



AIR/SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES

Volume IV - Guidance for Ambient Air Monitoring at Superfund Sites (Revised)

AIR/SUPERFUND NATIONAL TECHNICAL
GUIDANCE STUDY SERIES

Report ASF-4

GUIDANCE FOR AMBIENT AIR MONITORING
AT SUPERFUND SITES

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Preface

This is one in a series of manuals dealing with air pathway assessments at hazardous waste sites. This document was developed for the Office of Air Quality Planning and Standards in cooperation with the Office of Emergency and Remedial Response (Superfund). It has been reviewed by the National Technical Guidance Study Technical Advisory Committee and an expanded review group consisting of State agencies, various groups within the U.S. Environmental Protection Agency, and the private sector. This document is an interim final manual offering technical guidance for use by a diverse audience including EPA Air and Superfund Regional and Headquarters staff, State Air and Superfund program staff, Federal and State remedial and removal contractors, and potentially responsible parties in analyzing air pathways at hazardous waste sites. This manual is written to serve the needs of individuals having different levels of scientific training and experience in designing, conducting, and reviewing air pathway analyses. Because assumptions and judgements are required in many parts of the analysis, the individuals conducting air pathway analyses need a strong technical background in air emission measurements, modeling, and monitoring. Remedial Project Managers, On Scene Coordinators, and the Regional Air program staff, supported by the technical expertise of their contractors, will use this guide when establishing data quality objectives and the appropriate scientific approach to air pathway analysis. This manual provides for flexibility in tailoring the air pathway analysis to the specific conditions of each site, the relative risk posed by this and other pathways, and the program resource constraints.

Air pathway assessments cannot be reduced to simple "cookbook" procedures. Therefore, the manual is designed to be flexible, allowing use of professional judgment. The procedures set out in this manual are not intended, nor can they be relied upon, to create rights substantive or procedural, enforceable by any party in litigation with the United States.

It is envisioned that this manual will be periodically updated to incorporate new data and information on air pathway analysis procedures. The Agency reserves the right to act at variance with these procedures and to change them as new information and technical tools become available on air pathway analyses without formal public notice. The Agency will, however, attempt to make any revised or updated manual available to those who currently have a copy through the registration form included with the manual.

Copies of this report are available, as supplies permit, through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711 or from the National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

Disclaimer

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SUPERFUND ABBREVIATIONS AND ACRONYMS

AAL	Ambient air level
AAM	Ambient air monitoring
ACGIH	American Conference of Governmental Industrial Hygienists
AMTIC	Ambient Monitoring Technology Information Center
APA	Air pathway assessment (or analysis)
ARARs	Applicable or Relevant and Appropriate Requirements
ATSDR	Agency for Toxic Substances and Disease Registry
AWMA	Air & Waste Management Association
CAA	Clean Air Act of 1990
CAAA	Clean Air Act Amendments
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CERI	Center for Environmental Research Information
CHIEF	Clearinghouse for Inventories and Emission Factors
CTC	Control Technology Center
DL	Detection Limit
DQO	Data quality objective
ECAO	Environmental Criteria and Assessment Office
EMTIC	Emission Measurement Technical Information Center
EPA	Environmental Protection Agency
ER	Emergency removal
FS	Feasibility study
FTIR	Fourier Transform Infrared
GFC	Gas filter correlation
GC	Gas chromatograph
HAP	Hazardous air pollutant
HRS	Hazard ranking system
HSL	Hazardous Substances List
IH	Industrial hygiene
IRIS	Integrated Risk Information System
ISC	Industrial source complex
IUR	Inhalation unit risk
MEI	Maximum exposed individual
met	Meteorological
NAAQS	National Ambient Air Quality Standards
NATICH	National Air Toxics Information Clearing House
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NESHAPS	National Emissions Standards for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Health and Safety
NPL	National Priorities List
NSPS	New Source Performance Standards

SUPERFUND ABBREVIATIONS AND ACRONYMS

NTG	National technical guidance
NTGS	National technical guidance study
NTIS	National Technical Information Services
NWS	National Weather Service
O&M	Operation and maintenance
OAQPS	Office of Air Quality Planning and Standards
OEL	Occupational exposure limit
OPM	Open path monitor
OSC	On-Scene Coordinator
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Removal
PA	Preliminary assessment
PAL	Point, Area, Line
PCBs	Polychlorinated biphenyls
PEL	Permissible exposure limit
PM	Particulate matter
PM ₁₀	Particulate matter of less than 10 microns in diameter
PNA _s	Polynuclear aromatic compounds
ppb	Parts per billion
ppbv	Parts per billion on a volume basis
PPE	Personal protective equipment
PSD	Prevention of significant deterioration
PUF	Polyurethane foam
QA	Quality assurance
QC	Quality control
RA	Remedial action
RAGS	Risk Assessment Guidance for Superfund
RCRA	Resource Conservation and Recovery Act
RD	Remedial design
RfC	Reference concentration
RfD	Reference dose
RI	Remedial investigation
RISC	Risk Information Support Center
RI/FS	Remedial investigation/feasibility study
ROD	Record of Decision
RPM	Remedial Project Manager
SACM	Superfund accelerated cleanup model
SARA	Superfund Amendments and Reauthorization Act
SCBA	Self-contained breathing apparatus
SCRAM	Support Center for Regulatory Air Models

SUPERFUND ABBREVIATIONS AND ACRONYMS

SCREEN	(atmospheric dispersion model)
SI	Site inspection
SITE	Superfund Innovative Technology Evaluation
STEL	Short-term exposure limit
SVOC	Semi-volatile organic compound
TBC	To be considered
THC	Total hydrocarbons
TLV	Threshold limit value
TLV-C	Threshold limit value - ceiling
TLV-STEL	Threshold limit value - short term exposure limit
TLV-TWA	Threshold limit value - time weighted average
TNMHC	Total non-methane hydrocarbons
TO	Toxic organic
TRI	Toxic chemical Release Inventory
TSCREEN	(emission model/atmospheric dispersion model)
TSDF	Transfer, storage, and disposal facilities
TSP	Total suspended particulates
TTN	Technology Transfer Network
TWA	Time-weighted average
TWA-REL	Time-weighted average - recommended exposure limit
TWA-STEL	Time-weighted average - short-term exposure limit
UST	Underground storage tank
UV-DOAS	Ultraviolet - Differential Optical Absorbance Spectrometer
VOC	Volatile organic compound

SECTION 1

INTRODUCTION

This report presents the results of an EPA-sponsored study to develop guidance for designing and conducting ambient air monitoring at Superfund sites. By law, all exposure pathways - including the air pathway - must be evaluated for every Superfund site; therefore, some level of ambient air monitoring usually is necessary at each site. This introduction provides background information related to this study, identifies the objectives and scope of the study, and contains an overview of air monitoring at Superfund sites.

1.1 BACKGROUND

The Office of Air Quality Planning and Standards (OAQPS) directs a national Air/Superfund Coordination Program to help EPA Headquarters and the Regional Superfund Offices evaluate Superfund sites and determine appropriate remedial actions to mitigate their effects on air quality. Each Regional Air Program Office has an Air/Superfund Coordinator who coordinates activities at the Regional level. OAQPS has a number of responsibilities related to the Air/Superfund program, including preparation of national technical guidance (NTG) documents.

Among the documents that have been prepared are a four-volume series on air pathway assessments (APA).¹⁻⁴ These have been widely distributed and used. (A list of all Air/Superfund documents is given in Appendix A.) This document is a revision of the original Volume IV (EPA-450/1-89-004) of this series which was titled, "Volume IV - Procedures for Dispersion Modeling and Air Monitoring for Superfund Air Pathway Analysis". Because the APA documents were originally published in 1989, they reflect information available as of 1988. Improved sampling and analytical techniques have been developed since then and this revision of Volume IV was prepared to incorporate this new information.

This document has a narrower focus than the original Volume IV; it addresses air monitoring but not dispersion modeling. The guidance for dispersion modeling at Superfund sites will be updated at a later date and published as a stand-alone document. In the interim, the guidance on atmospheric dispersion modeling given to the old Volume IV is still valid.

