampling program. Additional information regarding each category follows the checklist.

I. Objectives of the Sampling Program and Implied Assumptions

- ___ A. Have clear, concise objectives for the sampling program been defined (such as those defined in section 2.2 of Chapter 2)?
- ___ B. Have the assumptions of the sampling program been defined (e.g., sampling under "worst-case" conditions, sampling under "typical" conditions, sampling under a routine, periodic schedule, etc.)?
- ___ C. Other: _____

II. Selection of Sampling and Analytical Methods

- ___ A. Selection of Target Compounds
 - 1. Has background site information been consulted?
- ___ B. Selection of Method (sampling and/or analytical)
 - 1. Can selected methods detect the probable target compounds?
 - 2. Do the selected analytical methods have detection limits low enough to meet the overall objectives of the sampling program?
 - 3. Would the selected methods be hampered by any interfering compounds?
- ___ C. Will the selected methods, when applied to the projected sampling location(s), adequately isolate the relative downwind impact of the site from that of other upwind sources?
- ___ D. Are the selected methods logistically feasible at this site?
- ___ E. Other: _____

III. Location(s) and Number of Sampling Points

- ___ A. Does the selection of locations consider all the potential on-site emission sources that have been identified from the initial site background information and from walk-through inspections?
- ___ B. Will the sampling locations take into account all the potential emission sources upwind from the site?
- ___ C. For short-term monitoring programs, has a forecast of the local winds been obtained for the day(s) of the program?
- ___ D. For a long-term monitoring program, have long-term air quality dispersion models and historical

- meteorological data been used to predict probable areas of maximum impact (when applicable)?
- E. Does the sampling plan take into account the effects of local topography on overall wind directions and potential shifts in direction during the day (e.g., valley effects, shoreline effects, hillside effects)?
 - F. Do the sampling location decisions take into account the effects of topography on surface winds, especially under more stable wind directions (e.g., channelization of surface winds due to buildings, stands of trees, adjacent hills, etc.)?
 - G. Can sampling equipment left at these locations be adequately secured?
 - H. Other: _____

IV. Time, Duration, and Frequency of Sampling Events

- A. When the sampling time periods (the actual days, as well as the time span during specific days) were selected, were the effects of the following conditions on downwind transport of contaminants considered:
 - Expected wind directions?
 - Expected atmospheric stability classes and wind speeds?
 - Evening and early morning temperature inversions?
 - Changes in atmospheric pressure and surface soil permeability on lateral, off-site migration of gases from methane-producing sources such as landfills?
 - (During indoor air investigations) gas infiltration rates into homes affected by changes in atmospheric pressure and by the depressurization of homes caused by many home heating systems?
 - Other: _____

- B. When the sampling time periods (the actual days, as well as the time span during specific days) were selected, were the following effects on potential site emissions considered:
 - Effect of site activities?
 - Effect of temperature and solar radiation on volatile compounds?
 - Effect of wind speeds on particulate-bound contaminants and on volatiles from lagoons?
 - Effect of changes in atmospheric pressure on landfills and other methane-producing emission sources?
 - Effect of recent precipitation on emissions of both volatile and particulate-bound compounds?
 - Other: _____

- C. Do the time periods selected allow for contingencies such as difficulties in properly securing the equipment, or public reaction to the noise of generators for high volume samplers running late at night?

- D. When determining the length of time over which individual samples are to be taken, were the following questions considered (when applicable):
 - Will sufficient sample volumes be taken to meet the desired analytical method detection limits?
 - Will the sampling durations be adequate either to cover the full range of diurnal variations in emissions and downwind transport, or to isolate the effects of these variations?
 - When applicable, do the selected time intervals take into account potential wind shifts that could occur due to local topography such as shorelines and valleys?
 - Other: _____

V. Meteorological Data Requirements

- A. Has a source of meteorological data been identified to document actual conditions at the time the sampling event takes place?
- B. Has the placement of an on-site meteorological station been considered in the sampling plan if no off-site station has been identified?

VI. QA/QC Requirements (see Chapter 5 for additional information on QA/QC requirements)

- A. What level of QA/QC will be required?
- B. Have the necessary QA/QC samples been incorporated into the sampling design to allow for the detection of potential sources of error?
- C. Does the QA/QC plan account for verification of the sampling design and the sample collection?

2.3.1 Objectives of the Sampling Program and Implied Assumptions

The sampling objectives must be addressed prior to developing the sampling plan. Does the sampling verify adequate levels of protection for on-site personnel, or address potential off-site impacts associated with the site or site activities? In addition to defining the sampling objectives, also define the assumptions associated with the sampling program. These assumptions include whether the sampling is to take place under "typical" or "worst case" conditions. If the conditions present at the time of sampling are different than those assumed during the development of the sampling plan, then the quality of the data collected may be affected.

The sampling objectives also determine the detection limits. A sampling program may require several detection limits for the same compound using various sampling methods. Sampling objectives and their associated methods and detection limits may include:

- **On-Site Health and Safety Assessment**
The primary sampling methods used are those of NIOSH and OSHA. These methods utilize low sample volumes with resultant high detection limits in the mg/m³ range.
- **Off-Site Acute Exposure Assessment**
The same methods used for on-site health and safety assessments are generally employed here. However, more sensitive methods are available which can yield lower detection limits in the range of mg/m³ to Fg/m³, depending on the compound.

- **Off-Site Chronic Exposure Assessment and Confirmatory/Odor Complaint Assessment**
Sampling methods used require detection limits of Fg/m³ to mg/m³, depending on the compound. These methods generally are the most complicated, and require large sample volumes and extended sampling periods.
- **Environmental Impacts**
For determination of environmental impacts, site-specific action levels (and associated detection limits) should be developed, though guidance may be limited. Procedures for evaluating environmental exposure may also apply to the evaluation of contaminant deposition onto cropland, which may present a potential human exposure pathway.
- **Source Evaluation**
Sources being sampled generally have an elevated pollutant concentration, so methods with mg/m³ ranges are adequate.

The following are some general assumptions regarding detection limits:

- The larger the sample volume, the lower the detection limit which can be achieved.
- The larger the sample volume, the larger and more complex the sampling equipment needed (in most cases).
- The lower the detection limit, the greater the risk of sample contamination.
- The larger the sample volume, the greater the chance of breakthrough problems with sample media

Each method has logistical constraints that need to be taken into account (see Chapter 4).

2.3.2 Selection of Sampling and Analytical Methods

Unless the site is considered to present an emergency requiring an immediate removal action, conduct a thorough review of relevant site information in addition to visiting the site, when feasible. This information will assist in identifying compounds likely to be encountered on site and can help identify potential interference problems with the selected methods. Time constraints often hinder comprehensive research; concentrate on the most important information first. A priority ranking of information follows:

- Possible target compounds on site
- Possible concentration ranges of target compounds
- Site maps
- Facility blueprints
- Data files including past and present storage, process, and waste disposal areas (i.e., potential emission sources)
- Area topographic maps
- Aerial photographs

Not all of the above information will be readily available. No site-specific meteorological data will be available for a site unless an air sampling program was previously conducted at that site or at a nearby meteorological station or large airport.

2.3.3 Location and Number of Individual Sampling Points

Choose the number and location of sampling points according to the variability or sensitivity of the sampling and analytical methods being utilized, the variability of contaminant concentrations over time at the site, the level of precision required, and cost limitations. Determine the number, locations, and placement of samplers by considering: the nature of the response; local terrain; meteorological conditions; location of the site in relation to other conflicting background sources; size of the site; and the number, size, and proximity of separate on-site emission sources and upwind sources. Meteorological effects and other factors are discussed in Section 2.4. Consider the following when placing samples:

- Location of potential on-site emission sources, as identified from the review of site background information or from preliminary on-site inspections.

- The impact of potential off-site emission sources located upwind of the sampling location(s). Study local wind patterns to determine the location of off-site sources.
- Location of topographic features which affect the dispersion and transport of airborne toxic constituents. Avoid natural obstructions when placing air monitoring stations, and account for channelization around those obstructions. (As a general rule, the distance away from the obstruction should be 10 times the height of the obstruction.)
- Proximity of large water bodies which affect atmospheric stability and dispersion of air contaminants.
- Roadways (dirt or paved) which may generate dust that could mask site contaminants. Traffic patterns may also affect results.
- Vegetation such as trees and shrubs which stabilize soil and slow the process of subsurface contaminants becoming airborne. Vegetation also affects air flow and scrubs some contaminants from the air. Thick vegetation can make an otherwise ideal air monitoring station location inaccessible.

Consider the duration of sampling activities when determining the location and number of samples collected. For example, if the sampling period is limited to a few hours, one or two upwind and several downwind samples may be adequate, especially around major emission sources. However, the shorter the sampling period the less likely it is that the plume will be detected and defined.

A short-term monitoring program can range from several days to a few weeks and generally includes gathering data for site assessments, removal or early actions, and source determination data (for further modeling). Activities involved in a short-term sampling strategy must maximize the limited possibilities for data collection. Consider moving upwind/downwind locations daily based on National Oceanic and Atmospheric Administration (NOAA) weather forecasts. Weather monitoring becomes critical where complex terrain and local meteorological effects frequently change wind direction. Often, alternative sampler placements can reduce weather-related sampling error.

Complex terrain situations commonly require an increased number of sampling locations. For

example, a complex valley requires more sampler locations to account for wind variation than does a valley where prevailing winds run its length. Site-specific situations may require innovative planning to collect representative samples. For example, to sample in an area affected by an ocean or lake, placing two sets of samplers next to each other (so that one set is activated during sea-breeze conditions and the other during no sea-breeze conditions) ensures sampling during all wind conditions. After the sampling event, the respective upwind and downwind samples are combined. Alternatively, sampling near a large body of water may be performed with automatic, wind-vector-operated samplers which turn on only when the wind comes from a specific direction. In another situation where sites are located on hillsides, wind will move down a valley and produce an upward fetch at the same time. Sampling locations may have to ring the site to measure the impact of the wind.

Figure 3 depicts sites where off-site sources could affect on-site monitoring. In these cases, on-site meteorological data, concurrent with sampling data, are essential for interpretation of the acquired data. Additional upwind sampler sites may be needed to fully characterize ambient background contaminant levels. Multiple off-site sources may require several monitoring locations, but in cases where the sources are at a sufficient distance from the site, only one monitoring location may be necessary.

Topography and weather are not the only considerations in the placement of samplers; the sampling sites must be secure from vandals and mishap. Secure all sampling locations to maintain chain of custody and to prevent sample tampering and loss of sampling units. High-volume sampling methods often require the use of 110 volt AC electric power. When portable generators are used, the power quality may affect sampler operation. Be aware that the generators themselves could be a potential pollution source if their placement is not carefully considered.

Air quality dispersion models can be used to determine the placement of samplers. The models incorporate source information, surrounding topography, and meteorological data to predict the general distance and directions of maximum ambient concentrations. Use modeling results to select sampling locations in areas of expected maximum pollutant concentrations.

2.3.4 Time, Duration, and Frequency of Sampling Events

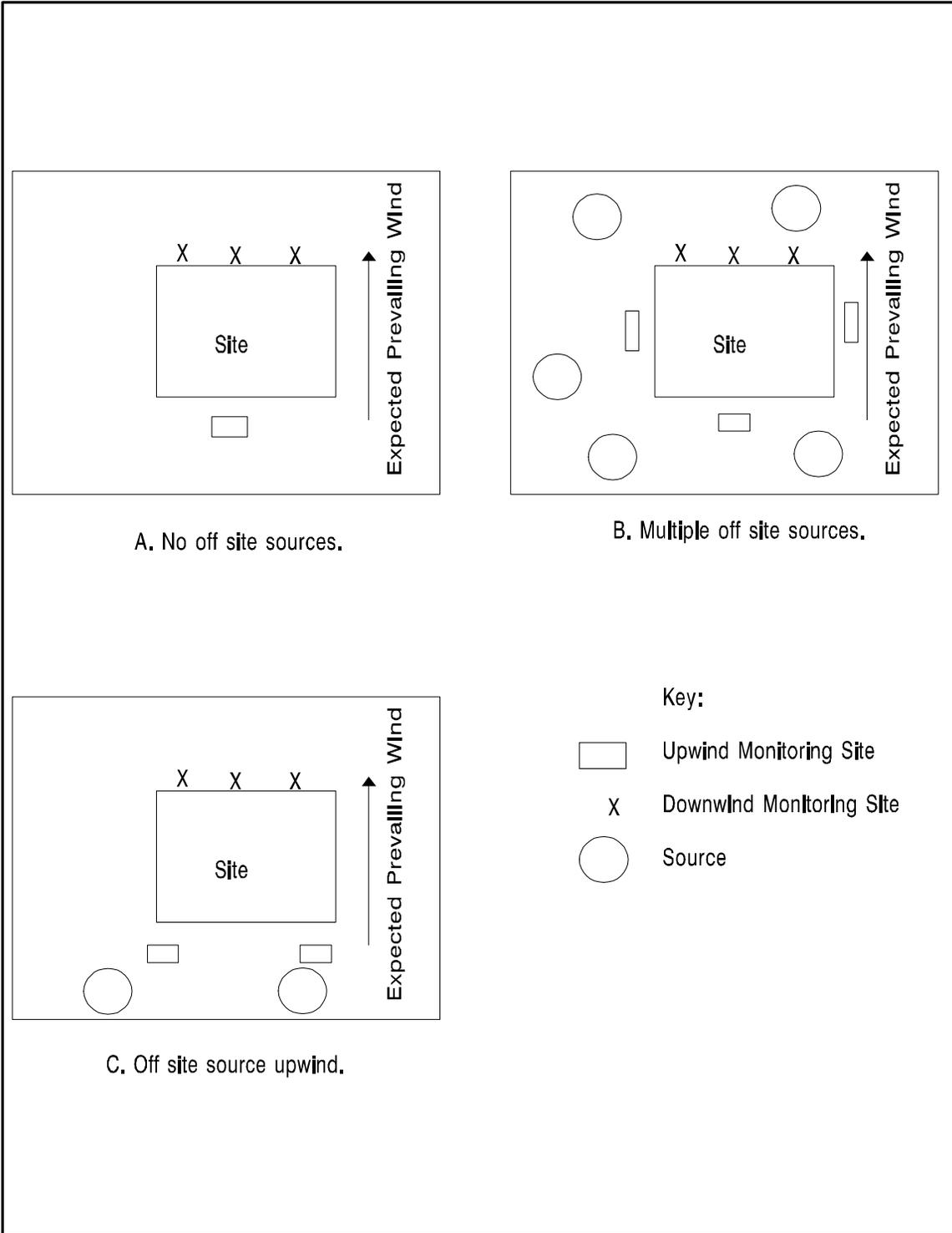
After choosing appropriate sampling or monitoring locations, determine the sampling frequency and the number of samples to be collected. The time of day and duration and frequency of sampling events are governed by:

- Effects of site activities and meteorology on emission rates
- Diurnal effect of the meteorology on downwind dispersion
- Time period(s) of concern as defined by the objective
- Variability in the impact from other non-site-related sources
- Degree of confidence needed for the mean or maximum downwind concentrations observed
- Precision requirements for single measurements
- Cost and other logistical considerations

The duration of the response action and the number of hours per day that site work is conducted determine sampling time, duration, and frequency. Short-term sampling programs may require daily sampling, while long-term programs may require 24-hour sampling every sixth or twelfth day. If the site will be undergoing response activities 24 hours a day, continuous air sampling may be warranted. If the site activities will go on for only 8 hours per day and there are no emissions likely during the remaining 16 hours, then appropriate sampling would begin prior to the start of daily activities, continue during operations, and end at the conclusion of the day's activities. An off-peak sample collection ensures that emissions do not persist after the conclusion of daily clean-up activities. For some sites, emissions are still a factor several hours after daily site activities have been completed. Because of the typically decreased downwind dispersion in the evening, higher downwind concentrations may be detected. For sites where this is a possibility, lengthen the sampling duration accordingly.

Air quality dispersion models can predict the maximum air contaminant concentration expected from a source. The meteorological and site conditions expected to cause the highest concentration are known as "worst-case" conditions and can be identified by analyzing the modeling results. Depending on the objective, sample at times when the model predicts worst-case conditions to exist.

Figure 3
Effects of Off-Site Contamination Sources on
On-Site Monitoring and Sampling



2.3.5 Meteorological Data Requirements

A meteorological monitoring program is an integral part of site monitoring activities. Meteorological data which define local terrain impacts on air flow paths should be examined in advance so they can be appropriately used to interpret air concentration data. Meteorological data may be available from an existing station located near the site (e.g., at a local airport). Otherwise, a station will need to be set up at the site. The meteorological data will document the degree to which samples collected were downwind, and verify whether other worst-case assumptions were met. This information then can be used to refine air quality dispersion models. Meteorological parameters to be monitored are, at minimum, wind speed and wind direction. Wind direction is used to calculate "sigma theta," which is the horizontal wind direction standard deviation (an indicator of atmospheric stability).

2.4 METEOROLOGICAL AND PHYSICAL/CHEMICAL CONSIDERATIONS

2.4.1 Meteorological Parameters

Meteorological parameters are major considerations when designing air sampling plans. Meteorological stability classes, wind speed, and wind direction are the most important parameters in the transport and dispersion of contaminants and the placement of monitoring sites. The remaining parameters primarily affect the amount of a contaminant available in the air. Appendix A contains a detailed overview of meteorological and physical effects on pollutants. Data collection for use with models is more comprehensive and costly than data collected to document basic meteorology (i.e., wind speed and direction).