1.2 OBJECTIVES AND SCOPE

The overall objectives of this study were to review the original Volume IV, identify portions of the document that needed to be revised or updated, and implement these changes. This was accomplished by:

- Performing a literature search to identify recent relevant citations on ambient air monitoring methods; and
- Conducting a telephone survey of selected EPA staff and EPA contractors to elicit suggestions for improving the document.

The recommendations for changes to the document included:

- Tables to help users select appropriate air monitoring and sampling/analytical methods for specific compounds or classes of compounds;
- Guidance on designing networks for ambient air monitoring studies;
- More detailed information on quality assurance and quality control for long-term and short-term ambient air monitoring efforts;
- Guidance for managing and using the large quantities of data generated by ambient air monitoring networks;
- Guidance on how to compare data from open-path monitors with data from more traditional measurement techniques; and
- Guidance on using ambient air monitoring data to derive emission source terms for use with dispersion models.

This document is an interim final manual that offers technical guidance for use by a diverse audience, including EPA Air and Superfund Regional and Headquarters staff, State Air and Superfund staff, federal and state remedial and removal contractors, and potentially responsible parties. This manual is written to serve the needs of individuals with various levels of scientific training and experience in selecting and using ambient air monitoring (AAM) methods in support of air pathway assessments. Assumptions and judgements are needed to develop air monitoring approaches, so the individuals involved in this activity would benefit from having a strong technical background in air emissions measurements, instrumentation, dispersion modeling, monitoring, and risk assessment. Remedial project managers, on-scene coordinators, and regional air program staff, supported by the technical expertise of their contractors, can use the information in this report when developing ambient air monitoring programs.

The development of an AAM program cannot be reduced to simple "cookbook" procedures. There is always a potential need for professional judgement and flexibility when developing compliance monitoring programs for specific Superfund sites. The information set forth in this manual is intended solely for technical guidance. This information is not intended, nor can it be relied upon, to create rights substantive or procedural, enforceable by any party in litigation with the United States.

1.3 OVERVIEW of AIR MONITORING at SUPERFUND SITES

The U.S. Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA), is required to develop and implement measures to clean up hazardous or uncontrolled waste sites. The Superfund process consists of three phases: pre-remedial, remedial and post-remedial. The cleanup of a contaminated site under the Superfund program proceeds via a series of actions (see Figure 1-1) designed to remove or stabilize the contaminated material in a controlled way. Activities related to an air pathway assessment for a Superfund site may be necessary during the Site Inspection (SI), Emergency Removal (ER), the Remedial Investigation (RI), the Feasibility Study (FS), the

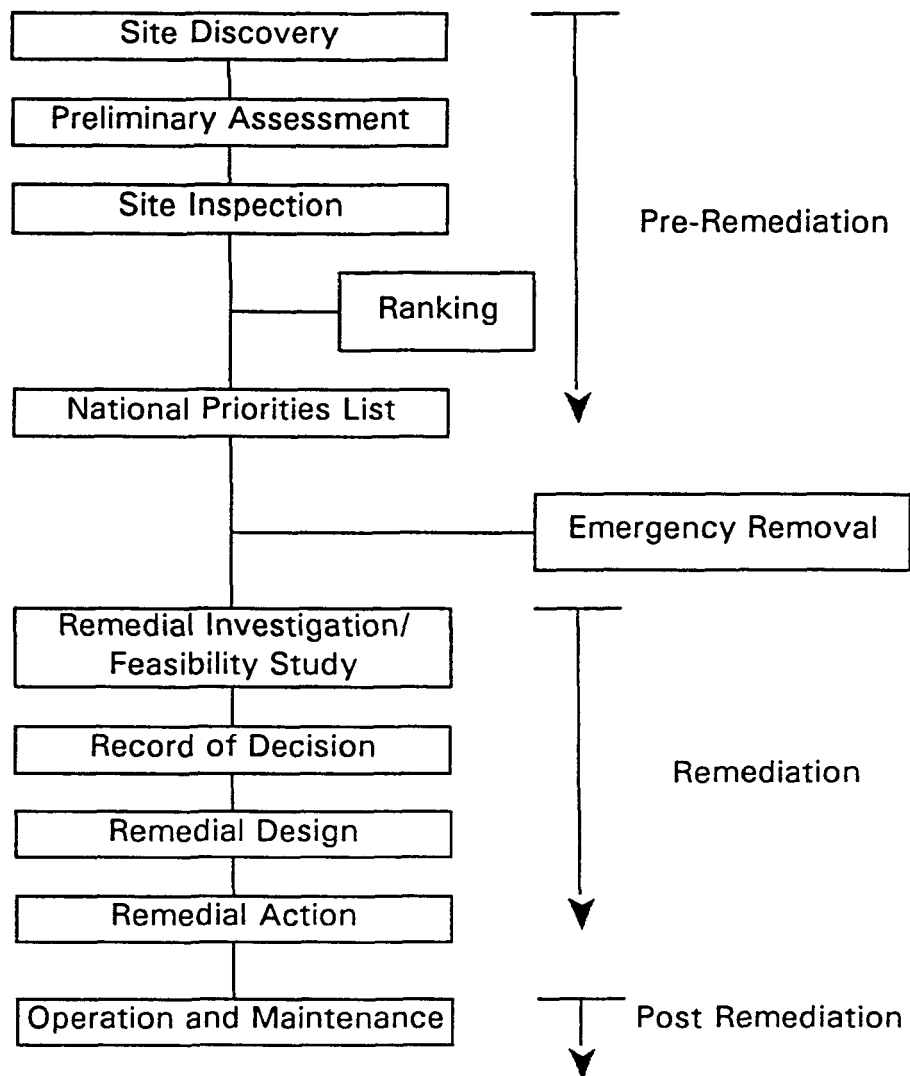


Figure 1-1. Phases of the Superfund Process.

Remedial Design (RD), the Remedial Action (RA) and the Post Remediation which is often called Operation and Maintenance (O&M). Typical air pathway assessment (APA) activities associated with each action are summarized in Table 1-1. An overview of air monitoring at Superfund sites adapted from a recent EPA publication is given below.¹

The overall goal of an APA is to evaluate a given site's actual or potential effects on air quality. The specific goal of any associated air monitoring work is typically to evaluate the exposure of on-site workers or the off-site populace and surrounding environment. The air monitoring issues related to these goals are discussed below, followed by a discussion of general air monitoring issues.

1.3.1 Evaluate Exposure of On-Site Workers

On-site workers at Superfund sites may be exposed to significant amounts of air pollutants in the course of performing their jobs. Any source of emissions at a site will result in an emissions plume. Fugitive air emission releases at Superfund sites usually occur at ground level and are not thermally buoyant; therefore, the maximum ambient air concentrations for such sources occur immediately downwind of the source and at ground level. Point sources such as air strippers may have relatively short stacks and nonbuoyant plumes; the maximum ambient air concentrations resulting from such sources often may occur within the site boundaries. It frequently is necessary for on-site workers to operate equipment or otherwise work in contact with such emission plumes. As a consequence, on-site workers must undergo training to recognize and respond to such potentially adverse exposures as part of their OSHA-mandated safety training.

On-site personnel may work close to emission sources and they also tend to move around over time, which makes it very difficult to accurately predict worker exposure using a modeling approach. Instead, monitoring is usually performed to determine worker exposure. This monitoring may entail the use of both portable monitoring instruments (e.g., THC or TNMHC hand-held analyzers) to provide immediate feedback on surrogate indicators such as total hydrocarbons, and industrial hygiene (IH) sampling to provide information on