- **Wind Speed**
When the contaminant of concern is a particulate, wind speed is critical in determining whether the particulate will become airborne, and how much and how far the contamination will travel from the source. Wind speed contributes to the volatilization of contaminants from liquid sources.
- **Wind Direction**
Wind direction highly influences the path of airborne contaminants. Variations in wind

direction increase the dispersion of pollutants from a given source.

- **Atmospheric Stability**
Atmospheric stability refers to the degree to which a parcel of air tends to dampen vertical and horizontal motion. Stable atmospheric conditions (e.g., in the evenings) dampen motion resulting in low dispersion, while unstable atmospheric conditions (e.g., on hot, sunny days) are less dampening and result in higher dispersion.
- **Temperature**
Increased temperature increases the rate of volatilization of organic and some inorganic compounds, and affects the initial rise of gaseous or vapor contaminants. Worst-case emission of volatiles and semi-volatiles occurs at the hottest time of day, or on the hottest day.
- **Precipitation**
Precipitation will scrub or remove airborne contaminants from the atmosphere. The effectiveness of this scrubbing depends on the length and intensity of the precipitation and the chemical and physical properties of the contaminant. Precipitation generally suppresses any generated particulate matter from becoming airborne.
- **Humidity**
High humidity affects water-soluble chemicals and particulates. Humid conditions may determine the sampling media for collecting the air sample, or may limit the volume of air sampled and thereby increase the detection limit.
- **Atmospheric Pressure**
Migration of landfill gases through the landfill surface and through surrounding soils is governed by changes in atmospheric pressure. Atmospheric pressure influences upward migration of gaseous contaminants from shallow aquifers into the basements of overlying structures. Otherwise, the effect of atmospheric pressure is generally minor.

2.4.2 Meteorological Effects

Normal diurnal variations, such as temperature inversions, affect the dispersion of airborne contaminants. Terrain features can enhance or create air inversions and influence the path and speed of air flow, complicating both transport and dispersion patterns.

- **Temperature Inversions**
In an inversion, when radiant heat leaves the lower (near ground) atmosphere, the temperature **increases** with altitude to a certain height. Above that height, the temperature begins to decrease with altitude. The top of the inversion becomes an effective cap where wind speeds above the inversion could flow in a different direction and at a much higher speed than those at the surface. In this very stable atmospheric condition, the cap effectively barricades pollutants, holding them either close to the surface or above the warm layer.

- **Valley Effects**
As the slopes of a valley cool at night by radiation, the air immediately adjacent to the slopes cools also and becomes more dense than the air over the center of the valley at the same elevation. This density imbalance induces convection, with winds flowing downslope to the valley floor. This is commonly referred to as drainage wind or drainage flow. The combination of stable atmospheric conditions, light drainage wind, and inversion can be a potentially dangerous scenario, where pollutants may not only be concentrated from a large area source, but also may be transported over considerable distance with little dispersion.

On clear days with light winds, an up-valley, upslope flow can develop due to the heating of the air adjacent to the sun-warmed slopes and valley floor. Channeling occurs most often when wind speeds are light to moderate and their direction is not perpendicular to the valley. During channeling, winds at the top of the valley may be different from winds at the valley floor.

- **Shorelines**
On summer days with clear skies and light winds, the land surface adjacent to a large lake or ocean is heated much more rapidly than the body of water. This results in a temperature difference, and consequently a density difference, between the air just above the land surface and the air above the water. Because of the density gradient, a local circulation is established with wind moving from the water toward the land. At night, the rapid cooling of the land causes a reverse wind flow toward the water.
- **Hills**
During stable atmospheric conditions, the air will tend to flow slowly around hills. Under unstable conditions, air tends to move faster over

obstructions, with less impact to hillsides.

2.4.3 Physical/Chemical Factors

The chemical characteristics of a contaminant affect its behavior in the atmosphere and can influence the method used to sample and analyze it.

- **Molecular Weight**
When the release involves a pure gas, its molecular weight may influence downwind transport.

- **Physical State**
Pressure and temperature are the predominant controllers of physical state. For sampling purposes, airborne contaminants may be grouped into three broad categories: gases, vapors, and particulates. Semi-volatile compounds can be distributed partially into each phase, as dictated by atmospheric conditions and the compounds' vapor pressures (compounds ranging from naphthalene to PCB could be found in each phase, depending upon conditions).

Particulates may exist as solids or liquids (such as aerosols). Particulates are frequently subdivided into dusts, mists, fumes, and smokes. The distinction between subgroups is based upon particle size, state, and means of generation.

The nature and state (solid, liquid, or gas) of the contaminant determines the sampling method. Gases and vapors are collected in an aqueous medium, on adsorbates, in molecular sieves, or in a suitable container. Particles are collected by filters, impingers, impactors, centrifugal devices (e.g., cyclones), settling chambers, electrostatic precipitators, thermal precipitators, and diffusion batteries.

- **Vapor Pressure**
Vapor pressures of target contaminants determines sampling media selection. As temperature increases, so does the vapor pressure, resulting in more liquid evaporating or vaporizing. Contaminants with high vapor pressures (> 1 mm Hg) volatilize much more readily than those with low vapor pressures. The vapor pressure determines whether the substance is found primarily in the vapor state, on the surface of particles, or in both states.

- **Temperature**
The temperature of contaminants at the time of their release affects the state, transport, and dispersion of the contaminant.
- **Reactive Compounds**
A reactive compound refers to a substance that undergoes a reaction in the presence of water or under normal ambient atmospheric conditions. Among these types of hazard are the pyrophoric liquids which can spontaneously ignite in ambient air without added heat, shock, or friction, and the water-reactive gases such as phosgene that will be decomposed by ambient humidity as they are transported downwind.
- **Photodegradation**
Some compounds undergo photolysis, where ultraviolet (UV) radiation provides enough energy to break bonds (e.g., PNAs).
- Extraneous anthropogenic contaminants (e.g., burning of fossil fuels; emissions from vehicular traffic, especially diesels; volatiles from petrochemical facilities; effluvia from smoke stacks)
- Photo-reactivity or reaction of the parameters of concern with non-related compounds (e.g., nitrogen compounds, sulfur compounds, polyaromatic hydrocarbons)

2.4.4 Environmental Interferences

When designing an air sampling/monitoring program, consider many environmental interferences. Note the following sources of potential environmental interference:

- Natural sources of pollution (e.g., pollen, spores, terpenes, biologically produced waste compounds such as hydrogen sulfide, methane, ore and mineral deposits)

2.5 SAMPLING QA/QC

Sampling QA/QC involves the collection of supplementary samples that will be analyzed in addition to the normal sampling program. Extra equipment and sample media are required to take the QA/QC samples. Chapter 4, Quality Assurance/Quality Control (QA/QC), provides a detailed overview of the types of QA/QC samples and their purpose.

3.0 SAMPLING AND ANALYTICAL TECHNIQUES

3.1 INTRODUCTION

Air sampling and monitoring equipment and techniques support Superfund Program objectives. This chapter provides information on advantages and disadvantages associated with their use. Given the wide range of chemicals with properties that can vary over time, the choice of available technologies is understandably complex. If the wrong technique is selected, the resulting data may be inappropriate or incorrect. This chapter provides a basic understanding of each air monitoring and sampling technique. The summaries focus on the applicability of a wide range of techniques for monitoring, sampling, and analysis of organic and inorganic chemicals in the air. This document does not address sampling and analytical techniques for radiation, radon, or asbestos, but direct reading instruments (radiation meters) are included in the discussion.

3.1.1 Air Sampling Methods Database

In conjunction with this document, an air sampling methods database has been developed to provide additional assistance in preparing air sampling plans. The Air Methods Database is a PC-based, self-contained software package which allows the user to access summarized standard methods for chemical analysis. The software allows the user to make quick determinations on which air sampling approach is appropriate and what equipment should be used to collect and analyze the sample. The database runs on an IBM-compatible personal computer with a hard drive and 640K RAM.

The database has the following features:

- It requires no other software for support (self-contained)
- It provides smooth user interface
- It can search by chemical name, CAS number, or by method
- It makes periodic updates available
- It generates hardcopy
- The user can add, delete, and edit methods

A copy of the database can be obtained by sending a request to:

U.S. EPA - Environmental Response Team
Environmental Resource Center
2890 Woodbridge Avenue
Edison, NJ 08837-3679

Questions regarding the database should be directed to the Environmental Protection Agency's Environmental Response Team in Edison, New Jersey.

3.1.2 Overview of the Methods and Techniques for Air Sampling

A wide range of sampling methods and techniques is available to support air monitoring and sampling activities. Selecting the most appropriate techniques for a given situation depends on the following factors:

- Type of sampling applications
- Chemicals to be sampled (volatile organic, semi-volatile organic, inorganic, corrosive, toxic, particulate, etc.)
- Duration of response action
- Acquisition time for daily data gathering
- Mobilization and set-up time needed to collect samples
- Weather conditions
- Specificity required in identifying chemicals
- Relative precision and accuracy attainable
- QA/QC objective required
- Detection levels attainable
- Cost

Tables 2 to 5 summarize the capabilities, advantages, and disadvantages of direct reading instruments and techniques, sampling equipment, sampling collection media/devices, and analytical techniques. These tables are not inclusive, since methods and techniques may be modified to fit a specific sampling scenario.

Key to Tables 2, 3, 4, and 5

Applications (see Chapter 2 for additional information on sampling applications)

A - On-site health and safety	E - Off-site chronic unknown exposure
B - Off-site acute known exposure	F - Confirmatory sampling
C - Off-site acute unknown exposure	G - Odor complaints
D - Off-site chronic known exposure	H - Source identification

Mobilization Time

Short - Less than 2 hours to set up equipment

Long - More than 2 hours to set up equipment

Data Acquisition Time

Hours - Data from samples are available within hours

Days - Data from samples usually take days to process

Weeks - Data from samples usually take weeks to process

Specificity

Non-specific - No information about compound type or identity

Class - Type or class of compound provided, but not identity

Compound - Identity of compound is provided

Cmpd. Qualified - Identity of compound is provided only if a reference standard for comparison is available

Relative Precision and Accuracy

Poor - Technique produces highly variable data

Fair - Technique produces acceptable data using the recommended QA/QC level

Good - Technique produces data with good precision and little bias using the recommended QA/QC level

Excellent - Technique produces data with high precision and little bias using the recommended QA/QC level.

Detection Levels (units within parentheses apply to Table 3.1)

Very low - Detection limits routinely less than 1 pg (fractional ppb(v) and lower)

Low - Detection limits routinely less than 1 Fg (ppb(v))

Medium - Detection limits routinely greater than 1 mg (fractional ppm(v) to low ppb(v))

High - Detection limits routinely greater than 10 mg (ppm(v))

Relative Cost

\$ - Instrumentation cost < \$1,000; Sample cost < \$50 per sample

\$\$ - Instrumentation cost \$1,000 - \$10,000; Sample cost \$50 - \$150 per sample

\$\$\$ - Instrumentation cost \$10,000 - \$50,000; Sample cost \$150 - \$500 per sample

\$\$\$\$ - Instrumentation cost > \$50,000; Sample cost > \$500 per sample

TABLE 2: Summary of Direct Reading Instruments and Techniques* (Part 1 of 2)

Instrument and Technique	Analyte Category	Applications	Data Turnaround Time	Relative Cost	Specificity	False Pos.	False Neg.	Precision and Accuracy	Detection Level
Flame Ionization Detector (FID)	VOCs, Semi-Volatiles	A,B,H	Minutes	\$\$ ⁽³⁾	Non-specific	No	No ⁽¹⁾	Fair	Medium ⁽²⁾
	Advantages: Easy to use; Inexpensive					Disadvantages: Generally not compound specific; Response varies among compounds.			
Photoionization Detector (PID)	VOCs	A,B,H	Minutes	\$\$ ⁽³⁾	Non-specific	No	Yes	Fair	High ⁽²⁾
	Advantages: Easier to use than FIDs.					Disadvantages: Unable to differentiate between chemicals and chemical classes; Cannot be used for aliphatic hydrocarbons; Response of instrument dependent on proper bulb selection; Methane and moisture distort reading.			
Electro-Chemical Monitors	VOCs	A,B,H	Minutes	\$ ⁽³⁾	Compound	No	Yes	Fair	Medium
	Advantages: Easy to use; Inexpensive; Compound-specific.					Disadvantages: Prone to interference from high ambient moisture; Affected by freezing temperature.			
Oxygen Meter	Oxygen	A	Minutes	\$\$ ⁽³⁾	Compound	Yes	Yes	Fair	High
	Advantages: Easy to use; Compound-specific.					Disadvantages: None significant.			
Lower Explosive Limit Meter	VOCs	A	Minutes	\$\$ ⁽³⁾	Non-specific	No	Yes	Fair	High
	Advantages: Easy to use.					Disadvantages: None significant.			
Particulate Monitor	Particulate Monitor	A,B	Minutes	\$	Non-specific	No	No	Fair	Medium
	Advantages: Easy to use.					Disadvantages: None significant.			
Radiation Meter (field)	Radio-nuclides	A,B,H	Minutes	\$ ⁽³⁾	Non-specific	No	Yes	Fair	N/A
	Advantages: Easy to use.					Disadvantages: None significant.			
Gold Film	Hydrogen Sulfide, Mercury	A,B,G,H	Minutes	\$\$ ⁽³⁾	Compound	No	Yes	Fair	Low
	Advantages: Easy to use; Good detection limits; Compound-specific.					Disadvantages: None significant.			

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages among analytical methods. (1) Only for selected halogenated compounds. (2) Affected by the variability of the background. (3) Cost of the instrument.

TABLE 2: Summary of Direct Reading Instruments and Techniques* (Part 2 of 2)

Instrument and Technique	Analyte Category	Application	Data Turnaround Time	Relative Cost	Specificity	False Pos.	False Neg.	Precision and Accuracy	Detection Level
Infrared Detectors	VOCs, Semi-Volatiles	A,B,H	Minutes	\$\$ ⁽³⁾	Class/Compound	Yes	Yes	Fair	High - Medium
	Advantages: Easy to use; Detects multiple compounds.					Disadvantages: Requires 115 VAC power; Target compounds should be known; Prone to interference.			
Colorimetric Tubes	VOCs, Inorganics	A,B	Minutes	\$ (\$30-\$60 box of ten)	Class/Compound	Yes	No	Poor	High - Medium
	Advantages: Easy to use; Inexpensive; Compound-specific.					Disadvantages: High detection limits; Prone to interference.			
Remote Optical Sensing	VOCs, Inorganics	B,C,D,E,F,G,H	Minutes	\$\$\$\$ ⁽³⁾	Compound	Yes	Yes	Good	Low
	Advantages: Provides new set of concentrations every 3-5 minutes; provides excellent flexibility; Measures large number of compounds at low detection limits; good for determination of the variation of emission rates over time.					Disadvantages: Expensive; Requires trained operator; Prone to interference; Used in conjunction with the collection of concurrent on-site meteorological data or with releases of tracer gases.			
TAGA	VOCs, Semi-Volatiles	B,D,G,H	Hours/Days	\$\$\$\$ ⁽³⁾ (Sample \$\$\$)	Compound	Yes	No	Excellent	Low
	Advantages: Mobile monitoring; Good detection limits for most solvents; Provides new set of concentrations every 2-3 seconds; Real-time plume delineation; Detects and identifies low levels of polar compounds.					Disadvantages: Target compounds should be known; Not capable of resolving certain individual groups of compounds; Used for approximately 12-14 hours per day; Only one unit currently available for use; Requires at least one day to switch from standard non-polar compound analysis to polar compound analysis.			
Portable GCs	VOCs, Semi-Volatiles	D,E,H	Hours	\$\$	Compound	Yes	No	Good	Low
	Advantages: Qualitative identification and quantitative determination of relative concentrations in the field.					Disadvantages: Many require AC power; Shelter or trailer needed. Direct air samples are not truly representative of either the average or maximum plume concentrations; therefore, the results can only be considered semi-quantitative.			

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages for the most common direct reading instruments and techniques available for use. (3) Cost of the instrument.

TABLE 3: Summary of Sampling Equipment*

Equipment	Analyte Category	Applications	Mobilization Time	Relative Cost	Advantages	Disadvantages
High Volume TSP Samplers	Metals, Particulates	B,C,D,E,F, H ⁽¹⁾	Short	\$\$ ⁽⁴⁾	Large air sample volume for low detection limits; Simple operation and rapid set-up; Weather-proof, but weather influences samples; Easily automated.	Requires 110 VAC power; Difficult to mobilize; Bulky.
PM-10 Samplers	Metals, Particulates	B,C,D,E,F, H ⁽¹⁾	Short	\$\$ ⁽⁴⁾	High volume yields low detection limits; Low volume X-Ray Fluorescence (XRF) analysis; Simple operation and easy set-up; Not affected by weather; Easily automated.	Requires 110 VAC power; Difficult to mobilize; Bulky (large unit size and weight).
High Volume PS-1 Samplers	Semi-Volatiles	B,C,D,E,F,G H ⁽¹⁾	Short	\$\$ ⁽⁴⁾	Provides detection at very low concentrations; Simple operation and rapid set-up; Not affected by weather; Easily automated.	No size selection inlet; Requires 110 VAC power; Difficult to mobilize; Bulky.
Personal Sampling Pumps	Metals, VOCs, Semi-Volatiles, Inorganics	A,B,C,D,E,F,G,H	Short	\$ ⁽⁴⁾	Rapid set-up for time average sampling; Small and compact; Portable, reliable, and versatile; Battery operated; Intrinsically safe.	Flow rates are too low to provide detection of some compounds; Pumps are not weather-proof; Requires frequent monitoring to ensure pumps are operating; Sampling periods longer than 8 hours usually require recharging the battery (can be run on AC operation).
Canister Samplers	VOCs	B,C,D,E,F ⁽²⁾ , G ⁽²⁾ ,H ⁽³⁾	Short	Positive Pressure Samplers \$\$\$ ⁽⁴⁾ Sub-Ambient Pressure Samplers \$-\$\$\$ ⁽⁴⁾	Reliable, flexible, and easy to operate; Large air sample volume; Weather-proof.	Pressurized units require 110 VAC or a battery to operate pump; Units without 110 VAC power may not work properly in sub-freezing weather; Units need to be checked for leaks before each field assignment; Rigorous QA/QC is required to ensure cleanliness of samplers, especially pressurized systems.