Table 1-1.
APA Activities During Various Superfund Actions

Action	Data Quality Needs	Typical Ambient Concentration Level	Typical Sampling Strategy/Network Design	Duration of AAM Effort	Data Turnaround Time	Air Modeling	Typical Uses of APA Data
SI	Qualitative (screening)	≤ 10 ppb	<ul style="list-style-type: none"> • IH monitoring • Limited fence-line monitoring 	1 + weeks	Not critical	Screening study	Assess type and general magnitude of site emissions.
ER	Quantitative	≥ 200 ppb	<ul style="list-style-type: none"> • IH monitoring • Fence-line monitoring • Monitoring at MEI 	1 + weeks	Critical to determination of compliance with short-term action levels	Evaluate evacuation options	Estimate risk to on-site workers and off-site populace.
RI	Semi-quantitative	≤ 10 ppb	<ul style="list-style-type: none"> • IH monitoring • Limited fence-line monitoring 	Several weeks	Not critical	Evaluate off-site exposure	Estimate risk to on-site workers and improve knowledge of emission sources, also estimate risk to off-site populace.
FS	Quantitative	100-200 ppb	<ul style="list-style-type: none"> • IH monitoring • Emission rate measurements 	Several weeks	Not critical	Input to risk determination and RD	Estimate air impacts during full-scale remediation.
RA	Quantitative	≥ 200 ppb	<ul style="list-style-type: none"> • IH monitoring • Fence-line monitoring • Monitoring at MEI 	Months	Critical to determination of compliance with short-term action levels	Provide regular estimates of downwind impacts	Estimate risk to on-site workers and off-site populace.
O&M	Semi-quantitative (screening)	≤ 10 ppb	<ul style="list-style-type: none"> • Limited fence-line monitoring 	1 + weeks	Not critical	Input to any final risk determination	Estimate risk to off-site populace.

exposure to specific compounds. IH sampling involves placing dosimeters or low-volume sampling pumps with sorbent tubes, filters, etc. on the workers and measuring the average concentrations of selected contaminants in the breathing zone over a given period (e.g., 8- to 10-hour worker shift). The IH type of sampling yields more detailed information than portable monitoring instruments do, but data turnaround time is usually at least 24 hours. For either type of sampling, the measured values can be compared with occupational exposure limits to determine whether worker exposure is within safe levels. In general, short-term acute exposure is more of a concern for on-site workers than is long-term chronic exposure. A series of action levels is often established that relate the level of required personal protective equipment (PPE) to specific ambient air concentrations. For example, workers may be required to put on respirators if the total hydrocarbon (THC) concentration in the breathing zone at the work area exceeds some level for a specified period (e.g., if the THC concentration exceeds 10 ppmv for 1 minute).

In many cases, the site health & safety plan requires a conservative (i.e., restrictive) approach. At the start of the project, on-site workers are required to wear adequate PPE to safely work under assumed worst-case levels of emissions. The PPE requirements are gradually reduced if the air monitoring data collected in and near the work zones indicate that no problems have been encountered, i.e., that no action levels have been exceeded. Information regarding on-site worker exposure can also be useful for estimating air impacts further downwind.

1.3.2 Evaluate Exposure of Off-Site Community/Environment

A major concern at Superfund sites is the potential exposure via the air pathway of residents and workers in the areas surrounding the site. The degree of concern varies from site to site, as discussed below, depending on the nature of the contamination, the proposed remedy, and the proximity of the off-site populace (receptors). The exposure of off-site receptors typically is evaluated at several steps of the Superfund process, and both modeling and monitoring approaches may be employed as part of the exposure assessment.

The evaluation of human exposure (due to inhalation) using a monitoring approach generally involves measuring the concentrations of target analytes at the fenceline of the site for ground-level emission sources and at the areas of maximum estimated ground-level impacts for elevated emission sources (e.g., thermal treatment unit smokestacks). Additional AAM may be conducted at selected receptor locations in the surrounding community (e.g., at nearby schools) or on site, if there is public access. Data are collected at locations upwind and downwind of the site. The data are compared with action levels to determine if there is cause for concern at downwind locations. If downwind concentrations exceed levels of concern, actions must be taken to reduce pollutant emissions. The difference in the concentrations measured downwind and upwind of the site yields an adjusted concentration considered to represent the contribution of the site emissions to the local air quality.

The evaluation of off-site exposure generally requires that monitoring be performed whenever significant air emissions may be released from the site. At sites that have the potential for adversely affecting the air, this is often addressed by performing a short baseline study, followed by continuous monitoring whenever active remediation is being conducted at the site. Usually, a fixed network of point samplers is located around the perimeter of the site, samples are collected continuously during on-site activities, and all samples are analyzed. Additional samplers may be located near the working areas. The number of sampling locations will depend on the size of the site, among other factors. For large sites surrounded by nearby residences, a twelve-station network may be used to provide nearly complete coverage of the fenceline (i.e., a station every 30 degrees). In some cases, only samples from stations located directly upwind or downwind of the site for a given sampling period will be analyzed to save time and money; samples collected at locations perpendicular to the emission plume(s) are not analyzed. Alternatively, a smaller number of AAM stations may be used, and these stations may be moved from day to day according to predicted wind patterns. If the predictions are wrong, however, the monitoring stations may not be in the emission plume as needed.

1.3.3 General Air Monitoring Issues

Typical APA activities at Superfund sites can be divided into the following four categories:

- 1) Screening evaluation of site emissions and their impacts on air quality under baseline or undisturbed conditions;
- 2) Refined evaluation of site emissions and their effect on air quality under baseline or undisturbed conditions;
- 3) Refined evaluation of emissions and their effect on air quality from pilot-scale remediation activities; and
- 4) Refined evaluation of the effects on air quality of full-scale remediation activities.

Other APA activities may be appropriate for specific site applications. Screening studies are performed to better define the nature and extent of a problem (i.e., to limit the number of questions to be considered for a site); refined studies are performed to find definitive answers to one or more air-related questions. While screening studies are less time- and resource-intensive than refined studies, they do not necessarily use different monitoring methods or approaches. Screening studies should not be thought of as being necessarily inexpensive, "quick-and-dirty," or qualitative in nature. Screening studies have more uncertainty associated with them than refined studies do, so their experimental design should be more conservative. For example, if only a few days of monitoring data are to be collected, it should be collected during periods of worst-case conditions.

Superfund sites often contain a complex mixture of contaminants. The potential adverse health effects vary from compound to compound, and the health-based action levels may vary by orders of magnitude between compounds with relatively similar structures and physical properties. Therefore, the most significant compounds at the site from a health risk standpoint may not necessarily be those compounds present in the highest concentrations in the soil or water at the site. The compounds addressed in the air monitoring program will typically be a subset of the contaminants present at the site, since it

is often prohibitively expensive to generate data for all the contaminants present. Risk assessments for the air pathway usually indicate that a relatively few compounds account for most of the risk.

The proposed remedy will greatly influence the potential emissions from a site. In general, in-situ remediation methods result in lower levels of air emissions than ex-situ remediation methods. Any activity that moves or disturbs the waste present at the site can potentially result in emissions of VOCs and PM. Public concern historically has focused on point sources of air emissions such as incinerator stacks, but fugitive sources of emissions such as materials handling operations may result in greater air emissions at many sites.

The appropriate monitoring methods used to check compliance with established action levels will vary from target compound to target compound and from site situation to site situation. Compliance monitoring for long-term action levels tends to involve the continuous collection of time-integrated samples at fixed locations; compliance monitoring for short-term action levels tends to involve the periodic collection of nearly instantaneous samples at various locations of interest. Long-term monitoring is intended more to document actual exposure than to provide feedback to on-site operations. Short-term monitoring is intended to provide information to on-site decision makers to help them select operating rates and decide whether emission control measures are needed.

In general, compliance with long-term action levels is based on daily samples collected at each location within an AAM network. Broad-based collection methods such as evacuated canisters, Tenax tubes, or charcoal tubes are usually selected for VOCs so that all the target analytes can be measured using only one or two sampling and analysis approaches. Alternatively, dedicated gas chromatographs (GCs) or gas chromatographs/mass spectrometers (GC/MSs) used as point samplers, or open path monitors (OPMs) may be used in some cases to provide near real-time data and to minimize unit analytical costs. Fewer options exist for standard PM₁₀, metals, and some SVOCs, although standard methods are available.

Selecting monitoring methods to document compliance with short-term action levels often is more difficult than selecting methods to determine compliance with long-term action levels. Dedicated GC, GC/MS, or OPM systems are the only realistic options for the cost-effective continuous or semi-continuous monitoring of individual volatile organic compounds. These methods require a relatively large capital investment and they may not be a viable option for certain compounds or mixtures of compounds. Several methods are commonly used for periodic compliance monitoring for short-term action levels. Fixed or portable broad-band analyzers for total hydrocarbons (THC) or total non-methane hydrocarbons (TNMHC) can be used if it is assumed that the instrument response (or some fixed fraction thereof) is wholly due to the most hazardous compound present. Compound-specific colorimetric tubes are available for many compounds, though usually only for relatively high concentration ranges (e.g., ppm levels). Short-term monitoring for SVOCs and metals cannot be performed directly. Instead, portable monitors for particulate matter can be used to measure total suspended particulate matter (TSP). An action level can be established if the average fraction of SVOCs or metals associated with the TSP is assumed.

The need to determine compliance with short-term action levels requires a timely turnaround of data. The most critical need for timely information is to compare AAM data with short-term action levels during remediation. As previously discussed, the most common solution is to use broad-band THC or TNMHC analyzers or to use colorimetric tubes. For sites where the concentration of specific analytes must be measured, dedicated gas chromatographs (GC) and GC/MS systems used as point samplers have until recently been the only realistic option. They can provide updated values every 30 minutes or so. The main drawbacks of the use of their instruments as short-term monitors have been the cost of the equipment (e.g., \$100,000 per station), the complexity of installing and controlling the monitoring network, maintenance requirements, and the labor required to reduce and manage the data.

A promising monitoring approach for Superfund remedial actions is the use of open path monitors (OPM).⁵ OPMs are spectroscopic instruments configured to monitor the open air over extended paths of hundreds of meters or more. They rely on the interaction of light with matter to obtain information about that matter. The potential advantages of OPMs compared with more conventional air monitoring approaches include: 1) there is rapid, essentially real-time data analysis; 2) no sample collection is required in the normal sense of the term; 3) no additional analytical costs are associated with each additional sampling episode; and 4) data are path-weighted concentrations rather than concentrations for specific sampling points. The first advantage implies that information is available to site decision makers within minutes and short-term fluctuations in ambient concentrations can be detected. The last advantage listed implies that it is less likely that an emission plume will evade the monitoring network and that source terms can be directly determined. Data management software is available for handling the very large quantities of data generated. The main disadvantages of OPMs at this time are the lack of standard operating procedures, the lack of qualified equipment operators, the lack of standardized procedures for dealing with spectral interferences, the lack of reference spectra for some compounds of interest, and detection limits that, for some compounds (e.g., benzene), are higher than those for conventional methods.

Detection limits are often a concern when selecting a monitoring device. Compliance monitoring for action levels generally requires that the detection limit of the sampling and analytical approach be lower than the action level concentration. Changes in ambient concentration due to emissions from the site must be distinguished from the sample-to-sample variability that is always present. Therefore, the precision of the measurement method is critical, but the precision of analytical methods tends to deteriorate as the detection limit is approached. There often is a trade-off between analytical data turnaround time and detection limit. Measurement methods that provide rapid data turnaround often are screening methods that provide rapid feedback for parts-per-million concentration levels rather than for parts-per-billion or lower concentration levels. The data accuracy and precision of such screening methods also tend to be more variable than those for non-screening methods. For example, portable THC analyzers may exhibit a large daily zero and upscale drift, especially

if they are exposed to very high concentration levels or if the internal batteries are allowed to fully discharge. As previously mentioned, dedicated GC, GC/MS, or OPM systems may be the best options to meet data turnaround and detection limit requirements at sites where potential adverse effects on air quality are a major concern.

The uncertainty of the AAM data also is an issue. The accuracy of the monitoring data must be adequate to determine whether action levels are exceeded. The AAM data must be precise enough to determine differences from ambient or upwind concentrations of the compounds of interest. If the action levels selected are at or near detection limits, the uncertainty of the analytical data usually will be greater than it would be for measurements of those compounds at higher concentrations.

SECTION 2

PROGRAM DESIGN

There is no universal approach to conducting an AAM program that would satisfy the needs of every air pathway assessment. Instead, each program should be designed to match the specific program needs and available resources. A framework for designing an effective ambient air monitoring (AAM) program consists of the eight basic steps listed in Table 2-1. This framework parallels earlier EPA guidance on applying the Data Quality Objectives Process for ambient air monitoring around Superfund sites.^{6,7} The first step to designing an AAM program consists of defining the program goals. Once these have been established, specific data needs in terms of target compounds, data quality, temporal resolution, and spatial resolution can be defined. The selection of appropriate monitoring equipment will depend on these specific data needs and therefore selection should occur only after an initial determination of the data requirements has been made. Guidelines for addressing five of the elements of program design are summarized in Table 2-2. An example checklist for developing an AAM plan is given as Figure 2-1. Detailed discussions of specific measurement methods, elements of quality assurance/quality control, and data management appear in subsequent sections of this document.

2.1 PROGRAM GOALS

Section 1.3 of this document gave examples of reasons to conduct air monitoring around Superfund sites. In each example, air monitoring data were used for comparison with certain risk-based action levels to determine the need for reducing the exposures of either on-site workers or the general public to pollutants. For an AAM program to be effective, goals should be defined in terms of certain key questions whose answers will depend on the outcome of the monitoring results. For example, "Has remedial activity caused the ambient air concentrations to exceed applicable risk-based concentration levels?"⁶ If the answer to this question is "yes," specific planned actions must be taken to reduce pollutant exposures. Such actions might be to: (1) institute additional emission controls, (2) temporarily halt remedial activities, or (3) evacuate the receptor population.

Table 2-1.
Eight Steps to Designing an Ambient Air Monitoring Project

Step	Description
(1)	Define program goals
(2)	Select target compounds
(3)	Establish data quality objectives
(4)	Select number and location of monitoring sites
(5)	Select duration and frequency of monitoring
(6)	Choose monitoring methods
(7)	Establish a quality assurance/quality control program
(8)	Establish a data management system

Table 2-2.
Summary of AAM Design Elements for a Typical¹ Superfund Site

Design Element	Typical ¹ Goal or Range of Values		
	Baseline Study	Monitoring During Remedial Activities	Post-Remediation Study
Number of Target Compounds	<ul style="list-style-type: none"> Multiple compound classes Full analyte list 	1-20	< 10
Data Quality Objectives	Identify compounds accurately; semi-quantitatively	Quantify level of specified compound(s).	Quantify level of specified compound(s).
Sampling: Period Duration Frequency	24-hour 5 days to 1 year Daily to once every 6 days	8-24 hours Duration of remediation Daily	24-hour 5 days to 1 year Daily to Quarterly
Number of Sampling Locations	4-12	4-12	4-12
Required Monitoring Method Characteristics	<ul style="list-style-type: none"> Low DLs Applicability to broad range of compounds 	<ul style="list-style-type: none"> Rapid Data-Turnaround Low DLs 	<ul style="list-style-type: none"> Low DLs

¹Superfund sites vary greatly from one to another in a number of relevant areas. The information in this table is intended to provide general guidance as to the design boundary conditions expected for most sites.

The following checklist consists of a series of questions to consider when developing the sampling program.

I. Objectives of the Sampling Program and Implied Assumptions

- ☐ A. Have clear, concise objectives for the sampling program been defined?
- ☐ B. Have the assumptions of the sampling program been clearly defined (e.g., sampling under "worst-case" conditions, sampling under "typical" conditions, sampling under routine, periodic schedule, etc.)?
- ☐ C. What will the data be used for (e.g., risk assessment, compliance with action levels)?
- ☐ D. 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. 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?
- ☐ B. Will the sampling locations account for all the potential emission sources upwind from the site?
- ☐ C. For short-term monitoring programs, was a forecast of the local winds for the day(s) of the program obtained?
- ☐ D. For a long-term monitoring program, were long-term air quality dispersion models and historical meteorological data used to predict probable area of maximum impact (when applicable)?
- ☐ 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)?
- ☐ F. Does 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.)?
- ☐ G. Can any sampling equipment left at these locations be adequately secured?
- ☐ H. Other _____

Figure 2-1. Air Sampling Plan Checklist⁸

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 direction?
- ☐ • 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 due to changes in atmospheric pressure and to 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 effects on potential site emissions listed below 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?
- ☐ • Are the sampling intervals consistent with the averaging period of the applicable action levels?
- ☐ • When applicable, do the selected time intervals account for 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 sample design to allow for the detection of potential sources of error?
- ☐ C. Does the QA/QC plan account for verification of the sample design and the sample collection?

Figure 2-1. (Continued)

The Remedial Program Manager (RPM) or On-Scene Coordinator (OSC) will usually take the lead role in defining program goals and determining what actions might be necessary if pollutant concentrations exceed levels of concern. During this initial stage of program design, the RPM or OSC should also discuss the goals of the program with the technical staff to make sure that these objectives can be reasonably accomplished within the limitations of available technical and financial resources. This will usually require a preliminary assessment (in very general terms) of the types of data required, the uses of the data, and any consequences of an incorrect decision, based on the measurement results. In some cases, program goals may have to be revised if inadequate resources are available.