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages for sampling equipment available for use.

(1) Requires the collection of multiple days of sampling with the concurrent collection of on-site meteorological data followed by a sophisticated statistical correlation analysis.

(2) Limited to only the non-polar and slightly polar compounds responsible for an odor complaint. (3) Sector sampler system. (4) Cost of the equipment only.

TABLE 4: Summary of Sampling Collection Media/Devices* (Part 1 of 3)

Media/ Device	Analyte Category	Applications	Relative Cost	Advantages	Disadvantages
Canisters	VOCs	C,D,E,F,G,H	\$\$ ⁽²⁾	Once samples are collected, there is little or no sample degradation for most compounds for up to 30 days; Sufficient sample volume for repeated analysis; Straightforward cleaning procedure; Excellent for non-polar VOCs; Good for some polar VOCs; Easily transported and operated; Detection limits 0.05 - 1.0 ppb by volume achieved; Obtain whole air sample with no possibility of breakthrough problems; Little sample degradation due to reactive component of air (e.g., ozone); No special extended holding times or shipment requirements.	Sample collection systems need to be rigorously cleaned to avoid cross-contamination; Not reliable for most polar (odorous) compounds; Requires special procedures for cleaning canisters when they are exposed to greater than ambient concentrations of a contaminant; Leaks in valves may develop over time.
Passive Dosimeters	VOCs, Inorganics	A,C,E,F,G	\$ ⁽²⁾	Easy to use; Non-obtrusive to wearer; Inexpensive.	Difficult to recover some compounds from dosimeters; Most relevant for industrial hygiene; Results after the fact; Relatively high detection limits.
Polyurethane Foam (PUF)	Semi-Volatiles, Non-Volatile Organics	A,B,C,D,E,F	\$ ⁽²⁾	Excellent for collection of heavier PCBs, most pesticides, dioxins, furans, and long-chain PAHs; With properly cleaned foam, excellent detection limits with little or no background contamination; Best when used with high volume sampling methods; Multiple analysis of extracts is possible.	Requires XAD backup when used for lighter PCBs and PAHs; Samples need to be chilled when stored and shipped; Care must be taken during setup, tear down, and cleanup to avoid contamination; Foam should be shipped ready for use in pre-cleaned glassware from analytical laboratory; Limited sample holding time.
Sampling Bags	VOCs	A,G,H	\$ ⁽²⁾	Large air sample volume; Excellent for fixed gases and methane; Inexpensive.	Difficult to ship and bags may break; Very limited holding time (maximum 1-2 days; less volatile compounds, 1-2 hours); Artifact formation; Background contamination (especially below 1 ppm); Sample loss from adsorption of some analytes to bag walls.

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages for types of sampling collection media/devices available for use. (2) Cost of the media only.

TABLE 4: Summary of Sampling Collection Media/Devices* (Part 2 of 3)

Media/ Device	Analyte Category	Applications	Relative Cost	Advantages	Disadvantages
Impingers	Inorganics, Gases	B,D,F,G	\$	Simple analysis; Good collection efficiency; Compound-specific.	More difficult to set up than most samplers; High detection limit ranges; Care must be taken during sampling to avoid spilling of impinger solution.
Thermally Desorbed Media					
Tenax Tubes ⁽¹⁾	VOCs, Some Semi-Volatiles, Inorganics, Non- Volatile Organics	A,B,C,D,E,F, G,H	\$ ⁽²⁾	Inexpensive, rugged, and reusable; Large number of VOCs and semi-volatiles can be sampled; Easy to use and easily automated; Low detection limits achievable.	Limited holding time for samples; Samples need to be chilled when stored and shipped; Breakthrough volumes vary by compound and temperature; Analytes are not always quantitatively desorbed; Background contamination, especially light aromatics due to breakdown of polymer; Artifact formation; One analysis per sample tube; Cleanup procedure time-consuming and easily contaminated.
Carbonized Polymers ⁽¹⁾	VOCs	C,D,E,F,G,H	\$ ⁽²⁾	Easy to use; Good detection limits achievable.	Limited number of compounds that can be sampled; Thermal desorption may not remove all compounds quantitatively or reproducibly; Easily contaminated; Only one analysis available from each tube.
Mixed Sorbent Tubes ⁽¹⁾	VOCs, Semi- Volatiles, Inorganics, Non- Volatile Organics	A,B,C,D,E,F, G,H	\$ ⁽²⁾	Easy to use; Quick set-up; Good for polar compounds; Sorbents can be silica gel and resins, and can be pretreated with specific chemicals; Optimized for specific classes of polar compounds.	High humidity can affect flow rate; Must know the compound to be monitored; Not recommended for general ambient air levels when using solvent extractions; Tenax/charcoal tubes require samples be kept chilled when stored and shipped.

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages for types of sampling collection media/devices available for use. (1) When solvent-extracted associated advantages and disadvantages will differ. (2) Cost of the media only.

TABLE 4: Summary of Sampling Collection Media/Devices* (Part 3 of 3)

Media/ Device	Analyte Category	Applications	Relative Cost	Advantages	Disadvantages
Solvent-Extracted Media					
Chemically Treated Silica Gel			\$(²)	Easy to use.	High humidity can affect results; Must chemically treat for specific compounds.
XAD-2 Polymers	Semi-Volatiles, Non-Volatile Organics	A,B,C,D,E,F,H	\$(²)	Excellent for the retention of short-chain semi-volatiles (PAHs); Soxhlet extraction, followed by concentration of the artifacts, provides excellent detection limits.	Samples need to be chilled when stored and shipped; Care must be taken during setup, tear down, and cleanup to avoid contamination; Only pre-cleaned resin furnished and certified by analytical laboratory should be used; Limited sample holding time after resin is cleaned or after a sample is collected; Artifacts from the polymer are usually present in measurable amounts; Resin may fracture after it has been cleaned.
Carbon Cartridges	VOCs	A,B,C,D,E,F,G,H	\$(²)	Large number of VOCs can be sampled; Quick set-up.	Loss of target analytes by irreversible sorption on the carbon; Loss of target analytes due to breakthrough of some VOCs; Background contamination; Requires two analyses (front and back section); Possible artifact formation and selected compound decomposition of lower concentrations.
Particulate Filters					
Particulate Filters	Particulates, Inorganics, Non- Volatile Organics	A,B,C,D,E,F,H	\$(²)	Collects various airborne particulates; Filters can be analyzed by various methods.	Some filters not applicable to specific analyses.

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages for types of sampling collection media/devices available for use. (2) Cost of the media only.

TABLE 5: Summary of Analytical Techniques*

Analytical Techniques	Analyte Category	Application	Data Turnaround Time	Relative Cost	Specificity	False Pos.	False Neg.	Precision and Accuracy	Detection Level
High Performance Liquid Chromatography (HPLC)	Semi-VOCs, Non-VOCs, Polars	A,B,C,D,E,F,G	Days/Weeks	\$\$\$ ⁽¹⁾	Compound	Yes	No	Good	Low to Very Low
	Advantages: Good for polar compounds, PAHs, high thermal energy compounds (explosives), and thermally unstable compounds; Good separation between similar compounds; Low detection limits.					Disadvantages: Interference problems; Less readily available method than GC.			
Gas Chromatography (GC)	VOCs, Semi-Volatiles	A,B,C,D,E,F,G,H	Hours/Weeks	\$\$\$ to \$\$\$\$ ⁽¹⁾	Compound	Yes	No	Good to Excellent	Low to Very Low
	Advantages: Easily automated; Best for non-polar compounds; Detects wide range of compounds with a single analysis; Good detection limits; Good quantitative and qualitative results; GC/MS provides better confirmation of contaminants and detection limits than less selective detectors; GC/MS in the SIM mode provides low detection limits and good selectivity.					Disadvantages: GC/MS is relatively expensive; In SIM mode the compound must be known and data on other compounds are not collected; When analyzing for a wide range of compounds resolution of similar compounds may be difficult.			
Wet Chemical/Photometric Analyses	Elements, Inorganics	A,D,E,F,H	Weeks	\$ to \$\$\$ ⁽¹⁾	Class	Yes	No	Fair	Med. to High
	Advantages: Easy to perform, even in the field; Reasonable quantitative results; Inexpensive.					Disadvantages: Non-specific; Prone to interference; High detection limits.			
Ion Chromatography (IC)	Elements, Inorganics	A,B,C,D,E,F,H	Weeks	\$ to \$\$\$ ⁽¹⁾	Class	Yes	No	Good	Low to Med.
	Advantages: Detects inorganic anions; Low detection limits.					Disadvantages: Prone to interference.			
Atomic Absorption (AA)	Metals	A,B,D,E,F,H	Days	\$ to \$\$\$ ⁽¹⁾	Element	No	No	Excellent	Low
	Advantages: Quantitative; Low detection limits.					Disadvantages: Only one metal can be analyzed at a time; Variability in analytical results for some metals.			
Inductively Coupled Plasma (ICP) Emission Spectrometer	Metals	A,B,C,D,E,F,H	Days	\$ to \$\$\$ ⁽¹⁾	Element	No	No	Excellent	Low
	Advantages: Automated analysis; Multiple elements detected in a single analysis; Detection limits comparable to Flame AA; Inexpensive.					Disadvantages: Detection limits are approximately an order of magnitude less than Graphite Furnace AA; Detection limits for some metals are poor (e.g., Cr).			
X-Ray Fluorescence (XRF)	Metals	A,B,C,D,E,F,H	Days	\$ to \$\$\$ ⁽¹⁾	Element	No	No	Good	Low
	Advantages: No interferences; Low detection limits; Multiple metals analysis.					Disadvantages: Costly if only a few elements desired; Semi-quantitative; Only Teflon filters are recommended; Sensitive to amount of particulate collected.			

* Exceptions to some of these classifications can be found. This table is designed to provide a quick reference showing relative advantages and disadvantages among analytical methods.
 (1) Cost of the sample.

3.2 DIRECT READING INSTRUMENTS AND TECHNIQUES

There are two general types of direct reading instruments: portable screening devices and specialized analytical instruments. All these techniques involve acquiring, for a specific location or area, continuous or sequential direct air concentrations in either a real-time or semi-real-time mode.

3.2.1 Portable Screening Devices

These portable instruments are useful for rapid screening methods. They involve simple, relatively inexpensive techniques. They are usually not very selective and can produce false positive results. None of these instruments can acquire true time-weighted average concentrations. They are not capable of acquiring simultaneous concentration readings at multiple locations, although several can sequentially analyze samples taken remotely from different locations.

- **Flame Ionization Detectors (FIDs)**
FIDs are sensitive to volatile organic vapor compounds such as methane, propanol, benzene, and toluene. They respond poorly to organic compounds lacking hydrocarbon characteristics. An example of an instrument using an FID is the Organic Vapor Analyzer (OVA).
- **Photoionization Detectors (PIDs)**
PIDs depend on the ionization potential of compounds. PIDs are sensitive to aromatic and olefinic (unsaturated) compounds such as benzene, toluene, styrene, xylenes, and acetylene. Greater selectivity is possible if low-voltage lamps are used.
- **Electrochemical Monitors**
Electrochemical monitors use an electrochemical sensor to determine the concentration of a compound in air. These monitors are compound-specific and operate in a limited concentration range. High humidity may produce low-bias results in some models.
- **Oxygen Meters**
Oxygen meters use an electrochemical sensor to determine the air's oxygen concentration. The meters are calibrated for sea level and may indicate a false negative (i.e., lower O₂

content) at higher altitudes.

- **Lower Explosive Limit (LEL) Meters**
LEL meters measure the concentration of a flammable vapor or gas in air and present this measurement as a percentage of the LEL. The measurements are temperature dependent. The calibration gas determines sensitivity.
- **Radiation Meters**
Radiation meters determine the presence and level of radiation. The meters use a gas or solid ion detection medium which becomes ionized when radiation is present. The meters are normally calibrated to one probe.
- **Gold Film (H₂S and Hg Monitors)**
H₂S and Hg monitors operate on the principle that electric resistivity increases across a gold film as a function of H₂S and Hg concentration. These monitors provide rapid and relatively low detection limits for H₂S and Hg in air. After extensive sampling periods or exposure to high concentrations of H₂S and Hg, the gold film must be heated to remove contamination and to return the monitor to its original sensitivity.
- **Infrared Detectors**
Infrared detectors such as the Miniature Infrared Analyzer (MIRAN) use infrared (IR) absorption as a function of specific compounds. MIRAN instruments are useful when contaminants are identified but their concentrations are unknown. The MIRAN-C, however, is a screening model which can be useful for identifying unknowns in simple mixtures. MIRAN instruments generally require AC power.
- **Colorimetric Tubes**
Colorimetric tubes are small, calibrated glass tubes filled with various reactive ingredients. They can identify the presence of specific vapors by a color change in the tube when contaminated air is pumped or passively diffused through the tube. Diffusion detector tubes clipped to clothing can provide contaminant measurements over time without pumps. Colorimetric tubes are not continuous monitors and can determine concentration only in a grab sample.

3.2.2 Specialized Analytical Instruments

The continuous monitors already described provide qualitative measurements of air contaminants. To collect quantitative measurements in the field, more sophisticated instruments, such as the portable Gas Chromatograph, are used for analysis of grab samples.

- **Direct Air Sampling Portable Gas Chromatographs (GCs)**

Portable GCs use gas chromatography to identify and quantify compounds. The time it takes for a compound to move through a chromatographic column is characteristic of that specific compound or group of compounds. A trained technician with knowledge of the range of expected concentrations of compounds can utilize a portable GC in the field to analyze grab samples. Operation of GCs generally requires AC power and shelter. The accuracy of this method is limited by the representativeness of the short-term grab sample.

- **Remote Optical Sensing**

This technique, also referred to as open-path monitoring, involves using either an infrared or an ultraviolet light beam across a long open path and measuring the absorbance at specific wavelengths. This technique is capable of analyzing any pre-selected organic or inorganic volatile compound which can be resolved from compounds naturally occurring in ambient air. Projected Superfund applications include perimeter monitoring during site cleanups and measurement of emission source concentrations during site assessments (Minnich, et al. 1990).

- **TAGA Direct Air Sampling Mass Spectrometer**

The Toxic Ambient Gas Analyzer (TAGA), which is operated by the U.S. EPA Environmental Response Team (ERT), is capable of real-time detection of pre-selected organic compounds at low parts per billion concentrations. The instrument has been successfully used by ERT for isolating individual emission plumes and tracing those plumes back to their sources.

3.3 SAMPLING EQUIPMENT

3.3.1 High Volume, Total Suspended Particulate (TSP) Samplers

High volume, TSP samplers collect all suspended particles by drawing air across an 8 by 10 inch glass-quartz filter. The sample rate is adjusted to 40 cubic feet per minute (cfm), or 18.9 liters per second, and held constant by a flow controller over the sample period. The mass of TSPs is determined by weighing the filter before and after sampling. The composition of the filter varies according to the analysis method and the detection limit required.

3.3.2 PM-10 Samplers

PM-10 samplers collect particulates with a diameter of 10 microns or less from ambient air. Particulates of this size represent the respirable fraction, and thus are of special significance. PM-10 samplers can be high volume or low volume. The high volume sampler operates in the same manner as the TSP sampler at a constant flow rate of 40 cfm, drawing the sample through a special impactor head which collects particulates of 10 microns or less. The particulate is collected on an 8 by 10 inch glass-fiber filter. The low volume sampler or low volume PM-10 sampler operates at a rate of approximately 17 liters per minute. The flow must remain constant through the impactor head to maintain the 10 micron cut-off point. The low volume PM-10 collects its sample on 37-mm Teflon filters.

3.3.3 High Volume PS-1 Samplers

High volume PS-1 samplers draw a sample through polyurethane foam (PUF), or a combination foam and XAD-2 resin plug, and a glass-quartz filter at a rate of 5 to 10 cfm, or 2.4 to 4.7 liters per second. This system is excellent for measuring low concentrations of semi-volatiles, PCBs, pesticides, or chlorinated dioxins in ambient air.

3.3.4 Personal Sampling Pumps

Personal sampling pumps are reliable, portable sampling devices that draw air samples through a number of sampling media including resin tubes, impingers, and filters. Flow rates are usually adjustable from 0.1 to 4 liters per minute and can remain constant for up to 8 hours on one battery charge, or continuously with an AC charger/converter.

3.3.5 Canister Samplers

Generally, there are two types of canister samplers. *Evacuated systems* simply use the pressure differential between the evacuated canister and ambient pressure to bleed air into the canister. The sample is bled into the canister at a constant rate over the sampling period until the canister is near atmospheric pressure, using either a critical orifice, mechanically compensated regulator, or a mass-flow control device. *Pressure systems* use a pump to push air into the canister. To maintain a higher, more controlled flow, the pump typically controls the pressure differential across a critical orifice at the inlet of the canister, resulting in a pressurized canister at the completion of sampling.

3.4 SAMPLING COLLECTION MEDIA/DEVICES

Some of the more common sampling collection media/devices used in air sampling are discussed below. The advantages and disadvantages of each medium/device, and its unique sample preservation needs and holding times are identified in Table 2.