2.2 TARGET COMPOUNDS

After the goals of the air pathway assessment have been defined, a list of analytes should be determined. Superfund sites often contain a complex mixture of contaminants, and not every contaminant will pose a significant risk via the air pathway. Factors that affect the magnitude of any risk posed by a particular contaminant include the concentration of the compound in the buried waste or soil, the compound's volatility or the rate at which the compound is emitted to the air, and the toxicity or unit risk factor of the particular compound.

Certain compounds typically are considered to "drive" the risk assessment at Superfund sites, i.e., they pose the most significant risk. Air pathway assessment studies, therefore, will typically focus available resources on those compounds thought to pose the most significant risk at a site, rather than include an evaluation of every compound found at the site. The selected analytes are sometimes referred to as target compounds or compounds of potential concern. Compounds of frequent concern at Superfund sites include:

- Volatile organic compounds (VOCs), especially benzene and chlorinated solvents such as vinyl chloride, methylene chloride, chloroform, etc.;
- Semi-volatile organic compounds (SVOCs), such as polychlorinated biphenyls (PCBs), polynuclear aromatic compounds (PNAs), and pesticides;

- Semi-volatile inorganic compounds such as those containing mercury; and
- Nonvolatile compounds such as asbestos and cyanides; and heavy metals, such as lead, chromium, cadmium, zinc, beryllium, copper, and arsenic.

Of course, not every compound listed above is present in significant quantities at every Superfund site. Site records must be reviewed to determine the nature of the buried waste. Wastes are typically classified according to RCRA codes that are defined with respect to compound constituents in the Code of Federal Regulations (40 CFR, Part 261). If site records are unavailable, soil sampling and analysis must be conducted to determine which compounds are present in significant enough quantities to possibly warrant air monitoring.

The rate at which soil contaminants are emitted to the air depends in part on their volatilities (for gaseous contaminants only), which in turn depend on vapor pressures and Henry's Law constants. Highly volatile compounds will typically be emitted at a higher rate than compounds of similar concentration in the soil but lower volatility. Computer models that rely in part on compound vapor pressure and Henry's Law data as input are often used to estimate potential emissions to the air. Emission rates can then be used as input to an atmospheric dispersion model to gauge both short-term (e.g., one-hour) and long-term (e.g., one-year) concentration levels at the facility fenceline and off-site receptors. Semi-volatile and non-volatile compounds may also be of concern whenever they exist in significant concentrations and there is the potential for the dispersion of wind-blown dust.

It often is not practical to monitor for every compound present in the soil or ambient air, because of the limitations of available technical or financial resources. In these cases, potential target compounds must be ranked in terms of predicted concentration levels and applicable health-based action levels. Note that the potential adverse health effects vary from compound to compound, and the health-based action levels may vary by orders of magnitude between compounds with relatively similar structures and physical properties. For example, 1,2-dichloroethane is considered to be a much more potent carcinogen than 1,1-dichloroethane, and benzene is considered to pose a much more significant risk than equal

amounts of toluene or xylene. Therefore, the most significant compounds at the site from a health risk standpoint might not necessarily be those present in the highest concentrations in the soil or water. To prepare a list of potential target compounds, the potential health risks associated with each compound can be ranked in terms of a hazard index (HI), where HI is the ratio of the predicted concentration to the applicable action level. Measurement resources should be focused on those compounds with the highest hazard indices.

Emission and dispersion models can be limited in their ability to predict actual environmental conditions because of inherent simplifications and assumptions in both the model and the model's input. Therefore, the most effective, albeit more costly, way to determine which compounds may or may not be of concern is to conduct a short-term intensive monitoring effort to screen for a comprehensive list of potential high-risk compounds. Based on the results of this initial screen, a more realistic ranking of the potential hazards associated with each compound can usually be made.

2.3 DEFINING DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are statements of the level of uncertainty a decision maker is willing to accept where making decisions based on the air monitoring data.⁶ Note that DQOs differ from data quality indicators such as measurement precision and accuracy in that they express the limits of the overall uncertainty of a project's results in terms of the probability and consequences of making a wrong decision (rather than as the limits of certainty about specific measurements). How data quality objectives relate to accuracy and precision is described in the following paragraphs.

Establishing DQOs must be one of the first steps in the design of an AAM program. This must be done before sampling and analytical methods are selected for performing the measurements. EPA has adopted a three-stage process for establishing DQOs for ambient air monitoring around superfund sites.^{6,7} Combined, the three stages of the DQO process take into account all of the eight elements of project design to ensure that sufficient, valid data are collected to achieve the goals of the program. During the first stage of the

DQO process, the goals of the APA are defined in terms of certain critical decisions that require ambient measurement data, and the feasibility of achieving those goals within the constraints of the available technical and financial resources are determined. During the second stage, specific data requirements in terms of temporal resolution, spatial resolution, and data quality are defined. At the third stage of the DQO process, a viable data collection program that meets the Stage I and Stage II objectives is designed. Guidelines for defining the temporal and spatial resolutions of the measurement domain are addressed in Sections 2.4 and 2.5, respectively, and guidelines for selecting appropriate measurement methods are given in Section 2.6. The remainder of Section 2.3 pertains to defining the limits of data quality.

Data quality objectives are expressed in terms of acceptable probabilities that the measurement results will lead to incorrect decisions. Two general types of incorrect decisions can occur: false positive errors and false negative errors. False positive errors result in decisions to take action to reduce pollutant exposures when the true concentrations are actually below levels of concern. False negative errors result in not taking action when, in fact, concentration levels are above those thought to pose a serious risk. While false negative errors are usually more detrimental because of the health risks that might unknowingly be imposed on the public, false positive errors are also counterproductive because of the money and time wasted taking unnecessary action. Data quality objectives, therefore, place limits on the acceptable probabilities that either a false positive or false negative error will be made. The acceptable probability that a measurement result will lead to an incorrect decision should depend on the seriousness of the consequences of the incorrect decision. The following examples of APA data quality objectives demonstrate the relationship between acceptable probability rates and the seriousness of the incorrect decision¹:

- At a true concentration of $\frac{1}{2}$ the level of concern, the probability of a **false positive** finding should be less than 10% (i.e., at least 90% of the time, the data would correctly indicate that there is no problem).
- When the true concentration is $1\frac{1}{2}$ times the level of concern, the probability of a **false negative** finding should be less than 5% (i.e., at

least 95% of the time, the monitoring data would correctly indicate that there is a problem).

- When the true concentration is 2 times the level of concern, the probability of a **false negative** finding should be less than 1% (i.e., at least 99% of the time, the monitoring data would correctly indicate that there is a problem).

The probability of a false finding is directly and quantitatively related to the accuracy and precision of the measurement method. For instance, in the examples above, a measurement method with a precision of 20% (expressed as relative standard deviation) and no systematic biases would be needed to satisfy each of the three conditions. More details on applying the DQO process to AAM around Superfund sites are given in References 6 and 7.

In addition to quantitative limits of data quality, data quality objectives must also be defined qualitatively in terms of representativeness and comparability. Representativeness refers to the specific conditions of space and time to which measurement value is intended to relate. For example, if data are to be compared with 30-minute inhalation-based action levels, the measurement values must be representative of conditions in the typical breathing zone (i.e., approximately 5' to 6' above ground in an area with unrestricted air flow) and averaged over 30-minute intervals. Comparability refers to assurances that the measurement results are expressed in a manner and format that enables direct comparison with applicable action levels (i.e., standardized units) or, if necessary, with other, similar types of data.