Before employing a specific sampling method, consult the laboratory that will conduct the analyses, if possible. Many of the methods can be modified to provide better results, or a wider range of results.

3.4.1 Canisters

Canisters are highly polished, passivated stainless steel containers. One method of canister preparation, the SUMMA electro-polishing process, cleans and reduces the inner surface area of the canister and causes the formation of chromium and nickel oxides on the surface so that the adsorption of VOCs is reduced. The canister is cleaned and evacuated in the laboratory prior to sampling. At the sampling site, the canister is often placed in a sampler that is designed for time-integrated collection at constant flow rates. Samples can be collected by allowing air to bleed into or be pumped into the canister. Canisters come in various sizes, most commonly 6 and 15 liters. Evacuated canisters can be opened in the field to collect a grab sample.

3.4.2 Passive Dosimeters

Passive dosimeters are clip-on vapor monitors (samplers) with specially prepared, active surfaces

which absorb the diffused contaminants. Industrial hygienists commonly use dosimeters to obtain time-weighted averages/concentrations of chemical vapors because they can trap over 130 organic compounds. Selective dosimeters have been developed for a number of chemicals including formaldehyde, ethylene oxide, hydrogen sulfide, mercury vapor, nitrogen dioxide, sulfur dioxide, and ozone. Dosimeters must be analyzed in a laboratory.

3.4.3 Polyurethane Foam (PUF)

PUF is a sorbent used with a glass or quartz filter for the collection of semi-volatile and non-volatile organic compounds such as pesticides, PCBs, chlorinated dioxins and furans, and polynuclear aromatic hydrocarbons (PAH). Fewer artifacts (chemical changes that occur to collected compounds) are produced than with some other solid sorbents. PUF is used with the PS-1 sampler and EPA method TO-13. Breakthrough of the more volatile PCBs and PAHs may occur when using PUF.

3.4.4 Sampling Bags

Sampling bags, like canisters, transport an air sample to the laboratory for analysis. Samples are generally pumped into the bags, but sometimes a "lung" system is used which uses a pump to create a vacuum around the bag in a drum. This in turn draws air from the source into the bag without the potential for cross-contamination from the pump. This vacuum method is used for volatile organic compounds (VOCs), fixed gases (CO₂, O₂, and N₂), and methane.

3.4.5 Impingers

Impingers allow an air sample to bubble through a solution which collects a specific contaminant by either chemical reaction or absorption. During long sampling periods, the impinger may need to be kept in an ice bath to prevent the solution from evaporating during sampling. A sampling pump draws the sample through the impinger or, in more elaborate sampling trains, through multiple impingers. Take care to avoid spilling impinger solution during sample collection, storage, and shipping.

3.4.6 Sorbent Tubes/Cartridges

Various sampling media are available in sorbent tubes, which are used primarily for industrial hygiene. A few examples are carbon cartridges, carbon molecular sieves, Tenax tubes, and the XAD-2 polymer. Depending upon the sorbent material, tubes

can be analyzed using either solvent extraction or thermal desorption. The former technique uses standard laboratory equipment and allows for multiple analyses of the same sample. The latter technique requires special, but readily available, laboratory equipment and allows only one analysis per sample. Thermal desorption typically allows for lower detection limits (by two or more orders of magnitude) than solvent extraction. Whenever sorbent tubes are used for thermal desorption, they should always be certified as clean by the analytical laboratory.

Thermally Desorbed Media

Thermally desorbed media use high temperature gas streams to remove the compounds collected on a sorbent medium. The gas stream is injected and often cryofocused into an analytical instrument, such as a GC, for compound analysis. The following are examples of thermally desorbed media:

- **Tenax Tubes**
Tenax tubes are made from a commercially available polymer (p-phenylene oxide) packed in glass or stainless steel tubes through which air samples are drawn or sometimes pumped. The tubes are used in EPA Method TO-1 and VOST. These collection media are appropriate for sampling volatile, nonpolar organics; some polar organics; and some of the more volatile of the semi-volatile organics. Tenax tubes are not appropriate for many of the highly volatile organics (i.e., with vapor pressures greater than approximately 200 mm Hg).
- **Carbonized Polymers**
The carbonized molecular sieve, a carbonized polymer, is a commercially available carbon sorbent packed in glass or stainless steel sampling tubes through which air samples are drawn or pumped. These are used in EPA Method TO-2 for highly volatile nonpolar compounds which have low breakthrough volumes on other sorbents. High thermal-desorption temperatures may cause more variability in analysis when used with carbonized molecular sieves than with other sorbents.
- **Mixed Sorbent Tubes**
Sorbent tubes can contain two types of sorbents. Combining the advantages of each sorbent into one tube increases the types of compounds that can be sampled. The combination of two sorbents can also reduce

the chance that highly volatile compounds will break through the sorbent media. An example of a mixed sorbent tube is the combination of Tenax and charcoal with a carbonized molecular sieve. A potential problem with mixed sorbent tubes is the breakthrough of a compound from an earlier sorbent (from which it cannot be desorbed) to a later sorbent.

Solvent-Extracted Media

Solvent-extracted media use the principle of chemical desorption to remove compounds collected on a sorbent medium. The chemical solvent is injected into an instrument such as a GC for analysis of compounds. Examples of solvent-extracted media follow:

- **Chemically Treated Silica Gel**
Silica gel is a sorbent which can be treated with various chemicals before being used to sample for specific compounds in air. Examples of chemically treated silica gel include the DNPH-coated silica gel cartridges used with EPA Method TO-11.
- **XAD-2 Polymers**
XAD-2 polymers usually are placed in tubes, custom packed sandwich-style with polyurethane foam, and prepared for use with EPA Method TO-13 or the semi-VOST method. The polymers are used for the collection of semi-volatile polar and nonpolar organic compounds. The compounds collected on the XAD-2 polymer are chemically extracted for analysis.
- **Carbon Cartridges**
Carbon cartridges, consisting of primary and backup sections, trap compounds by adsorption. Ambient air is drawn through them so that the backup section verifies that breakthrough of the analytes on the first section did not occur, and that therefore the sample collection was quantitative. Quantitative sample collection is evidenced by the presence of target chemicals on the first carbon section, and their absence on the second section. The adsorbed compounds must then be eluted, usually with a solvent extraction, and analyzed by GC with a detector such as a mass spectrometer (MS).

- **Tenax Tubes**
Tenax tubes are used in OSHA and NIOSH methods in a manner similar to carbon cartridges; they are typically used for less volatile compounds.

3.4.7 Particulate Filters

Particulate filters collect particulates present in the air pumped through them. The filter is then analyzed for particulate mass, or chemical or radiological composition. Particulate filters are made from a variety of materials which are described below. An example of a common use for each filter is also given.

- **Mixed Cellulose Ester (MCE)**
MCE is manufactured from mixed esters of cellulose which are a blend of nitro-cellulose and cellulose acetate. MCE filters are used primarily for particulate sampling, with subsequent analysis for metals or asbestos.
- **Glass Fiber**
Glass fiber is manufactured from glass fibers without a binder. Particulate filters with glass fiber provide high flow rates, wet strength, and high, solid holding capacity. Glass fiber filters are generally used for gravimetric analysis of particulates.
- **Polyvinyl Chloride**
Particulate filters with polyvinyl chloride are resistant to concentrated acids and alkalis. Their low moisture pickup and light tare weight make them ideal for gravimetric analysis.
- **Teflon**
Teflon is manufactured from polytetrafluorethylene. Particulate filters with Teflon are easy to handle and exceptionally durable. Teflon filters are used for metal collection and analysis.
- **Silver**
Particulate filters manufactured from pure silver have high collection efficiency and uniform pore size. These filters are used for mercury, chlorine, chrysene, and coal tar collection and analysis.
- **Cellulose**
Particulate filters with cellulose contain less than 0.01 percent ash. These filters are used to collect particulates.

3.5 ANALYTICAL TECHNIQUES

This section describes types of analyses that are used for air samples.

3.5.1 High Performance Liquid Chromatography (HPLC)

HPLC is a technique that separates organic compounds by passing a solution containing organics through a tube column packed with an adsorbing material (packing). The solvent or mobile phase (usually water or a water/solvent mixture) is pumped through the tube under high pressure, forcing the compounds through the column. By the time the individual compounds reach the end of the column, they have separated because of their relative adsorption on the packing. The solvent then pushes the compounds into the detector, which generates a signal proportional to the quantity of each compound present. The most commonly used detector is the ultraviolet/visible (UV/Vis) absorbance detector which responds to nanogram quantities of many organics. The second most commonly used detectors are fluorescence and electrochemical detectors, which respond to more selective classes of organic compounds in the sub-nanogram to sub-picogram quantities. Other detectors used include conductivity (inorganic compounds), infrared (IR), and mass spectrometry (MS) (the last two for organic compounds).

3.5.2 Gas Chromatography (GC)

GC separates mixtures of volatile and semi-volatile chemicals by vaporizing them and passing them through long tubes (contained in an oven) that are either packed (packed columns), or coated (open tube capillary columns) with various substances. A carrier gas (nitrogen or helium) sweeps the vapor through the column as the temperature in the oven is gradually increased. The chemicals are separated by affinity for the column coating and/or by their boiling points in the column, and are then eluted to a detector.

There is a wide variety of detectors. FIDs are general purpose, non-specific detectors which are not very sensitive to halogen-containing compounds. PIDs respond to compounds that contain one or more double bonds which are ionized by the photons emitted from the PID source. Electron capture detectors (ECDs), which are not compound-specific, are very sensitive to halogen-, oxygen-, and sulfur-containing compounds but considerably less sensitive to hydrocarbons. Nitrogen/phosphorus detectors

(NPDs) are specific and sensitive to those elements. Halogen-specific electroconductivity detectors (HECDs) are selective and very sensitive to halogenated compounds. Flame Photometric Detectors (FPDs) are selective for sulfur and phosphorous compounds. Mass spectrometry (MS), the most selective and the most general-purpose detector, is also the most expensive. When operated in the full scan mode, MS will respond to nanogram levels of all organic compounds while retaining the ability to differentiate between co-eluting compounds based upon different unique fragmented ions. Use of an MS in the full scan mode allows for the tentative identification of unknown non-target compounds. If sub-nanogram detection limits are needed, the MS can be operated in the selected ion monitoring (SIM) mode, but then identification of non-target compounds cannot be made.

3.5.3 Wet Chemical/Photometric Analyses

Colorimetric analysis identifies and quantifies several anions and cations. Various reagents are usually automatically mixed with the samples interspersed with standards. After undergoing color-producing reactions, the mixture is passed through a colorimeter. The absorption of light at specific wavelengths in the visible range compared to established standards measures the amount of chemical present.

3.5.4 Ion Chromatography (IC)

The only differences between IC and HPLC are: (1) IC is typically used to separate inorganic ions while HPLC is used to separate organic compounds; and (2) IC can be performed using either low or high pressure systems. A column containing ion exchange resins separates anions (e.g., nitrate, sulfate, chloride) from one another and measures their concentration.

3.5.5 Atomic Absorption (AA) Spectrometry

An AA instrument measures one element at a time, most commonly metals. An acid-digested solution is either aspirated into a flame by flame atomic absorption spectrometry (FAAS), or placed in a graphite vessel and heated in a furnace by graphite furnace atomic absorption spectrometry (GFAAS). GFAAS provides better detection limits than FAAS by an order of magnitude, but at much higher cost. Glass-fiber or glass-quartz air sampling filters are usually used in conjunction with this method. Teflon filters are not recommended for AA analysis since the filter cannot be digested.

3.5.6 Inductively Coupled Plasma (ICP) Emission Spectrometry

The ICP emission spectrometer analyzes about 40 elements simultaneously. An acid-digested solution of the sample is aspirated into an argon plasma where the heat is so intense that it produces an emission (light) spectrum of the elements. The spectrum is used to identify the individual elements and to quantitate them based on their light intensity. ICP-MS yields better accuracy and detection limits than standard ICP, but at a greater cost.

3.5.7 X-Ray Fluorescence (XRF)

The XRF irradiates a sample with X-rays, inducing the atoms present to give off light. To use XRF for the air medium, a sample would be collected on a filter and then analyzed. When used with a high-resolution instrument, this method provides excellent detection limits for a variety of metals. Cost is on a filter by filter basis, not on a given element. As a result, XRF can be a cost-effective method to define specific contaminants of concern.

3.6 OVERVIEW OF AIR ASSESSMENT MODELS

A number of references are available on the selection and uses of various air assessment models. Two general categories of air modeling are discussed here: emission rates models and atmospheric dispersion models.

3.6.1 Emissions Models

The Air/Superfund National Technical Guidance Series on Air Pathway Assessments Volume I (Revised) provides recommended models for estimating emission rates for various sources. The procedures and recommendations made in that volume supersede guidance provided in the earlier Volume II of the series. The models were compiled for Superfund applications.

Emissions models cited in the series require site-specific data such as soil or water contaminant concentrations, and physical property data such as vapor pressure and Henry's Law constant.

3.6.2 Atmospheric Dispersion Models

General procedures for atmospheric dispersion modeling are also well established; Volume V of the Air/Superfund National Technical Guidance Series provides information for performing a detailed modeling study for a Superfund site. That volume also provides lists of models suitable for various applications and further references.

Screening modeling for volatiles emissions can be performed using EPA's SCREEN or TSCREEN computer models. Refined modeling for volatiles emissions is typically performed using EPA recommended models, such as the ISC model or the Point, Area, Line (PAL) model.

One of the most difficult aspects of air dispersion modeling is determining how to approximate the area or volume of a source. Volume I (Revised) of the series provides an overview on completing such approximations.

4.0 QUALITY ASSURANCE/QUALITY CONTROL EVALUATION

4.1 INTRODUCTION

The goal of representative sampling is to produce analytical results which accurately depict site conditions during a given time frame. The goal of quality assurance/quality control (QA/QC) is to implement appropriate methodologies in order to limit the introduction of error into the sampling and analytical procedures and, consequently, into the analytical data and conclusions regarding the impact on air quality. QA/QC procedures allow site managers to evaluate the quality and adequacy of the data in terms of how accurately they represent ambient site conditions and how well they satisfy sampling objectives.

QA/QC samples allow personnel to: (1) evaluate the degree of site variation; (2) determine whether samples were cross-contaminated during sampling or sample handling; (3) assess if a discrepancy in sample results is due to laboratory handling and analysis procedures; and (4) evaluate the sampling procedure. Refer to EPA's *Quality Assurance/Quality Control Guidance for Removal Activities* for further information.

4.2 DATA CATEGORIES

EPA has established data quality objectives (DQOs) which ensure that the precision, accuracy, representativeness, and quality of environmental data are appropriate for their intended application. Superfund DQO guidance defines two broad categories of analytical data: **screening** and **definitive**.

Screening data are generated by rapid, less precise methods of analysis with less rigorous sample preparation. Sample preparation steps may be restricted to simple procedures such as dilution with a solvent, rather than elaborate extraction/digestion and cleanup. At least 10 percent of the screening data are confirmed using the analytical methods and QA/QC procedures and criteria associated with definitive data. Screening data without associated confirmation data are not considered to be data of known quality. To be acceptable, screening data must include the following: chain of custody, initial and continuing calibration, analyte identification, and analyte quantification. Streamlined QC requirements are the defining characteristic of screening data.

Definitive data are generated using rigorous analytical methods (e.g., approved EPA reference methods). These data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce tangible raw data (e.g., chromatograms, spectra, digital values) in the form of paper printouts or computer-generated electronic files. Data may be generated at the site or at an off-site location, as long as the QA/QC requirements are satisfied. For the data to be definitive, either analytical or total measurement error must be determined. QC measures for definitive data contain all of the elements associated with screening data, but also may include trip, method, and rinsate blanks; matrix spikes; performance evaluation samples; and replicate analyses for error determination.

For further information on these QA/QC objectives, please refer to EPA's *Quality Assurance/Quality Control Guidance for Removal Activities* or EPA's *Data Quality Objectives Process for Superfund*.

4.3 SOURCES OF ERROR

Sampling errors which affect the success of a representative air sampling program can be introduced in the planning or implementation of the program, or during sample collection, handling, and analysis.

Identifying the source of error in a sampling program is difficult. Generally, three potential sources of error exist:

- **Sampling design** -- Sample representativeness
- **Sampling methodology** -- Sample collection, handling, shipment
- **Analytical procedures** -- Sample storage preparation, analysis

4.3.1 Sampling Design

Site variation includes variation both in the types and in the concentration levels of contaminants present. Representative sampling should accurately identify and reflect these variations. Error can be introduced by the design of a sampling plan which does not take this variation into account.

4.3.2 Sampling Methodology

Error can be introduced by the sampling methodology and sample handling procedures, such as cross-contamination from inappropriate use of sample collection equipment, unclean sample media, improper sampling equipment decontamination and shipment procedures, and other factors. Standardized procedures for collecting, handling, and shipping samples allow for easier identification of the source(s) of error, and can limit error associated with sampling methodology. The use of standard operating procedures ensures that all sampling tasks for a given matrix and analyte will be performed in the same manner regardless of the individual sampling team, date, or location of sampling activity. Trip blanks, field blanks, replicate samples, and rinsate blanks are used to identify errors due to sampling methodology and sample handling procedures.

4.3.3 Analytical Procedures

Errors which may originate in analytical procedures include cross-contamination, inefficient extraction, and inappropriate methodology. Matrix spike samples, replicate samples, performance evaluation samples, and associated quality assurance evaluation of recovery, precision, and bias can be used to distinguish analytical error from error introduced during sampling activities.