2.4 SAMPLING PERIODS AND FREQUENCIES

The temporal resolution of the measurement domain is defined by the sampling period and frequency. Sampling period refers to the length of time to which each measurement value is referenced (e.g., 30-minute, one-hour, 24-hours, etc.). The sampling frequency is the number of sampling periods conducted within a given time interval (e.g., daily, one every third day, etc.). For typical APA monitoring programs, the sampling period may range from a few seconds to 72-hours, depending on the specific goals and data

requirements of the program. Sampling periods of a few seconds are performed using real-time or grab sampling techniques, whereas longer sampling periods are usually performed using integrated methods. For real-time monitoring, the sampling frequency is usually continuous, although sampling may be limited to certain times of the day when remedial activity is occurring. Integrated sampling may be performed continuously (i.e., back-to-back sample collection), or at intermittent, discrete intervals. Specific program goals and available funding will normally dictate whether continuous or intermittent sampling intervals are performed. Grab sampling is only performed when an instantaneous, spot check of the air constituents is required (e.g., as a pre-monitoring screen for constituent compounds).

Sampling periods must be chosen for comparability with relevant action levels or ARARs. For example, if the measurement data are to be compared with a 30-minute action level, a 30-minute sampling period is normally required (alternatively, continuous, real-time monitoring can be performed and the resulting data averaged over 30-minute intervals). Compliance with long-term action levels usually is determined using a series of 24-hour sampling periods. In some cases, sampling periods also may depend on the amount of sample volume needed to achieve acceptable detection limits. For instance, a one-hour sampling period will yield a detection limit twice as low as the same technique operating with the same flow rate for 30 minutes.

The required frequency of sample collection depends primarily on: (1) the temporal variability of emission rates with respect to the temporal scale of the action level, (2) the variability of meteorological and other factors that might affect pollutant dispersion, (3) the level of confidence needed for determining mean or maximum downwind concentrations, and (4) the level of available funding. When action levels are based on short-term averages and the pollutant concentrations are expected to vary significantly over time, continuous sample collection may be needed to achieve an acceptable level of confidence that action levels are not exceeded. Note that the level of confidence required in the measurement results may depend on how close the measured ambient concentration levels are to the action level concentrations (i.e., the higher the measured concentrations, the greater the confidence required). For determining compliance with long-term action levels, a

minimum sampling frequency of once every sixth day is normally required. However, if the measured concentration levels are near levels of concern, a greater frequency of collection, perhaps daily, will be required (e.g., operating schedule for PM₁₀ sampling given in 40 CFR, Part 58.13).

2.5 NUMBER AND LOCATIONS OF SAMPLING SITES

The spatial resolution of the measurement domain is defined by the number and locations of the sampling sites. Factors that influence the required number and locations of monitoring sites are: (1) the locations of potential on-site emission sources; (2) the locations of topographic features that affect the dispersion and transport of site emissions; (3) the variability of local wind patterns; (4) the locations of sensitive receptors such as schools, hospitals, and concerned citizens; (5) the level of confidence needed to ensure that the maximum concentration levels are observed; and (4) the level of available funding.

Typically, programs designed for determining long-term concentration levels (e.g., annual or lifetime exposures) will require fewer monitoring locations than those intended to monitor compliance with short-term action levels. This is because the long-term prevailing wind directions are usually more predictable than day-to-day wind patterns, and sampling sites therefore can be more accurately situated for measuring significant long-term effects. For example, the dispersion modeling of source emissions, using climatological wind data as input, can be performed to determine the most appropriate sampling locations (i.e., areas of maximum or significant effects).

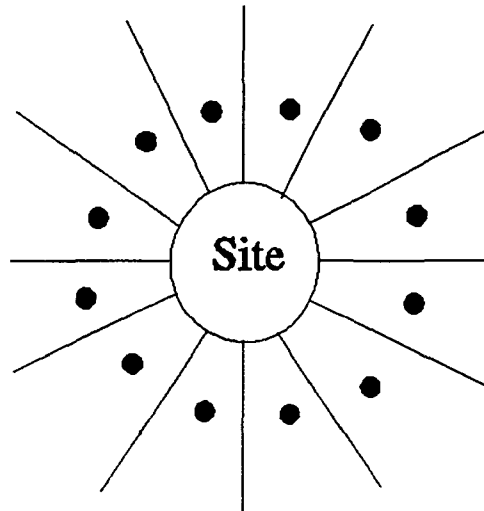
For determining concentration levels with respect to short-term effects, a fixed network of sampling sites ideally should be located around the perimeter of the waste site, with additional samplers located near working areas and near sensitive receptors. The number of sampling sites will depend, in part, on the size of the waste site. For large sites surrounded by nearby residences, a 12-station network would provide nearly complete spatial coverage of the fenceline (i.e., one sampling station every 15 degrees). In some cases, only samples from stations located directly upwind or downwind of the site for a given sampling

period will need to be analyzed. Alternatively, a smaller number of stations may be used and these stations moved from day to day according to predicted wind patterns. If predictions are wrong, however, the monitoring stations may not be in the emission plume as needed. The minimum and maximum number of recommended monitoring locations for a typical site are shown in Figure 2-2.

In many cases, constraints on placing samplers can be encountered because of wind flow obstructions caused by nearby buildings, trees, hills, or other obstacles. Other constraints might be related to security, the accessibility of electrical power, as well as the proximity to roadways or other pollution sources that might affect the representativeness of the sample for measuring the waste site's effects on air quality. Specific guidelines for selecting sites to achieve representative conditions are⁹:

- The most desirable height for sampler inlets is near the breathing zone (i.e., about 5' to 6' above ground). Practical factors such as high impermeable fences surrounding the waste site may sometimes require that sampling inlets be placed slightly higher (at least 1 meter above the top of the fence).
- Samplers should be located at least 20 meters from the dripline of nearby trees and **must** be at least 10 meters from the dripline of trees when the trees act as an obstruction to airflow.
- Samplers must be located away from obstacles and buildings such that the distance between the obstacles and the sampler inlet is at least twice the height that the obstacle extends above the sampler inlet. Airflow must be unrestricted in an arc of at least 270° around the sampler, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270° arc.
- The sampler and nearby roadways must be sufficiently separated to avoid the effects of dust reentrainment and vehicular emissions on measured air concentrations.
- Stations for measuring particulate matter should not be located in an unpaved area unless there is vegetative ground cover year round so that the effect of locally reentrained or fugitive dusts will be kept to a minimum.

Maximum - One Station Every 30°



Minimum - One Upwind and Three Downwind Stations

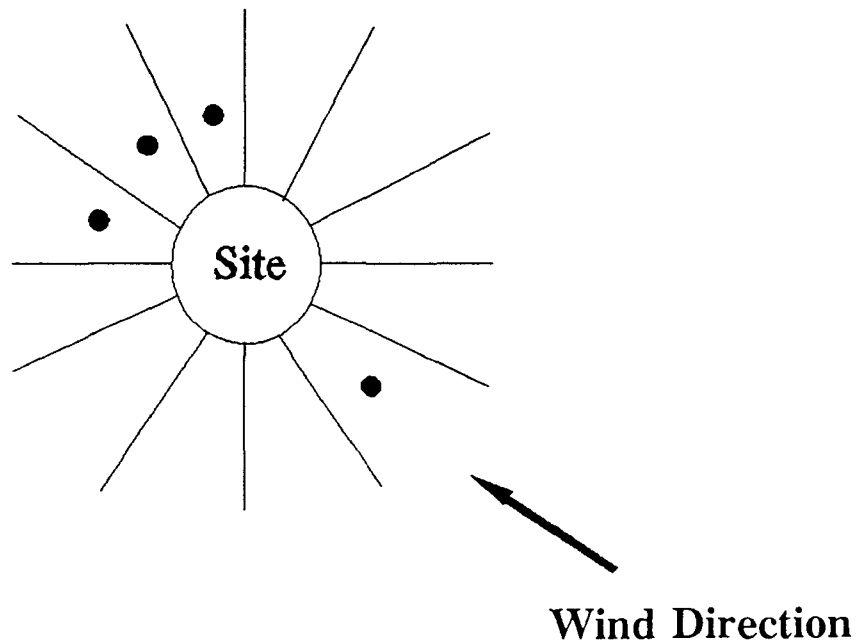


Figure 2-2. Depiction of Maximum and Minimum Number of Recommended Monitoring Locations for a Typical Site

2.6

SELECTING APPROPRIATE MONITORING METHODS

Because of the wide variety of data needs that may be encountered when designing an APA monitoring program, there is no single monitoring method that applies equally to every situation. Factors that might influence the selection of appropriate monitoring methods to suit particular data needs are: (1) target compounds, (2) data turnaround time, (3) detection limits, (4) data quality, (5) temporal resolution, (6) spatial resolution, and (7) cost. The merits and limitations of various conventional and novel measurement methods are given in Section 3.0. The factors that should be considered when selecting a measurement method are discussed below.