4.4 REPRESENTATIVENESS OF THE SAMPLES (QA/QC OF THE METHOD)

To determine the adequacy or representativeness of air samples, compare the meteorological and emission source conditions during sampling activities with those required to satisfy the sampling objectives defined in the sampling plan. During most Superfund Program applications, representative sampling demands collection of air samples during periods of expected high contaminant concentration, such as worst-case meteorological conditions and/or periods of high pollutant emissions.

If a sample design is based on a prevailing wind direction, wind speed, and/or atmospheric stability class during sampling, the meteorological data collected during the sampling program are reviewed to determine if these meteorological conditions did in fact occur, and the percentage of time they occurred during the sampling. If these meteorological

conditions did not persist during most of the sampling time, the data may not be representative of site conditions.

If a sample design is based upon a specific rate or duration of emission, then it is necessary to document that the specific rate or duration of emission occurred during sampling. The sample design and application must correspond in order to evaluate the representativeness of the samples.

4.5 QA/QC SAMPLES

QA/QC samples provide information on the variability and reliability of environmental sample results. Various QA/QC samples may be collected to detect error. This section briefly describes the types and uses of QA/QC samples collected in the field, and those prepared for or by the laboratory. QA/QC samples submitted for analysis with the field samples help to identify the origin of analytical discrepancies. The site manager can utilize these QA/QC samples to determine how the analytical results should be employed.

Replicate, collocated and background samples are the most commonly collected QA/QC field samples. Performance evaluation samples and matrix spikes provide additional measures of QA/QC data control. QA/QC results may suggest the need for modifying sample collection, preparation, handling, or analytical procedures if the resultant data do not meet site-specific quality assurance objectives. Refer to data validation procedures in EPA's *Quality Assurance/Quality Control Guidance for Removal Activities* for guidelines on utilizing QA/QC results.

Field blanks, trip blanks, lot blanks, reagent/method blanks, replicate/collocated samples, breakthrough samples, and distributed volume samples are the most common field QA/QC samples. Blanks, surrogate spikes, matrix spikes, blind spikes, and performance evaluation samples are prepared either for or by the laboratory to provide additional quality control measures for the data generated. Table 6 summarizes the application of the various QA/QC samples and the frequency of their use.

- **Field Blank**
A field blank sample undergoes the full handling and shipping process of an actual sample. It is designed to detect sample contamination that can occur during field operations or during shipment. The field blank must be associated with an actual sampling period.

When using adsorbent media that is sealed by the manufacturer, the field blank is opened with the other sample media, resealed, and carried through the sample handling process. Tedlar bag field blanks are filled with zero air and carried with other samples during sampling activities. When canister samples are collected using critical orifices or as grab samples, evacuated canisters are carried out to the field with the sampling canisters and serve as field blanks. However, if the canister samples are collected using more complex systems, such as mass flow controllers or stainless steel bellows pumps (e.g., Anderson sampler), the field blanks should test the full sampling system. Do this by purging humidified zero air through the sampling system into the field blank canister. Impinger field blanks consist of an aliquot of reagent that is prepared prior to going into the field and then carried into the field with the actual impinger solutions and taken through the sample handling process.

- **Trip Blank**

A trip blank sample detects whether samples are contaminated during shipping and storage. Trip blanks are used only when sampling for volatile organic compounds (VOCs). Trip blanks are typically used in conjunction with field blanks to isolate sources of sample contamination already noted in previous field blanks. The trip blank is prepared and added to the site samples after sampling has been completed, just prior to shipping the samples for analysis. If the adsorbent tubes are manufacturer-sealed, their seals should be broken at this point. For sorbent tubes that have been recycled and resealed by the laboratory, there is no need to break these temporary seals prior to shipping. Canister trip blanks are evacuated containers that are shipped to and from the site with the canisters used for air sampling. A trip blank for an impinger-based sampling method consists of an aliquot of impinger reagent that is shipped back to the laboratory with the samples.

- **Collocated Sample**

Collocated sampling involves placing two identical samplers next to each other. A collocated sample can be collected in one of two ways: (1) air is drawn from one source and split with a manifold; or (2) two adjacent pumps are set up so that each collects a sample at the same flow rate. Depending upon the method used to collect and analyze the samples, collocated samples can determine the variation due to both sampling error and imprecision in the analyses

(e.g., when using thermally desorbed adsorbent tubes), or can be used to isolate the variation due to sampling error only (e.g., when using solvent-extracted tubes and SUMMA canisters).

- **Breakthrough Sample**

A breakthrough sample detects false negative results and significant negative biases in the data. These problems arise when compounds elute from the sampling media before the sampling run is completed. The two types of breakthrough samples are serial media samples and spiked media samples. To collect a serial media sample, a sampling train is set up with a primary sampling device and backed by a secondary sampling device. A spiked media breakthrough sample is obtained by pulling air through a sampling train that was either spiked in the field with a standard solution or spiked in the laboratory prior to being shipped to the field. A breakthrough sample typically is used to determine whether the first sampling device has retained all of the compounds of concern.

- **Distributed Volume Sample**

A distributed volume sample detects problems arising from the actual pulling of air through a sorbent; these samples are particularly useful for detecting sample breakthrough and sample decomposition due to reactive species in the air. A distributed volume sample involves setting up collocated samplers that sample at flow rates which differ by a factor of two or more. If there are no problems associated with the actual sampling, then the calculated concentrations for all the distributed volumes should agree within the experimental error range of the method.

- **Performance Evaluation (PE) Sample/Blind Spike**

A PE sample evaluates the overall accuracy of the analytical laboratory and detects any bias in the analytical method used. The PE sample contains a quantity of analyte(s) which is known to the sampling team but unknown to the laboratory. The sample is usually prepared by a third party and always undergoes some type of certification analysis. The analyte(s) used to prepare the PE sample is the same as the analyte(s) of concern. The laboratory's accuracy is evaluated by comparing the percentage of analyte identified in the PE sample with the analytical results of the site samples.

A blind spike is a rarely used proficiency sample that is prepared and sent "blind" to a laboratory to

undergo the same analyses as the other samples. A blind spike is used when: (1) the desired frequency of check samples for the laboratory exceeds the number of available PE samples; (2) the background matrix of the PE does not truly reflect the background matrix of the samples (e.g., high summer-time humidity or the exhaust from soil vapor extraction or methane gas collection systems); or (3) many or all of the compounds of concern are not readily available in

a PE sample. In the last case, because of uncertainties of the stability and half-lives of "new" compounds in or on the sample media, the preparing laboratory must both certify the blind spikes which will be shipped to the field, and hold back a few spike samples for re-certification analyses in the same time period as the actual sample analyses. A blind spike should be prepared by an individual who is proficient in its preparation.

TABLE 6: Types of QA/QC Samples

QA/QC Sample Type	Suggested Minimum Frequency	Responsible Party	Application
Field Blank	Method dependent, typically not less than 5%	Field Crew	Used to detect contamination during field operations and shipping.
Trip Blank	5% or minimum of 1 per shipment (0 if field blank used in lieu of trip blank)	Field Crew	Used to detect contamination during shipping.
Replicate/ Collocated Sample	5% or minimum of 1 per sampling event	Field Crew	Used to determine variation due to sample collection and/or ambient conditions.
Breakthrough Sample	Minimum of 1 per event unless supplanted by distributed volume sampling	Field Crew	Indicates when the medium has become saturated. Typically required when atmospheric conditions may cause saturation of the sampling tubes.
Distributed Volume Sample	When applicable, minimum of 1 per day	Field Crew	Used with adsorbent-based sampling methods - especially tube samples. Detects both breakthrough, compound degradation, and compound formation caused by the sampling event itself.
Performance Evaluation Sample/ Blind Spike	1 per week when user requires more stringent QC controls, when available	Field Crew	Used to evaluate laboratory capability. In addition, a blank spike evaluates air matrix and sorbent, if used for sampling.
Lot Blank	Minimum of 1 per event per lot, 3-6 whenever new lot of absorbent acquired	Laboratory	Used whenever manufacturers supply one lot of samplers or when a fresh lot of sampling media is cleaned.
Reagent/Method Blank	1 per reagent blank per batch	Laboratory	Used for impinger samples and for solvent desorbed sorbent media.
Surrogate Spike	Every sample when used	Laboratory	Used to verify that bias results are not being reported high or low due to problems with a specific analysis.
Matrix Spike	10% when user requires more stringent QC controls	Laboratory	Not appropriate for total particulates. Very appropriate for particulate bound pollutants. Used to verify retention times, concentrations, percent recovery, analytical error, and matrix interference.

Caution: Because of the great potential for errors and the difficulty in calculating the amount of spike needed and the distribution of spike compound throughout the sample, it is not recommended that field/blind spikes be used to evaluate laboratories. If they are used, the preparing lab must take all precautions to ensure accuracy and to reanalyze samples if there are any discrepancies.

- **Lot Blank**

A lot blank detects contamination producing false positive results due strictly to the sampling medium itself. It consists of a sample device from the same lot as the sample devices used during a particular day or time period. The lot blank comes from the manufacturer or laboratory with the seal intact. It is included with the samples when they are delivered to the laboratory. Whenever a set of canisters is cleaned by the laboratory for reuse, the previously most-contaminated canister should be re-analyzed as a lot blank at least 24 hours later in order to check the cleanliness of that lot of "cleaned" canisters. Whenever a new sampler system (e.g., Anderson stainless steel bellows pump) is initially received from the manufacturer or from a laboratory, a lot blank should be pulled off the system using humidified zero air or humidified nitrogen. In a similar manner, whenever a sampler system is cleaned, the sampler(s) that had generated the most contaminated canister sample(s) should be checked with humidified zero air.

- **Reagent/Method Blank**

A reagent/method blank is a reagent sample used in sample analyses. Unlike field and trip blanks, a reagent/method blank is prepared in the laboratory and is designed to detect contamination that could arise from the reagents and laboratory equipment used in the analysis. This would include the reagents used in preparing impinger solutions and the reagents used in the extraction and cleanup of solvent extracted adsorbent media.

- **Surrogate Spike**

A surrogate spike, which is typically used only with GC-, GC/MS-, and HPLC-based methods, is designed to detect potential quantitative errors in the actual analysis of each sample. The surrogate compounds, which are usually non-target compounds that elute throughout the analyses, are typically spiked into each sample prior to its analysis. The surrogate results are used to check retention times, concentrations, percent recovery, and matrix interferences.

- **Matrix Spike**

A matrix spike is designed to test the ability of the method to detect known concentrations of the target compounds. As a laboratory-prepared sample, a matrix spike contains known concentrations of the target compounds which are spiked into a sample prior to its analysis. The matrix spike results are used to verify retention times and percent recoveries in the extraction procedure and to determine the degree to which matrix interferences will affect the overall identification and quantification of the target compounds.

Appendix A -- Other Factors Affecting Sampling Design Parameters

1.0 METEOROLOGICAL PARAMETERS

Understanding meteorological parameters is important to the development of an effective ambient air monitoring scenario. Wind speed, wind direction, and atmospheric stability determine the transport and dispersion of contaminants and thus dictate the placement of sampling and monitoring sites to measure those contaminants. Other parameters (temperature, precipitation, humidity, etc.) primarily affect the amount of a contaminant emitted into the air. Additional discussion on these parameters is contained in Chapter 3.

1.1 Wind Speed

When the contaminant of concern is a particulate, wind speed is critical to measuring if and how much of the contaminant becomes airborne, and how far the contamination travels from the source. Wind speed may affect the number of samples needed to ensure that at least one location is truly representative of the downwind plume. Wind speed may be a factor in determining whether "worst-case" conditions existed at the site when samples were collected.

Wind speed plays a role in the volatilization of contaminants from liquid sources. Calm or low wind speeds may reduce volatilization from a liquid surface by creating a saturated layer near the surface, while higher wind speeds increase volatilization.

Wind speed affects the dispersion of downwind concentrations for a given source. Low wind speeds (less than 5 mph) or calm conditions result in little dispersion of airborne contaminants and provide for worst-case conditions. The concentration of air pollutants directly downwind of a source is inversely proportional to wind speed during most meteorological conditions.

1.2 Wind Direction

Wind direction heavily influences the path in which airborne contaminants travel. Terrain features, large bodies of water, and localized meteorological conditions cause changes in surface wind direction. Wind directions change rapidly in the vicinity of weather fronts and the onset or end of localized meteorological events (e.g., inversions, sea breezes). Variable winds increase the dispersion of pollutants from a given source. Worst-case conditions would result from light winds and constant direction, such as channelized winds or valley effects. Under very light evening winds, the plume can follow terrain features, resulting in higher concentrations in these areas.

1.3 Atmospheric Stability

Atmospheric stability refers to the degree to which the atmosphere tends to dampen vertical and horizontal motion. It may affect the time of day samples should be taken, as well as the average "width" of the expected plume, a determining factor in obtaining a worst-case condition sample. Stable atmospheric conditions result in little dispersion; conversely, unstable atmospheric conditions result in greater dispersion. Dispersion depends on several interrelated factors, including wind speed, variability of wind direction, vertical temperature profile, and incoming solar radiation.

Figure A-1 illustrates the effect of stability on downwind concentrations. The logarithm of concentration is plotted for four different stability conditions versus downwind distance for a point source with constant emissions. A class F stability (moderately stable) shows less dispersion of contaminants by two orders of magnitude, at a distance of one kilometer, than does a class A stability.

Figure A-1: Effect of Typical Stability Data on Downwind Concentrations From the Same Source

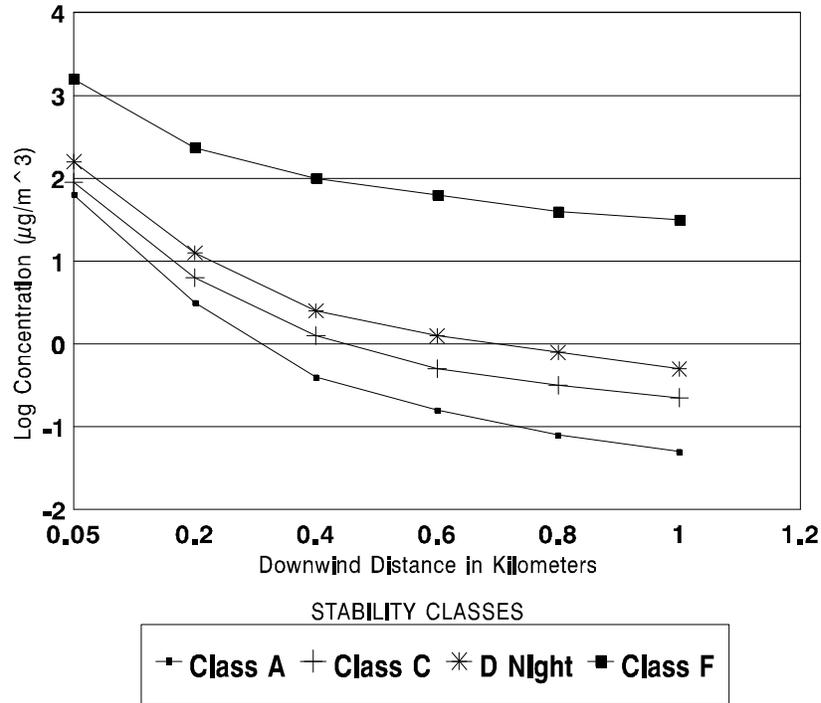


Table A-1: Key to Stability Classes

A - Extremely unstable conditions
 B - Moderately unstable conditions
 C - Slightly unstable conditions
 D - Neutral conditions*
 E - Slightly stable conditions
 F - Moderately stable conditions

Surface wind speed, mph	<u>Daytime Conditions</u>			<u>Nighttime Conditions</u>	
	Strong	Moderate	Slight	Thin Overcast or $\geq 4/8$	$\leq 3/8$ Cloudiness**
				Cloudiness**	
< 4.5	A	A-B	B		
4.5	A-B	B	C	E	F
9	B	B-C	C	D	E
13.4	C	C-D	D	D	D
>13.4	C	D	D	D	D

* Applicable to heavy overcast, day or night.

** The degree of cloudiness is defined as that fraction of the sky above the local apparent horizon which is covered by clouds.

Table 7 illustrates the commonly used Pasquill stability classification. If the sampling plan design is based on worst-case downwind dispersion from a constant emission source, some nighttime sampling under the most stable conditions may be warranted.

1.4 Temperature

Increased temperature typically increases the rate of volatilization of organic and some inorganic compounds. It also affects the initial rise of gaseous or vapor contaminants. Therefore, when determining the day or time of day to collect worst-case air samples, ambient temperature is an important consideration.

1.5 Precipitation

Precipitation will scrub the atmosphere of airborne contaminants. It physically scrubs the air of particulate matter and chemically reacts with airborne compounds such as SO₂ to produce acid rain. The effectiveness of this scrubbing is dependent on the length and intensity of the precipitation and the chemical and physical properties of the contaminant.

Precipitation decreases the potential for contaminated particulate matter to become airborne. Because wet soils tend to coalesce, thereby increasing the wind speed required to make their particles become airborne, transport of contaminated particulate matter is generally not a concern when the surface soil is wet. Wet soil also reduces volatilization of contaminants from the soil surface and sub-surfaces. However, during the onset of a rain storm, emission of volatiles increases for a short period of time, followed by a decrease in emission. This flux is caused by the rain displacing gases in the near-surface soil. Precipitation may be significant in determining whether worst-case or representative plumes will be present during a planned air sampling program.

1.6 Humidity

Humidity generally does not affect generation and transport of air contaminant plumes, but water-soluble chemicals and particulates may be affected by high humidity. Particulates act as condensation nuclei for water vapor which causes the particles to settle. Water-soluble chemicals often behave in a similar manner. Humid conditions can dictate the sampling media used for air sample collection, as well as limit the volume of air sampled, thereby increasing the detection limit (e.g., 0.05 ppm to 10 ppm).

1.7 Atmospheric Pressure

The effect of atmospheric pressure on air contaminants is generally negligible with the exception of landfill emissions. Migration of landfill gases through the landfill surface can be governed by changes in atmospheric pressure. The landfill can off-gas at much higher rates following a drop in atmospheric pressure, and may cease off-gassing altogether when the atmospheric pressure suddenly rises. Significant lag times are associated with this phenomenon, and each landfill behaves differently. It may be necessary to measure methane fluxes versus time in order to determine how long it will be before the landfill responds to atmospheric pressure changes.

Changes in atmospheric pressure can significantly affect the infiltration of subsurface vapors into homes. Since the internal pressures of homes almost always relate to outdoor atmospheric pressures, drops in atmospheric pressure will temporarily increase the tendency of subsurface vapors to infiltrate basements. Also, landfill gases tend to migrate off site in response to atmospheric pressure increases. When estimating worst-case conditions at a site (especially landfills), be sure to monitor changes in atmospheric pressure.

2.0 METEOROLOGICAL EFFECTS

In many cases, local meteorology complicates the transport and dispersion of air pollutants. Normal diurnal variations, such as temperature inversions, affect dispersion of airborne contaminants. Terrain features potentially

create or enhance air inversions, and also influence the movement and path of air flow, causing more intricate transport and dispersion patterns.

2.1 Temperature Inversions

Temperature inversions generally occur during fair weather. They start as early as late afternoon, endure through the night and slowly dissipate, ending by mid-morning. In an inversion, radiant heat leaves the lower (or near ground) atmosphere so that temperature **increases** with altitude to a certain height. Above that height, the temperature begins to decrease with altitude. The top of the inversion becomes an effective cap where wind speeds above the inversion could flow in a different direction and at a much higher speed than those at the surface. This cap is an effective barrier to pollutants, which are held close to the surface under this very stable atmospheric condition. Inversions generally result in a worst-case scenario for pollutants. However, if the pollutant source is able to penetrate the inversion by means of stack height or effective stack height (the height the plume reaches by means of velocity and thermal buoyancy), the inversion will effectively keep pollutants from affecting the surface "below" the inversion top. The height of an inversion can range from several meters to several hundred meters. Once the inversion breaks, wind speed and direction are more uniform.

2.2 Valley Effects

During clear nights when the prevailing wind is light, the slopes of a valley cool by radiation. Air immediately adjacent to the slopes cools and becomes denser than air over the center of the valley at the same elevation. The density imbalance induces convection, which causes winds to flow downslope to the valley floor. This situation is commonly referred to as drainage wind or drainage flow. The combination of stable conditions, light drainage wind, and inversion is a scenario where pollutants may not only be concentrated from a large source area, but also may be transported over considerable distance with little dispersion.

On clear days with light winds, an opposite circulation pattern develops. An up-valley, upslope flow is due to the heating of the air adjacent to the sun-warmed slopes and valley floor. Valleys are prone to temperature inversions because of their natural protection from winds. Valleys can also channel the prevailing wind to coincide with orientation of the valley. Channeling occurs most often when wind speeds are light to moderate and the direction is not perpendicular to the valley. During this situation, winds at the top of the valley may be different than winds at the valley floor.

2.3 Shorelines

During light winds, differences in heating and cooling of land and water surfaces and the air above them result in air circulation. On summer days with clear skies and light winds, the land surface adjacent to a large lake or ocean is heated much more rapidly than the body of water. A temperature difference and consequently a density difference results between the air just above the land surface and the air over the water. Because of the density gradient, a local circulation is established with wind moving from the water toward the land. There is usually some upwind motion over the land and subsidence over the water accompanying the sea breeze or lake breeze. These breezes more likely occur and tend to be stronger when land/water temperature differences are greatest (normally during the spring and early summer). Strong breezes may extend inland 5 to 10 miles; however, they usually extend less than one mile.

Shoreline effects alter the sampling plan. At night, the rapid cooling of the land causes lower temperatures above the land surface than above the water surface. Thus a land breeze may result in a reverse flow. A land breeze does not usually achieve as high a velocity or inland extent as a lake breeze. Wind may shift 180 degrees with the onset of the breezes. Sampling locations and periods may require adjustment to obtain upwind or downwind samples. Since the breezes are circular, pollutants can build up over the time period of these breezes, but not to the levels associated with many other meteorological conditions.

2.4 Hills

The influence of hills on the transport of contaminants depends upon a number of factors, complicating the siting of sample locations. During stable atmospheric conditions, air tends to flow around obstructions and affect the facing slope. This situation provides worst-case conditions, especially if the hillside location lies in the path of an elevated plume, or if an inversion top intersects the hillside where pollutant concentrations are higher. Under unstable conditions, air tends to move over obstructions. Airborne contaminants can accumulate in eddies formed on the lee side of a hill.

3.0 PHYSICAL/CHEMICAL FACTORS

The chemical characteristics of a contaminant affect its behavior in the atmosphere and influence the sampling and analytical method. This section discusses some of the more important physical and chemical parameters which affect the behavior of a contaminant, particularly those factors which should be considered before selecting sampling methods and procedures.

3.1 Molecular Weight

Molecular weight is an important factor when the release involves a pure gas. Pure dense gases (having a molecular weight greater than air) do not mix rapidly with the atmosphere and generally follow the terrain based on mean wind direction and gravity until diluted to below percent level concentrations. If released indoors, the gases tend to accumulate near the floor. Pure light gases, if released indoors, accumulate near the ceiling; outdoors, they rapidly disperse.

3.2 Physical State

Materials in their pure state pose special but predictable problems. If a contaminant of interest is immersed or dissolved in another matrix, then sampling varies from the approach used to sample a material in its pure state. Pressure and temperature are the predominant controllers of physical state.

For sampling purposes, airborne contaminants may be grouped into three broad categories: gases, vapors, and particulates. However, most compounds are distributed partially into each phase, as dictated by atmospheric conditions.

Particulates may exist as solids or gas mixed with liquids, such as aerosols. Particulates are frequently subdivided into dusts, mists, fumes, and smokes. The distinction between subgroups is based upon particle size, state, and means of generation.

- Dusts are formed from solid materials which have been reduced in size by mechanical processes such as grinding, crushing, blasting, drilling, and pulverizing; these particles range in size from the visible to the sub-microscopic.
- Mists are formed from either the mechanical disturbance of liquid or the evaporation and condensation of a liquid. These particles range in size from the visible to the microscopic.
- Fumes are formed from solid materials by evaporation and condensation and by gas phase molecular reactions; particles generally range in size from 1.0 μm to 0.0001 μm .
- Smokes are products of incomplete combustion of organic materials and are characterized by optical density; the size of smoke particles is usually less than 0.5 μm .

The nature and state (solid, gas, or gas mixed with liquid) of the contaminant determines the sampling method. Gases and vapors are collected in an aqueous medium, on adsorbates, in molecular sieves, or in a suitable container.

Particles are collected by filters, impingers, impactors, centrifugal devices (e.g., cyclones), settling chambers, electrostatic precipitators, thermal precipitators, and diffusion batteries.

3.3 Vapor Pressure

Vapor pressure is a measure of the pressure exerted by a vapor against the sides of a closed container. Vapor pressure is temperature dependent: as temperature increases, so does the vapor pressure, resulting in more liquid evaporating or vaporizing. The lower the boiling point of the liquid, the greater the vapor pressure it will exert at a given temperature. Values for vapor pressure are most often given as millimeters of mercury (mm Hg) at a specific temperature.

In general, contaminant volatilization is a function of vapor pressure. Contaminants with high vapor pressures (> 1 mm Hg) volatilize much more readily than those with low vapor pressures. The vapor pressure determines whether the substance is found primarily in the vapor state (volatile), on the surface of particles (non-volatile), or in both states (semi-volatile). The vapor pressure also determines whether a particulate-bound compound is capable of volatilizing off the particulates during sampling with filters.

3.4 Aerodynamic Size

The ability of a particle to become and remain airborne is a function of its size and aerodynamic diameter. In general, larger particles require greater force (typically wind) to become entrained in the air. Larger particles also tend to settle more rapidly.

3.5 Temperature

The temperature of contaminants at the time of their release affects the state of the contaminant as well as its transport and dispersion. Gaseous or vapor phase contaminants with a temperature greater than ambient air temperature will have thermal buoyancy that will cause the contaminant to exhibit an initial vertical rise above its point of release. As the contaminant cools, it will sink to, or even below, its original release point. If the temperature of a contaminant is significantly below ambient air temperature, the contaminant may sink and act in a manner similar to a dense gas, remaining close to the ground and settling in low-lying pockets.

3.6 Reactive Compounds

A reactive material can undergo a chemical reaction under certain specified conditions. Generally, the term *reactive hazard* refers to a substance that undergoes a violent or abnormal reaction in the presence of water or under normal ambient atmospheric conditions. Among these types of hazard are the pyrophoric liquids which can spontaneously ignite in ambient air without added heat, shock, or friction, and the water-reactive flammable solids which undergo a spontaneous and possibly violent reaction upon contact with water (e.g., sulfur trioxide and sodium metal).

3.7 Photodegradation

Some compounds undergo photolysis where UV radiation provides enough energy to break bonds. It may be necessary to sample with opaque cassettes or to cover tubes with aluminum foil to prevent the photolysis of certain compounds. This is a problem with polynuclear hydrocarbons and many pesticides and herbicides.

4.0 ENVIRONMENTAL INTERFERENCES

When designing an air sampling/monitoring program, consider the potential effects of environmental interferences on sampling. Sources of potential environmental interferences include:

- Natural sources of pollution (e.g., pollen, spores, terpenes, biologically produced waste compounds such as hydrogen sulfide, methane, ore and mineral deposits, etc)
- Extraneous anthropogenic contaminants (e.g., emissions from burning of fossil fuels, emissions from vehicular traffic, especially diesels, volatiles from petrochemical facilities, effluvium from smoke stacks)
- Photo-reactivity or reaction of the parameters of concern with non-related compounds (e.g., nitrogen compounds, sulfur compounds, and polyaromatic hydrocarbons)

Appendix B -- Representative Air Sampling Plan: Example Sites

Example Site 1 -- Wood Preserving Facility

1.0 SITE BACKGROUND INFORMATION

The Wood Preserving Company, Inc., began operation in 1950 when a swamp area was graded and converted to land suitable for wood storage. In the early 1970s, pentachlorophenol (PCP) began to be used in the wood preserving process. The facility also used creosote in its process through the 1980s.

Land use and zoning in the area surrounding the facility is mixed. An industrial area is located south of the site and residential areas are located to the north and west.

Several surface impoundments were used for disposal operations at the facility. Contact cooling waters were placed in two ponds, and process wastewaters were discharged into another large impoundment. A creosote recovery unit received some wastewater until its use was discontinued in the late 1980s. The discharge of wastewater containing hazardous constituents into these impoundments over the years created hazardous sludge.

The wood preserving process generates drippage at two points: immediately after the treated wood is removed from the treatment cylinders while it is held in the drip track area, and when the wood is retained in on-site storage after treatment has been completed. Because the facility utilized both creosote and PCP over its operational life, these drippage areas are cross-contaminated.

In 1986, EPA conducted Phase I of an emergency removal action to stabilize the three unlined surface impoundments. The sludges and contaminated soils were stabilized with cement kiln dust and stockpiled on site for future treatment or disposal during Phase II of the removal action.

Phase II involves bioremediation of the stockpiled contaminated soil. This treatment process includes screening of waste media, mixing with water, slurring in bioreactors, and final treatment in a land treatment unit. During Phase II, air sampling will be conducted to address health and safety concerns for on-site personnel and to monitor off-site acute exposure.

The selection of air sampling locations will be based in part on an updated conceptual site model. Historical information (e.g., activities during the Phase I emergency removal action) and knowledge of planned activities for Phase II will be incorporated into the original model for the site (which described sources, pathways, and potential receptors). This process will allow the conceptual site model to continue as a useful tool in selecting sample locations.

2.0 SAMPLING OBJECTIVES

The air sampling objectives for Phase II varied with changing activity at the site. During the initial three months when soil screening, slurring, and sludge application were taking place, the contaminant released to the air was unknown. The sampling objectives then were to determine the types of pollutants encountered and their concentrations. During land treatment activity at the site when soil was tilled, the sampling objectives were to document how well control measures were working and how releases to the air from the tilling were minimized.

The following have been identified as air monitoring and sampling objectives for Phase II activities:

1. Assess the health and safety of response personnel. Because of the planned nature of the response, sufficient sampling and monitoring equipment will be available at the site. Health and safety guidelines will be determined for the three months of land application and six months of tilling.

2. Assess the off-site, acute exposure of the public, particularly those residences across the street from the site. Off-site, acute exposure will be assessed for worst-case meteorological conditions during land applications, and for normal or expected meteorological conditions during soil tilling operations.

3.0 SAMPLING PLAN DESIGN

3.1 Selection of Sampling and Analytical Methods

During Phase I, soil/water samples were collected to identify the contaminants present at the site. The response team used this contaminant information to develop the sampling plan for Phase II activities. The contaminants of concern were PCP and creosote (aromatic hydrocarbons, PAHs/PNAs). Preliminary research into the chemical and physical properties of the compounds present included the following information:

Pentachlorophenol (PCP) C_6Cl_5OH

OSHA PEL -- 0.5 mg/m³

IDLH -- 150 mg/m³

Sample Collection -- Filter with impinger, methanol solvent

Instrument -- HPLC/UVD

Method -- NIOSH 5512

Creosote -- (aromatic hydrocarbons, PAHs/PNAs):

Aromatic Hydrocarbons

Sample Collection -- Carbon tubes/personal sampling pumps

Instrument -- HPLC

Method -- NIOSH 1501

PAHs/PNAs

Sample Collection -- Carbon tubes/personal sampling pumps

Instrument -- HPLC

Method -- NIOSH 5506, 5515

The above information was used to select the sampling and analytical methods for assessing on-site health and safety and off-site acute exposure. The equipment and methods selected for sampling activities are listed in section 5.0. To ensure the safety of the response personnel, monitoring was performed using HNu and OVA portable gas analyzers prior to initiating any site activities. No readings above background values were encountered anywhere on site, even when the probes were placed near areas of disturbed soil. A Real-time Aerosol Monitoring (RAM) instrument was used for particulate monitoring. Above-background readings were obtained only when soils were disturbed near the instrument.

The RAM instrument reads total particulate matter concentrations. These readings can be ratioed by the known concentration of a specific compound in soil which yields an estimate of the concentration for that compound in the air as a fraction of the total particulate matter. The estimated compound-specific concentration can then be compared to an action limit such as a TLV or PEL to assess air quality levels.

To assess off-site acute exposure, portable personal sampling pumps that were capable of collecting 8-hour, time-integrated air samples were used.

3.2 Meteorological and Topographic Considerations

The site was located in a generally open area, with the only rise in elevation occurring towards the western border of the site. A monitoring station was established to collect meteorological data (wind speed, wind direction, temperature, sigma theta) during sampling. The wind data helped to determine if the off-site sampling locations were

exposed to air that passed over the site, to document any shifts in winds during sampling due to topographic features, and to calculate changes in atmospheric stability. Figure B-1 is a map of the site.

3.3 Time, Duration, and Frequency of Sampling

Sampling for on-site health and safety was performed during all on-site activities. Sampling for off-site acute exposure was performed during the Phase II soil screening, slurry, and land application (three months), and tilling operations (six months). During screening activities, increased volatilization and dust generation was anticipated. Eight-hour, time-integrated samples were collected during days when site operations were in progress. Sampling was conducted at four locations around the site border, with one close to the private residence nearest the site.

During land application, the sludge applied to the land treatment area became drier late in the day and released more volatile compounds. During the late afternoon when the atmosphere became more stable and less mixing occurred, higher ambient concentrations of contaminants existed. To address this potential elevation of pollutant concentrations, an additional daily sampling period running from late afternoon (4 to 5 p.m.) to early evening (6 to 7 p.m.) was established at a location downwind of the land treatment area during land application activities (initial three months).

3.4 Location of Sampling Points

Four locations on the perimeter of the site (sampling locations 1 to 4) were selected for sampling with the personal sampling pumps and charcoal tubes. The sampling equipment was placed at each of the four compass points (north, south, east, and west) from the site and along the site boundary. This configuration enabled the collection of upwind and downwind air samples during Phase II activities. A fifth sampling location (sampling location 5) northwest of the site was situated near the residence closest to the site. Sampling at this location documented the exposure of the nearest residence to any emissions during Phase II site activities.