Data turnaround time is one of the most important factors to consider when choosing appropriate measurement technology. In contrast to typical non-Superfund applications where data turnaround times may be several weeks, data turnaround during remediation at Superfund sites typically must be within one or two days for comparison with long-term action levels and within hours for comparison with short-term action levels. Data turnaround times are most stringent when the monitoring data are being compared with short-term action levels during remediation. In these cases, immediate or real-time feed back of ambient concentration levels is usually required. In these situations, the most appropriate monitoring method will be a broad-band total hydrocarbon (THC) or total non-methane hydrocarbon (TNMHC) analyzer. For sites where the concentration of specific analytes must be measured, dedicated on-site GC, GC/MS, or OPM systems may be the only applicable option. For long-term monitoring programs, data turnaround time can be as much as 48 hours. This may also require a dedicated on-site laboratory because of the large number of samples likely to be analyzed during the course of the program.

Detection limits are another factor that must strongly influence the selection of appropriate monitoring methodology. Compliance monitoring for action levels generally requires that the detection limit be lower than the action level concentration. Note that there is often a tradeoff between detection limits and data turnaround times. For instance, measurement methods that provide real-time or near real-time results often are screening

methods that provide rapid feedback for parts-per-million concentration levels. This might be adequate for some programs designed for determining short-term risks; however, it would usually not be adequate for long-term assessment programs for which levels of concern are often on the order of parts-per-billion or less.

When selecting appropriate measurement technology, one must first decide on the necessary turnaround time and the required detection limits. Once these are defined, other factors such as temporal resolution, spatial resolution, data quality and cost can be considered. Temporal resolution differs from data turnaround time in that it relates to the time period during which a sample is collected (sample integration period) rather than how fast the sample can be analyzed and reported. Some methods may require a long integration period in order to acquire sufficient volume of sample to achieve acceptable detection limits. Other methods may achieve the same detection limits with a shorter sampling period.

Spatial resolution must also be considered when determining the measurement methodology. A high degree of spatial resolution in ambient air concentrations may be needed in some cases, such as when multiple emission sources are in close proximity to receptors. The higher the degree of spatial resolution required, the more sampling locations are needed. Increasing the number of sampling locations will increase the cost of the AAM program, if the sampling methods and frequency are held constant. Obviously, OPM systems provide the most complete coverage for monitoring emissions at a site boundary; however, OPMs provide a path-integrated measurement and might not be as accurate as other techniques for determining the peak concentration of a narrow plume.

Note that many interacting factors must be considered when selecting appropriate measurement methods. These factors must be ranked so that those issues most important to the particular needs of a specific program are given the appropriate attention.

2.7

METEOROLOGICAL MONITORING

Meteorological measurements will often be required along with ambient air quality data when assessing the risks associated with waste site air pathway emissions. At a minimum, wind direction and wind speed should be measured so that the direction of air pathway migration from the site can be assessed during all times that ambient air quality data are collected. Other meteorological parameters that are relevant to the air pathway assessment because of their effects on emission rates or dispersion of pollutants are: temperature, precipitation, relative humidity, barometric pressure, and sigma theta (standard deviation of the wind direction).

Meteorological measurements must be collected with similar concerns for quality assurance and quality control as the air pollutant measurements. That is, measurements must be: (1) representative of the atmospheric conditions that affect pollutant emissions, transport and dispersion; (2) comparable across the measurement network; and (3) of sufficient quality to support meaningful interpretations of the air pollutant data.

Meteorological measurements must be representative of the conditions at the source and at the locations of the sampling stations. In areas of uniform terrain, one meteorological monitoring station may be sufficient to represent the entire source and sampling domain. In some cases, meteorological data from an existing, off-site monitoring station (e.g., at a local airport) may serve this purpose. However, one should recognize that off-site data from other sources may not always be obtained with the same concerns for quality control and data management as data collected specifically to support the APA.

In regions of complex terrain or near large bodies of water where local topographical features can influence air flow and temperature, more meteorological monitoring stations are usually required to represent the different local domains. Assurances must also be made that the meteorological sensors are exposed to atmospheric conditions that are indeed characteristic of the area that the data are intended to represent. This requires that sensors be mounted away from the immediate influence of trees, buildings, steep slopes,

ridges, cliffs, and hollows. Sensors located in the vicinity of any such obstructions should be mounted at a horizontal distance at least 5 to 10 times the height of the obstruction⁹.

Comparability of meteorological measurement data across the monitoring network is achieved by adhering to a standard set of guidelines or criteria for monitoring site selection and sensor exposure. Detailed siting guidelines for meteorological instrumentation are given in Volume IV of EPA's Quality Assurance Handbook for Air Pollution Monitoring Systems. Typically, a 10 meter sensor height is recommended for wind speed and wind direction measurements, however, for short term screening studies when fixed monitoring stations may not be practical, a 2-3 meter sensor height is usually adequate. Additional guidelines for siting temperature, relative humidity, precipitation, and solar radiation sensors are given in the QA handbook.

Meteorological sensors must be capable of providing data of sufficient accuracy and resolution to enable a meaningful interpretation of the monitoring results. Recommended system accuracies for various measurement parameters are given in Table 2-3. The accuracies of meteorological sensors should be checked periodically during the course of a long-term measurement program (e.g., every three months or every six months) as part of the quality assurance audit program (e.g., see Section 4.0).

Table 2-3.

Recommended Meteorological Data Quality Objectives:
Accuracies and Resolutions⁹

Meteorological Variable	System Accuracy	Measurement Resolution
Wind Speed	$\pm(0.2 \text{ m/s} + 5\% \text{ of observed})$	0.1 m/s
Wind Direction	± 5 degrees	1 degree
Ambient Temperature	$\pm 0.5^{\circ}\text{C}$	0.1°C
Dew Point Temperature	$\pm 1.5^{\circ}\text{C}$	0.1°C
Precipitation	$\pm 10\%$ of observed	0.3 mm
Pressure	$\pm 3 \text{ mb}$ (0.3 kPa)	0.5 mb
Time	± 5 minutes	---

SECTION 3

SAMPLING AND ANALYTICAL METHODS

In this section, appropriate sampling and analytical methods for monitoring air emissions from Superfund sites under baseline conditions or during remediation are discussed. The sampling and analytical methods are divided into categories according to the class of target chemical. The four categories addressed are volatile organic compounds, semi-volatile organic compounds, particulate matter, and inorganic compounds.

Methods for volatile organic compounds (VOCs) are divided into categories for aromatic, halogenated, and oxygenated organic compounds. For semi-volatile organic compounds (SVOCs), specific sampling and analytical methods are described for polynuclear aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), and polychlorinated dibenzo(p)dioxins/polychlorinated dibenzo(p)furans (PCDDs/PCDFs). Methods for total particulate matter (PM) and for PM of less than 10 micron aerodynamic diameter (PM₁₀) are also described. The inorganic compounds addressed in this section are heavy metals, including mercury, and soluble salts of cyanide.

EPA has prepared a compendium of sampling and analytical procedures for many toxic organic compounds.¹⁰ The "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" gives general guidance for sampling and analyzing of many compounds listed in this document; however, experience has shown that, in some instances, the methods need to be modified to obtain the highest quality data.

Sampling methods are described first, followed by a discussion of analytical methods. For each, a general overview is given, followed by a discussion of specific methods.

3.1 SAMPLING METHODS

3.1.1 Overview of Sampling Methods

A variety of sampling methods can be used to monitor for the types of compounds found around Superfund sites. The methods vary by sample type (i.e., volatile compounds, semi-volatile compounds, and particulate borne compounds). Each method has various advantages, disadvantages, and specific uses. The greatest number of available methods for any one type are for VOCs. Semi-volatile organic compounds (SVOCs) may exist in both the particulate and vapor phases, so appropriate sampling methods are limited to those that apply to both phases. The concentration of particulate-borne contaminants can be estimated from the data for total particulate matter (PM) loadings; however, these values are extremely conservative.