3.5 QA/QC Requirements

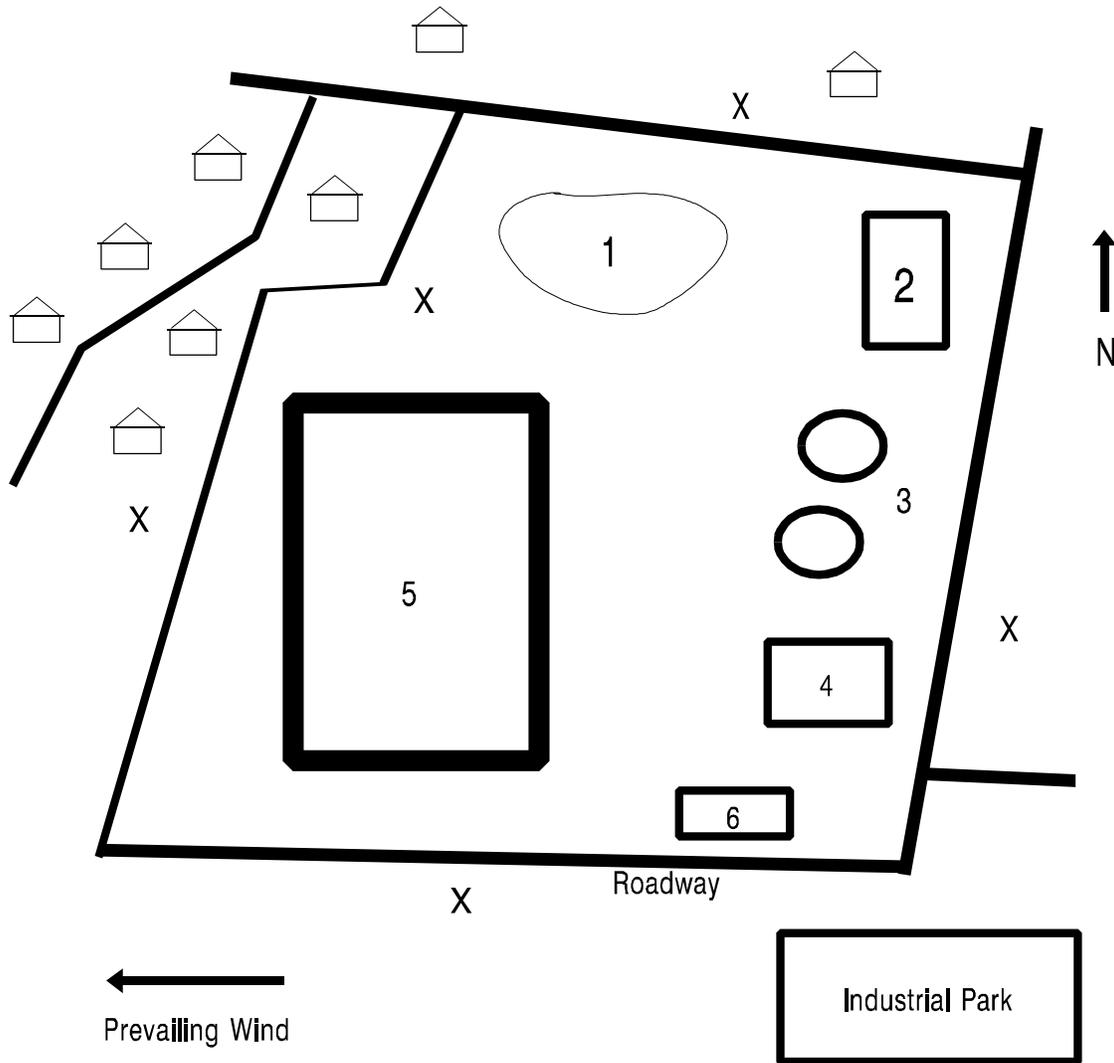
The QA/QC requirements covered field equipment calibrations, field sampling activities, laboratory analytical activities, and evaluations of meteorological conditions during sampling. All monitoring equipment was calibrated prior to its use in the initial assessment of health and safety conditions.

During sampling activities, trip blanks, field blanks, collocated samples, distributed volume samples, and breakthrough samples were utilized. Field samples were confirmed by definite analyses, including a performance sample, lot blank, method blank, surrogate spike, and matrix spike.

The meteorological data collected with the on-site monitoring station were utilized for QA/QC and data validation. The collected data helped to determine which of the sampling locations surrounding the site were upwind and which were downwind during each 8-hour sampling period, as well as to determine if samples were collected during worst-case meteorological conditions. A comparison of the sampling results between upwind and downwind locations was used to determine if the site emissions were significantly affecting air quality levels.

An air quality modeling analysis performed by the EPA Regional meteorologist was used to evaluate the representativeness of the sampling locations for identifying the maximum air concentrations due to emissions from the land treatment unit. The result of this analysis determined if air sampling locations corresponded to areas of maximum concentration predicted by the model. If sampling locations did not include these areas, the information provided by the model would be utilized for siting additional sampling locations.

**Figure B-1
Wood Preserving Company Site Map**



Key:

- | | |
|------------------------------------|-----------------------------|
| 1 - Contaminated Soil Pile | 5 - Land Treatment Unit |
| 2 - Soil Suspension System (Tanks) | 6 - Decontamination Trailer |
| 3 - Bioreactors | X - Sampling Location |
| 4 - Water Management Tank | 🏠 - Residences |

4.0 SAMPLING PLAN DEVELOPMENT CHECKLIST

I. Objectives of the Sampling Program and Implied Assumptions

- Yes A. Have clear, concise objectives for the sampling program been defined?
Yes B. Have the assumptions of the sampling program been clearly defined (e.g., sampling under "worst-case" conditions, sampling under "typical" conditions, sampling under a routine, periodic schedule, etc.)?
NA C. Other: _____

II. Selection of Sampling and Analytical Methods

- Yes A. Selection of Target Compounds
1. Has background site information been consulted?
Yes B. Selection of Method
1. Can selected methods detect the probable target compounds?
Yes 2. Do the selected analytical methods have detection limits low enough to meet the overall objectives of the sampling program?
Yes 3. Would the selected methods be hampered by any interfering compounds?
Yes C. Will the selected methods, when applied to the projected sampling location(s), adequately isolate the relative downwind impact of the site from that of other upwind sources?
Yes D. Are the selected methods logistically feasible at this site?
NA E. Other: _____

III. Location(s) and Number of Sampling Points

- NA A. Do the locations account for all the potential on-site emission sources that have been identified from the initial site background information and from walk-through inspections?
NA B. Will the sampling locations account for all the potential emission sources upwind from the site?
NA C. For short-term monitoring programs, has a forecast of the local winds been obtained for the day(s) of the program?
Yes D. For a long-term monitoring program, have long-term air quality dispersion models and historical meteorological data been used to predict probable area of maximum impact (when applicable)?
Yes E. Does the sampling plan account for the effects of local topography on overall wind directions and for potential shifts in direction during the day (e.g., valley effects, shoreline effects, hillside effects)?
Yes F. Do the sampling location decisions account for the effects of topography on surface winds, especially under more stable wind directions (e.g., channelization of surface winds due to buildings, stands of trees, adjacent hills, etc.)?
Yes G. Can any sampling equipment left at these locations be adequately secured?
NA H. Other: _____

IV. Time, Duration, and Frequency of Sampling Events

- A. When the sampling time periods (the actual days, as well as the time span during specific days) were selected, were the effects of the following conditions on downwind transport of contaminants considered:
C Yes Expected wind directions?
Yes C Expected atmospheric stability classes and wind speeds?
C Yes Evening and early morning temperature inversions?
C NA Changes in atmospheric pressure and surface soil permeability on lateral, off-site migration of gases from methane-producing sources such as landfills?
C NA During indoor air investigations, gas infiltration rates into homes due to changes in atmospheric pressure and to the depressurization of homes caused by many home heating systems?
C NA Other: _____

- B. When selecting the sampling time periods (the actual days, as well as the time span during specific days), were the effects on potential site emissions listed below considered:
- Yes C Effect of site activities?
C Yes Effect of temperature and solar radiation on volatile compounds?
C Yes Effect of wind speeds on particulate-bound contaminants and on volatiles from lagoons?
C NA Effect of changes in atmospheric pressure on landfills and other methane-producing emission sources?
NA C Effect of recent precipitation on emissions of both volatile and particulate-bound compounds?
C NA Other: _____
- Yes C. Do the time periods selected allow for contingencies such as difficulties in properly securing the equipment, or public reaction to the noise of generators for high volume samplers running late at night?
- D. When determining the length of time over which individual samples are to be taken, were the following questions considered (when applicable)?
- Yes C Will sufficient sample volumes be taken to meet the desired analytical method detection limits?
C Yes Will the sampling durations be adequate either to cover the full range of diurnal variations in emissions and downwind transport, or to isolate the effects of these variations?
YesC When applicable, do the selected time intervals account for potential wind shifts that could occur due to local topography such as shorelines and valleys?
C NA Other: _____

V. Meteorological Data Requirements

- NA A. Has a source of meteorological data been identified to document actual conditions at the time the sampling event takes place?
Yes B. Has the placement of an on-site meteorological station been considered in the sampling plan if no off-site station has been identified?

VI. QA/QC Requirements

- Yes A. Are screening data confirmed by definitive data at a minimum of a 10% rate?
Yes B. Have the necessary QA/QC samples been incorporated into the sample design to allow for the detection of potential sources of error?
Yes C. Does the QA/QC plan account for verification of the sampling design and of sample collection?

5.0 SAMPLING PLAN DEVELOPMENT SUMMARY

Selected Direct Reading Instruments and Techniques:

- C Flame ionization detector
- C Photoionization detector
- C Particulate monitor

Selected Sampling Equipment:

- C Personal sampling pump

Selected Sampling Collection Media/Devices:

- C Mixed sorbent tubes
- C Impingers

Selected Analytical Techniques:

- C High performance liquid chromatography

Example Site 2 -- Emergency Response at a Train Derailment

1.0 SITE BACKGROUND INFORMATION

At 1900 hours on a Sunday evening in early May 1991, a Western Consolidated Freight train derailed outside of Jonesburg, Oregon. Three of the rail cars were leaking and impinged by the resultant fire. These three rail cars were tentatively identified to be carrying toluene, chloroform, and carbaryl (solid), respectively. The fire department initially responding was Jonesburg Engine Company 51. Upon arrival at the scene, the assistant chief of Engine Company 51 called for a half-mile evacuation zone and isolated the site awaiting mutual aid assistance.

Jonesburg is an old timber and pulp industry town of about 25,000 residents. The town is situated along a large lake which was once used to float logs to the mills. The city is served by a paid fire department. The regional Haz-Mat team and The County Health Department are located in the county seat, approximately 19 miles to the west. The State Department of the Environment is 40 miles to the north, and the nearest EPA regional office is approximately 200 miles away.

The potentially affected residential area to the immediate west consists of small scattered developments of new homes and condominiums. An elementary school is located one mile west of the incident. Interstate Highway 6 runs east-west approximately one mile north of the derailment.

2.0 SAMPLING OBJECTIVES

The emergency response personnel identified three initial air monitoring/sampling objectives:

1. Assess the health and safety of the response personnel. Because of the emergency nature of the response, this objective must initially be accomplished by the local fire department and county Haz-Mat team, often using a limited collection of air monitoring equipment. Generally, air sampling equipment is not available within the first six hours of an emergency response.
2. Assess off-site, acute exposure of the public and the staged response personnel (e.g., police). Decisions on the size of evacuation zone and method of notification depend on the location and movement of chemical vapors and particulates.
3. Use confirmatory sampling to confirm the identity of compounds suspected of being released. The air sampling methods used are compound-specific and provide lower detection limits.

A map detailing the sources (railcars), pathways (e.g., prevailing wind direction/speed), and potential receptors (location of nearby houses, schools, offices) will help in the selection of off-site sampling locations. In an emergency, even a simple conceptual site model can be quite useful. Figure B-2 is an example of a simplified conceptual site model.

3.0 SAMPLING PLAN DESIGN

3.1 Selection of Sampling and Analytical Methods

The chemicals were identified from the railroad shipping manifests. The impinged rail cars contained toluene, chloroform-n, and carbaryl pesticide. Preliminary research into the chemical and physical properties of each compound, using the air methods database and other references, included the following information:

Toluene C₆H₅CH₃ (1 tank car)

OSHA PEL -- 200 ppm

IDLH -- 2,000 ppm

Sample Collection -- Charcoal tube

Instrument -- GC/FID

Method -- NIOSH 1500

Chloroform CHCl₃ (1 tank car)

OSHA PEL -- 2 ppm

IDLH -- 1,000 ppm

Sample Collection -- Charcoal tube

Instrument -- GC/FID

Method -- NIOSH 1003

Note: Decomposition by fire may generate phosgene gas, which reacts with strong oxidizers to form phosgene and chlorine gas.

Chlorine Cl₂

OSHA PEL -- 0.5 ppm

IDLH -- 30 ppm

Sample Collection -- Midget impinger

Instrument -- Ion-specific electrode

Method -- OSHA ID-101

Phosgene COCl₂

OSHA PEL -- 0.1 ppm

IDLH -- 2 ppm

Sample Collection -- Midget impinger

Instrument -- Colorimetric

Method -- NIOSH P+CAM 219

Carbaryl -- (1 box car)

OSHA PEL -- 5 mg/m₃

IDLH -- 600 mg/m₃

Sample Collection -- Particulate filter

Instrument -- Visible spectrometry

Method -- NIOSH 5006

The above information was used to select the sampling and analytical methods for assessing on-site health and safety and off-site acute exposure. The equipment and methods selected for sampling activities are listed in Section 5.0.

Note: The time required for mobilization affects the level of expertise and equipment available at the initial site response.

Health and Safety assessment was conducted by the local fire department and county Haz-Mat team using available equipment consisting of a flame ionization detector (FID), explosimeter, calorimetric tubes, and chemical-specific

monitors. These instruments monitored continuously during site activities. Worst-case exposure scenarios were assumed pending the results of confirmatory sampling. Data from the monitoring were used to establish site response work zones, levels of personal protection equipment, and placement of the command post. Potential interference problems associated with these detection methods were taken into account when making decisions affecting impacting response personnel.

Off-site acute exposure was assessed by collecting 8-hour samples at locations established around the perimeter of the evacuation zone (see Section 3.4). The assumption of a worst-case situation and establishment of a one-half-mile evacuation zone reduced the potential for acute human exposure during the response.

Sampling was conducted to confirm the identity of suspected contaminants and to backup the results of screening methods. These methods involve the use of personal sampling pumps and various sorbent filter media. As a general rule, these samples are collected for an 8 to 12 hour period; however, because of the extremely time-critical nature of this information, sampling times were modified. Sampling was designed to be compound-specific and to provide lower detection limits than would Direct-Reading Instruments (DRIs). The sampling required analysis, thus laboratory availability and turnaround time information was gathered in the initial phases of the response and was factored into the sampling strategy.

3.2 Meteorological and Topographical Considerations

The site was on the west coast in a generally flat, open area one-half mile from a lake. Local weather history was obtained from the National Weather Service once EPA received notification of the incident. The predominant local meteorology displayed stable atmospheric conditions during the evening, with inversions setting up approximately one hour before nightfall. A westerly wind occurred during the day (not a sea breeze). A meteorological monitoring station was established near the incident to collect real-time meteorologic data which were integrated into a modeling program. The data helped to determine if the sampling locations were exposed to air that passed over the site and to document any shifts in winds during sampling due to local topographic features. Because of the potential for complex meteorological conditions at this site, a meteorologist was involved in the decision process. Figure B-2 is a map of the site.

3.3 Time, Duration, and Frequency of Sampling

On-site health and safety monitoring with real-time instruments was performed whenever response personnel were within the hot zone. Continuous sampling for off-site acute exposure assessment and confirmatory sampling were conducted during the fire, tank venting, and cleanup activities. Sampling was also conducted continuously with DRIs at the on-site command post and support areas. Based on measured meteorological conditions and the spilled quantities, the CAMEO model was used to predict the location and concentration of the chemical plume during the various atmospheric stability conditions over the two-day fire and ensuing cleanup. To account for potential inversions during the response, monitoring was conducted with DRIs to ensure the adequacy of the evacuation corridors. As weather conditions or forecast conditions changed, new plume predictions were made and sampling locations moved accordingly.

3.4 Location of Sampling Points

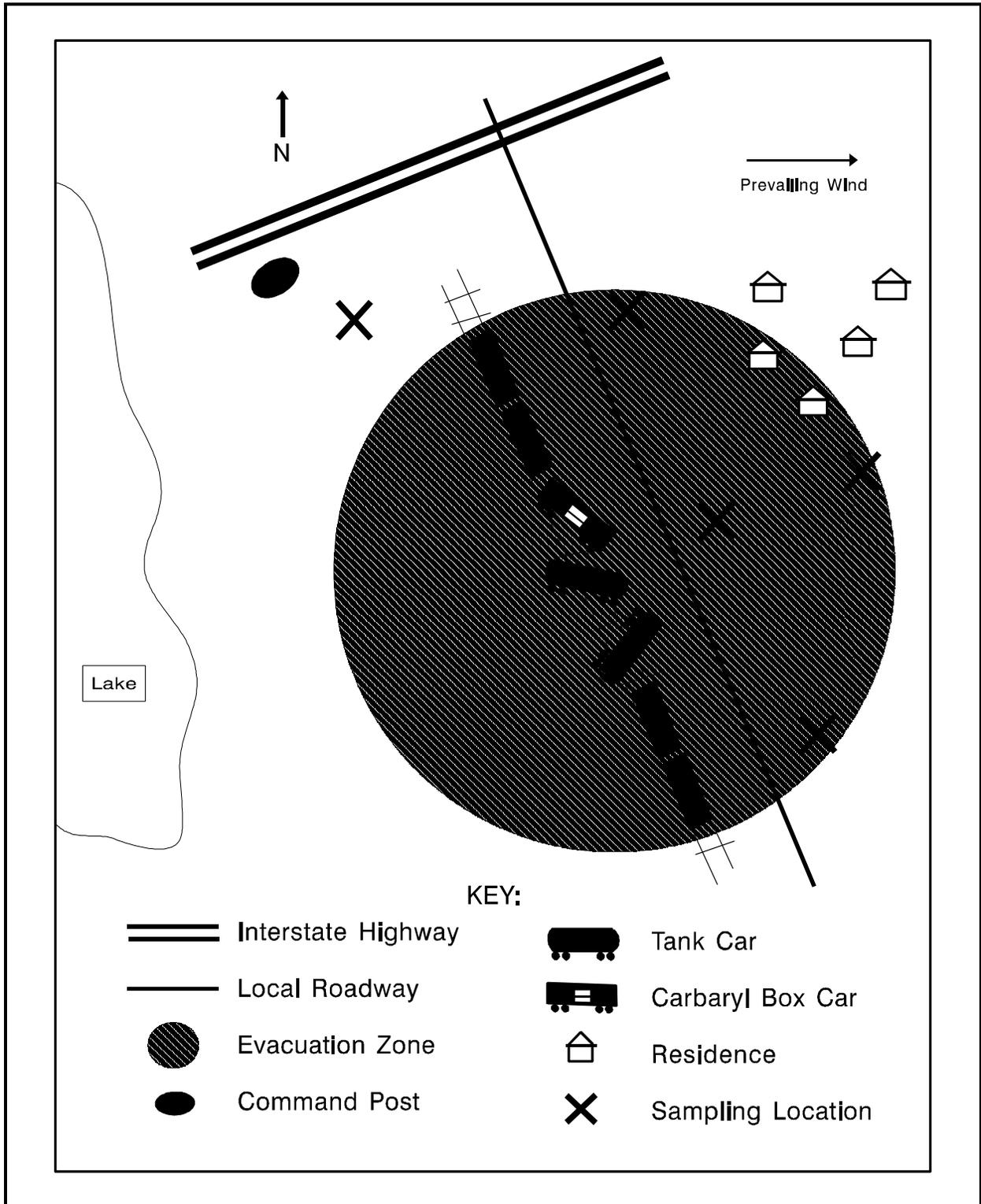
Five sampling locations were established: three points along the evacuation border of the site, one point at the command post, and one point inside the evacuation zone. The command post sample established a background level and determined the appropriate level of protective equipment for response personnel.

3.5 QA/QC Requirements

The QA/QC requirements covered field equipment calibrations, field sampling activities, laboratory analytical activities, and evaluations of meteorological conditions during sampling. All monitoring equipment was calibrated prior to its use in the initial assessment of health and safety conditions.

It is important to note that meeting specific QA objectives is not of paramount concern during an emergency response, primarily because of the presence of the contaminant in elevated concentrations (ppm).

Figure B-2
Train Derailment Emergency Response Site Map



4.0 SAMPLING PLAN DEVELOPMENT CHECKLIST

I. Objectives of the Sampling Program and Implied Assumptions

- Yes A. Have clear, concise objectives for the sampling program been defined?
NA B. Have the assumptions of the sampling program been clearly defined (e.g., sampling under "worst-case" conditions, sampling under "typical" conditions, sampling under a routine, periodic schedule, etc.)?
Yes C. Other: Emergency Response

II. Selection of Sampling and Analytical Methods

- Yes A. Selection of Target Compounds
Has background site information been consulted?
B. Selection of Method
Yes 1. Can selected methods detect the probable target compounds?
Yes 2. Do the selected analytical methods have detection limits low enough to meet the overall objectives of the sampling program?
Yes 3. Would the selected methods be hampered by any interfering compounds?
NA C. Will the selected methods, when applied to the projected sampling location(s), adequately isolate the relative downwind impact of the site from that of other upwind sources?
Yes D. Are the selected methods logistically feasible at this site?
NA E. Other: _____

III. Location(s) and Number of Sampling Points

- NA A. Do the locations account for all the potential on-site emission sources that have been identified from the initial site background information and from walk-through inspections?
NA B. Will the sampling locations account for all the potential emission sources upwind from the site?
Yes C. For short-term monitoring programs, has a forecast of the local winds been obtained for the day(s) of the program?
NA D. For a long-term monitoring program, have long-term air quality dispersion models and historical meteorological data been used to predict probable area of maximum impact (when applicable)?
Yes E. Does the sampling plan account for the effects of local topography on overall wind directions and for potential shifts in direction during the day (e.g., valley effects, shoreline effects, hillside effects)?
Yes F. Do the sampling location decisions account for the effects of topography on surface winds, especially under more stable wind directions (e.g., channelization of surface winds due to buildings, stands of trees, adjacent hills, etc.)?
Yes G. Can any sampling equipment left at these locations be adequately secured?
NA H. Other: _____

IV. Time, Duration, and Frequency of Sampling Events

- A. When the sampling time periods (the actual days, as well as the time span during specific days) were selected, were the effects of the following conditions on downwind transport of contaminants considered:
Yes C Expected wind directions?
Yes C Expected atmospheric stability classes and wind speeds?
C Yes Evening and early morning temperature inversions?
NA C Changes in atmospheric pressure and surface soil permeability on lateral, off-site migration of gases from methane-producing sources such as landfills?
NA C During indoor air investigations, gas infiltration rates into homes due to changes in atmospheric pressure and to the depressurization of homes caused by many home heating systems?
NA C Other: _____

- B. When selecting the sampling time periods (the actual days, as well as the time span during specific days), were the effects on potential site emissions listed below considered:
- Yes C Effect of site activities?
NA C Effect of temperature and solar radiation on volatile compounds?
Yes C Effect of wind speeds on particulate-bound contaminants and on volatiles from lagoons?
NA C Effect of changes in atmospheric pressure on landfills and other methane-producing emission sources?
NA C Effect of recent precipitation on emissions of both volatile and particulate-bound compounds?
NA C Other: _____
- Yes C. Do the time periods selected allow for contingencies such as difficulties in properly securing the equipment, or public reaction to the noise of generators for high volume samplers running late at night?
- D. When determining the length of time over which individual samples are to be taken, were the following questions considered (when applicable)?
- Yes C Will sufficient sample volumes be taken to meet the desired analytical method detection limits?
NA C Will the sampling durations be adequate either to cover the full range of diurnal variations in emissions and downwind transport, or to isolate the effects of these variations?
Yes C When applicable, do the selected time intervals account for potential wind shifts that could occur due to local topography such as shorelines and valleys?
NA C Other: _____

V. Meteorological Data Requirements

- NA A. Has a source of meteorological data been identified to document actual conditions at the time the sampling event takes place?
Yes B. Has the placement of an on-site meteorological station been considered in the sampling plan if no off-site station has been identified?

VI. QA/QC Requirements

- Yes A. Are screening data confirmed by definitive data at a minimum of a 10% rate?
NA B. Have the necessary QA/QC samples been incorporated into the sample design to allow for the detection of potential sources of error?
Yes C. Does the QA/QC plan account for verification of the sample design and of the sample collection?

5.0 SAMPLING PLAN DEVELOPMENT SUMMARY

Selected Direct Reading Instruments and Techniques:

- C Flame ionization detector
- C Explosimeter
- C Colorimetric Tubes
- C Chemical-specific monitors

Selected Sampling Equipment:

- C Personal sampling pump

Selected Sampling Collection Media/Devices:

- C Charcoal tubes
- C Impinger

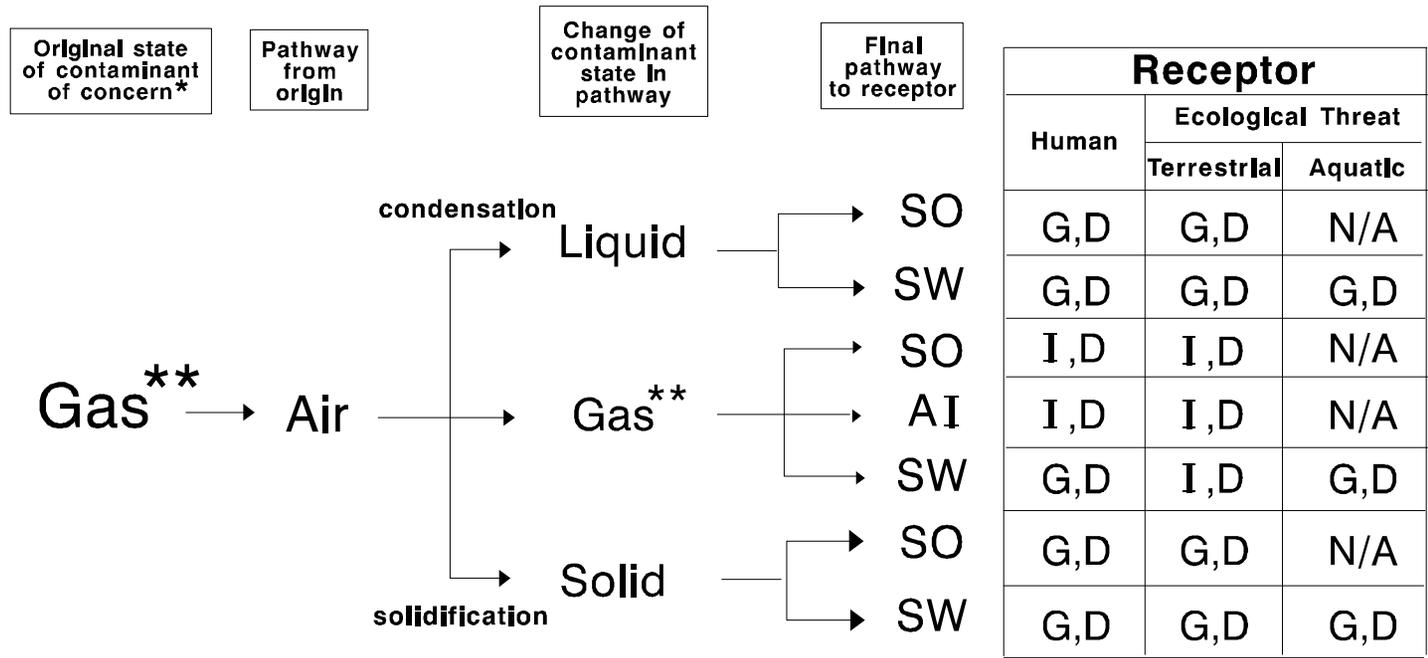
Selected Analytical Techniques:

- C Gas Chromatography/Flame Ionization Detector (GC/FID)

APPENDIX C -- Example of Flow Diagram For Conceptual Site Model

Figure C-1

Migration Routes of a Gas Contaminant from Origin to Receptor



* May be a transformation product
 ** Includes vapors

Receptor Key

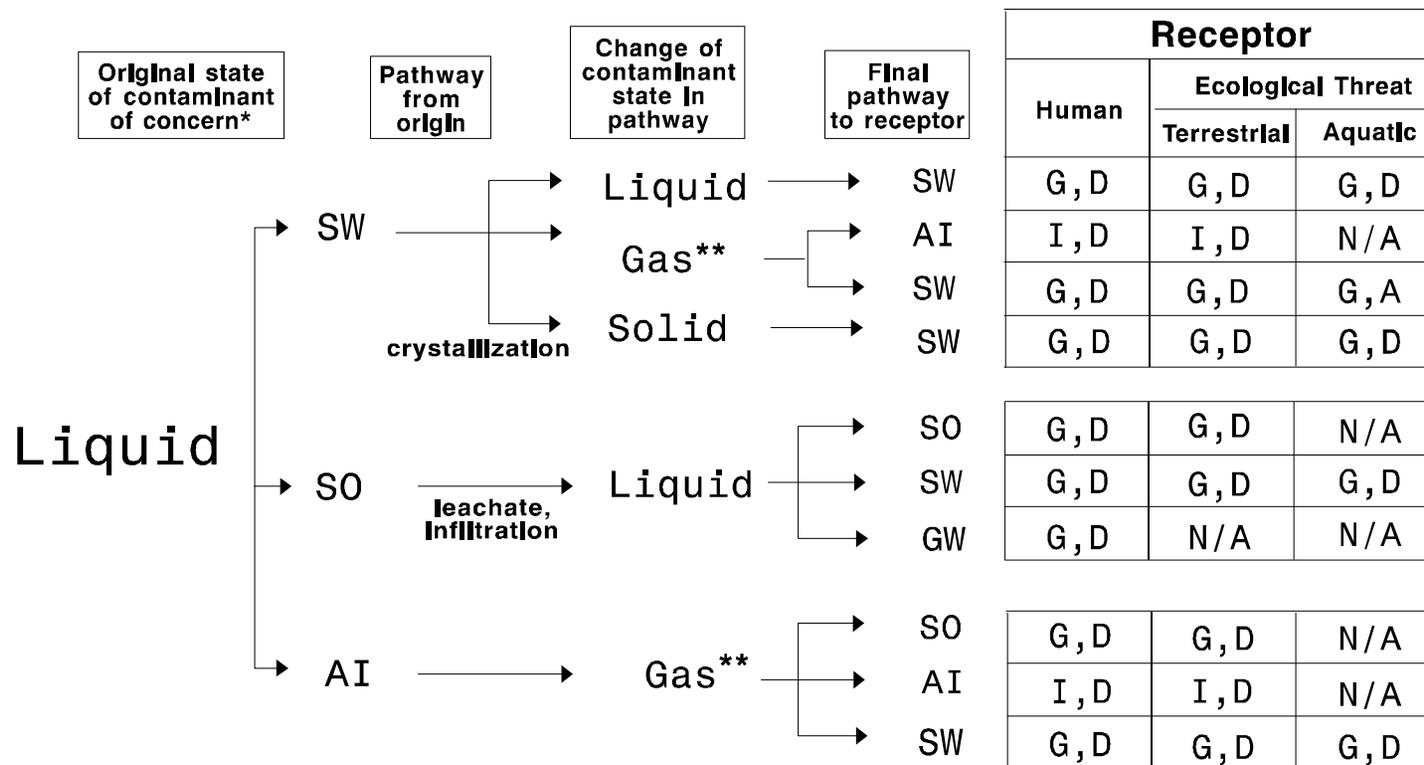
- D = Dermal Contact
- I = Inhalation
- G = Ingestion
- N/A = Not Applicable

Pathway Key

- AI = Air
- SO = Soil
- SW = Surface Water (including sediments)
- GW = Ground Water

Figure C-2

Migration Routes of a Liquid Contaminant from Origin to Receptor



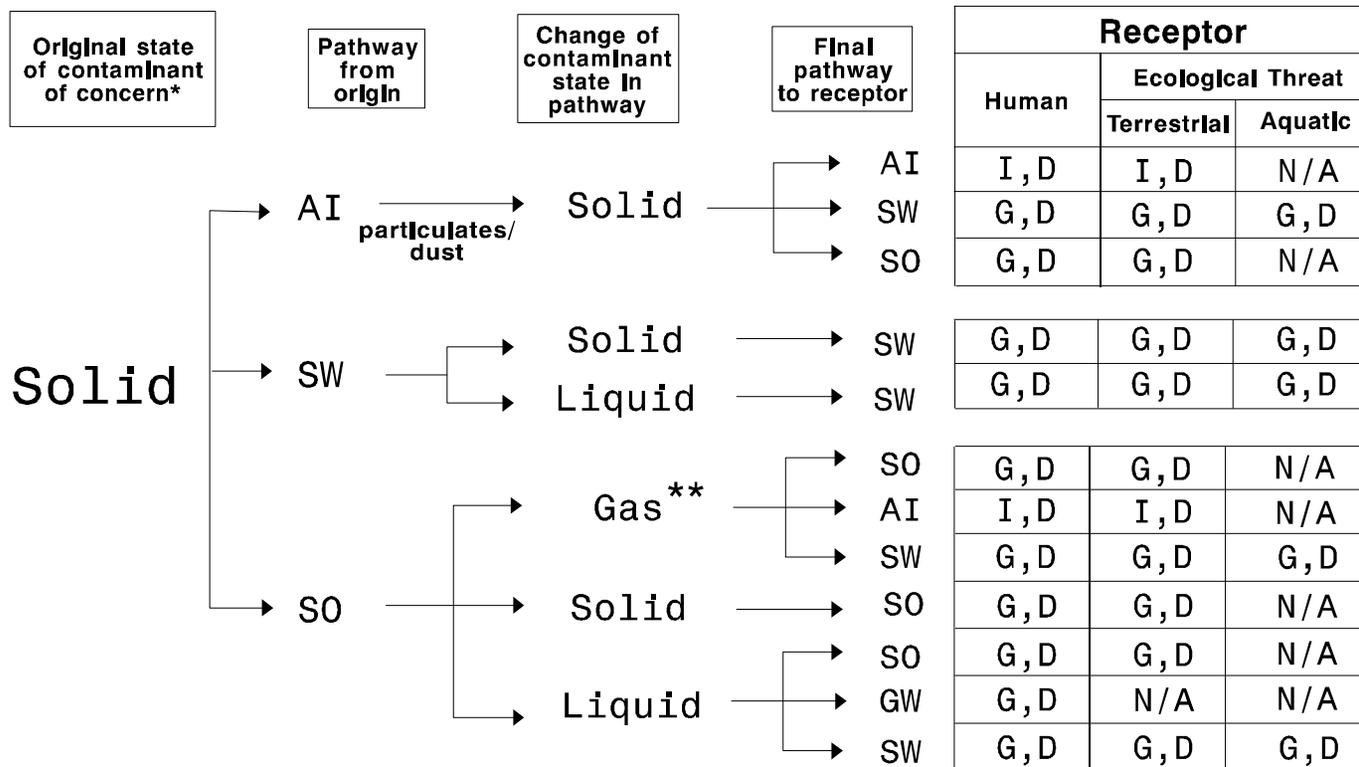
* May be a transformation product
 ** Includes vapors

Pathway Key
 AI = Air
 SO = Soil
 SW = Surface Water (including sediments)
 GW = Ground Water

Receptor Key
 D = Dermal Contact
 I = Inhalation
 G = Ingestion
 N/A = Not Applicable

Figure C-3

Migration Routes of a Solid Contaminant from Origin to Receptor



* May be a transformation product

** Includes vapors

Receptor Key	
D	■ Dermal Contact
I	■ Inhalation
G	■ Ingestion
N/A	■ Not Applicable

Pathway Key	
AI	■ Air
SO	■ Soil
SW	■ Surface Water (including sediments)
GW	■ Ground Water

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* For additional information or assistance, contact the Superfund Air Coordinator in your EPA Regional office.