Sampling techniques may be divided into two broad classes, regardless of the analytes of interest - integrated sampling and grab sampling:

- Integrated Sampling -- methods that involve the collection of a sample over a fixed time period (e.g., 8-hours or 24-hours) and provide a single, integrated (i.e., time-averaged) value. Included in this classification are sorbent tube collection methods and most particulate matter and semi-volatile compound collection methods.
- Grab Sampling -- methods that involve collection of an instantaneous whole air sample or real-time analysis.

Each of these classes of methods has certain advantages and disadvantages, depending on the monitoring objectives, the required detection levels, and the duration of the monitoring program. These two classes of sampling methods are briefly described below.

Integrated Sampling

Integrated sampling methods are among the most commonly used procedures for sampling air, since most contaminants are present in ambient air at relatively low levels, and some type of sample concentration is therefore necessary to meet detection limit criteria. Appropriate integrated sampling methods exist for collecting VOCs, SVOCs, and PM.

Integrated sampling methods can be useful for determining time-integrated pollutant concentrations, such as 8-hour OSHA PELs or other regulatory standards. When performing any integrated sampling, the sampling period must be long enough to collect sufficient analyte to achieve the desired detection limits. In general, the longer the sampling duration, the more analyte is trapped and the lower the detection limit. Therefore, integrated sampling methods may not be adequate for evaluating compliance with short-term (e.g., 15 minute, 1 hour) action levels. For example, even a high-volume particulate sampler generally will not be capable of collecting enough sample to determine compliance with short-term action limits for heavy metals. Similarly, most sorbent collection methods for VOCs will require sampling periods of several hours or more to achieve typical required detection limits.

The objectives of ambient air monitoring (AAM) at Superfund sites are different than those for compliance or PSD monitoring. As discussed in Section 1.3, the primary goal(s) usually is to evaluate the potential human health risk to on-site workers or the surrounding populace. For some analytes such as dioxins, a sampling period of 48 or even 72 hours may be needed to obtain adequate sample for the desired detection limits. Of course, the exact duration of sampling is not as important as achieving a compound detection limit capable of meeting the preset action limits.

One drawback of time-integrated sampling is the lack of immediate feedback, compared with the data that provided by real-time or automated continuous monitoring methods. Integrated sampling methods typically do not give site decision makers timely data so that they can determine worker and community exposure to pollutants or the need for implementing emission controls.

Grab Sampling

Grab sampling consists of collecting a single point-in-time sample. Among these methods are the collection of whole air samples in SUMMA® polished stainless steel canisters or Tedlar® bags and the collection of samples using colorimetric gas detection tubes, such as those made by Drager or Gastek Corporations. Samples are collected over a period of a few seconds to a few minutes. Real-time monitoring methods usually involve grab sampling.

Grab sampling is commonly used as a screening technique to identify contaminants that might be present in an area of interest and to determine the approximate concentrations of these contaminants. For example, grab samples may be collected during the SI using SUMMA® canisters and analyzed by GC or GC/MS to aid the development of a target analyte list for any long-term VOC monitoring.

Frequency of Data Updates

The categories of integrated sampling and grab sampling can be further subdivided according to the frequency with which the data values are updated (or the rapidity with which the data are reported): single value, real-time monitoring, and continuous or semi-continuous monitoring.

Single value methods involve the collection and analysis of a discrete sample. Included in this category are all methods that involve collecting the sample in a container or on a matrix and subsequently transporting the sample to an on-site or off-site laboratory for analysis.

Automatic continuous systems are methods that involve the semi-continuous, automated collection of samples followed by one or more detection methods. This approach usually is used as part of a fixed monitoring network to minimize the labor requirements

associated with sampling and analysis. The sampling and analytical methods tend to be similar to single value methods, except they are automated as far as possible.

The samples may be analyzed directly at the collection point, or the sample may be transported up to several hundred feet to an analytical device. In the latter case, a single analytical device may be used to analyze samples from multiple monitoring stations. The analyzer periodically cycles through the network. Automated analytical systems may involve gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), mass spectrometry/mass spectrometry (MS/MS), infra-red spectrometry (IR), Fourier Transform Infrared (FTIR) spectrometry, or ultra-violet, differential absorbance spectrometry (UV-DOAS).

Real-time monitoring refers to methods that provide (nearly) instantaneous values, so multiple measurements can be made over a period of minutes. A wide range of methods fall under this classification, including such widely used portable instruments as the FoxBoro Organic Vapor Analyzer (OVA) or the HNu Photoionization Detector (PID), and similar instruments. In addition, specialty gas monitors that measure specific compounds or compound classes also fit into this category. These usually are process-type monitors designed to continuously monitor for ppm or percent levels of specific analytes. Another real-time (or near real-time) monitoring approach is optical remote sensing using spectroscopic methods such as FTIR and UV-DOAS.

Real-time analyzers usually are used to monitor at or near areas of high emissions such as areas of active remediation, to give site decision makers timely information. Most of the portable real-time monitors react with entire classes of compounds and tend to not be specific for a given compound. For example, PIDs are very sensitive to aromatic hydrocarbons but significantly less sensitive to aliphatic hydrocarbons. Furthermore, they cannot differentiate between benzene and toluene if both compounds are present. In many instances, an action level will be set, based on a total response, as if the instrument response were due solely to benzene and not other aromatic compounds.

A guide has recently been published for selecting real-time ambient air monitoring instruments for use at Superfund sites.¹¹ Users should consult that publication for more detailed information about specific models of real-time instruments.

Method Selection

Information is given in the following subsections about specific methods for VOCs, SVOCs, etc. that will aid in the selection of a specific sampling method once the target analytes and their classification are known. Organic compounds can be grouped as VOCs, SVOCs, and non-volatiles as shown in Table 3-1.

A number of toxic organic (TO) sampling methods exist for VOCs and SVOCs, as shown in Figure 3-1. The detection limits and applicable range for these methods are given in Figure 3-2. Similar information for a wide range of sampling and analytical methods is given in Figure 3-3.

3.1.2 Sampling Methods for Volatile Organic Compounds (VOCs)

VOCs are among the most common type of contaminant of concern at Superfund sites. Three classes of VOCs generally are a concern at Superfund sites, and the specific class of VOCs present will dictate the appropriate sampling and analytical protocols. The VOC classes of most common interest are:

- Aromatic compounds such as benzene, toluene, ethylbenzene, and xylene(s) (BTEX);
- Halogenated hydrocarbons such as vinyl chloride, trichloroethylene, and 1,1,1-trichloroethylene; and
- Oxygenated compounds such as formaldehyde or acetone.

Table 3-1.

Characterization of Organic Compounds by Vapor Pressure

Vapor Pressure (kPa)	Vapor Pressures of Some Volatile Organic Compounds at 25°C			
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Aromatic
VOC				
100	Methyl chloride Vinyl chloride	Dimethylamine Phosgene Ethylene oxide	Butane	
10	Dichloromethane Chloroform Carbon Tetrachloride	Acrolein Acetone Acrylonitrile Methanol	Pentane Hexane	Benzene
1	Tetrachloroethylene	1,4-Dioxane	Heptane Octane	Toluene Xylenes
10 ⁻¹	Monochlorotoluenes	Methylmethacrylate Benzaldehyde	Decane	Styrene Mesitylenes
SVOC				
10 ⁻²	p-Dichlorobenzene Hexachlorobutadiene	Toluene-2,4-diisocyanate Aniline Toxaphene Phenol	Dodecane	
10 ⁻³	Tetrachlorobenzene 2,4,5-Trichlorophenol Dichlorvos	Nicotine p-Chloroaniline p-Cresol	Tetradecane	Naphthalene Biphenyl
10 ⁻⁴	Pentachlorobenzene	p-Nitroaniline	Hexadecane	Anthracene
10 ⁻⁵	Aroclor 1242 Pentachlorophenol Heptachlor	Diazinon Dibutyl-phthalate	Octadecane	Phenanthrene
10 ⁻⁶	Hexachlorobenzene Chlordane Aroclor 1260	Parathion Carbaryl Stearic Acid	Eicosane	
10 ⁻⁷	Dieldrin 2,3,7,8-Tetrachloro-dibenzo-p-dioxin	Anthraquinone	Hexacosane	Fluoranthene
Non-Volatile				
10 ⁻⁸	DDT	Di(2-ethylhexyl)-phthalate		Benz(a)anthracene

NOTE: 1 mmHg = 0.133 kPa

1 atm = 101 kPa

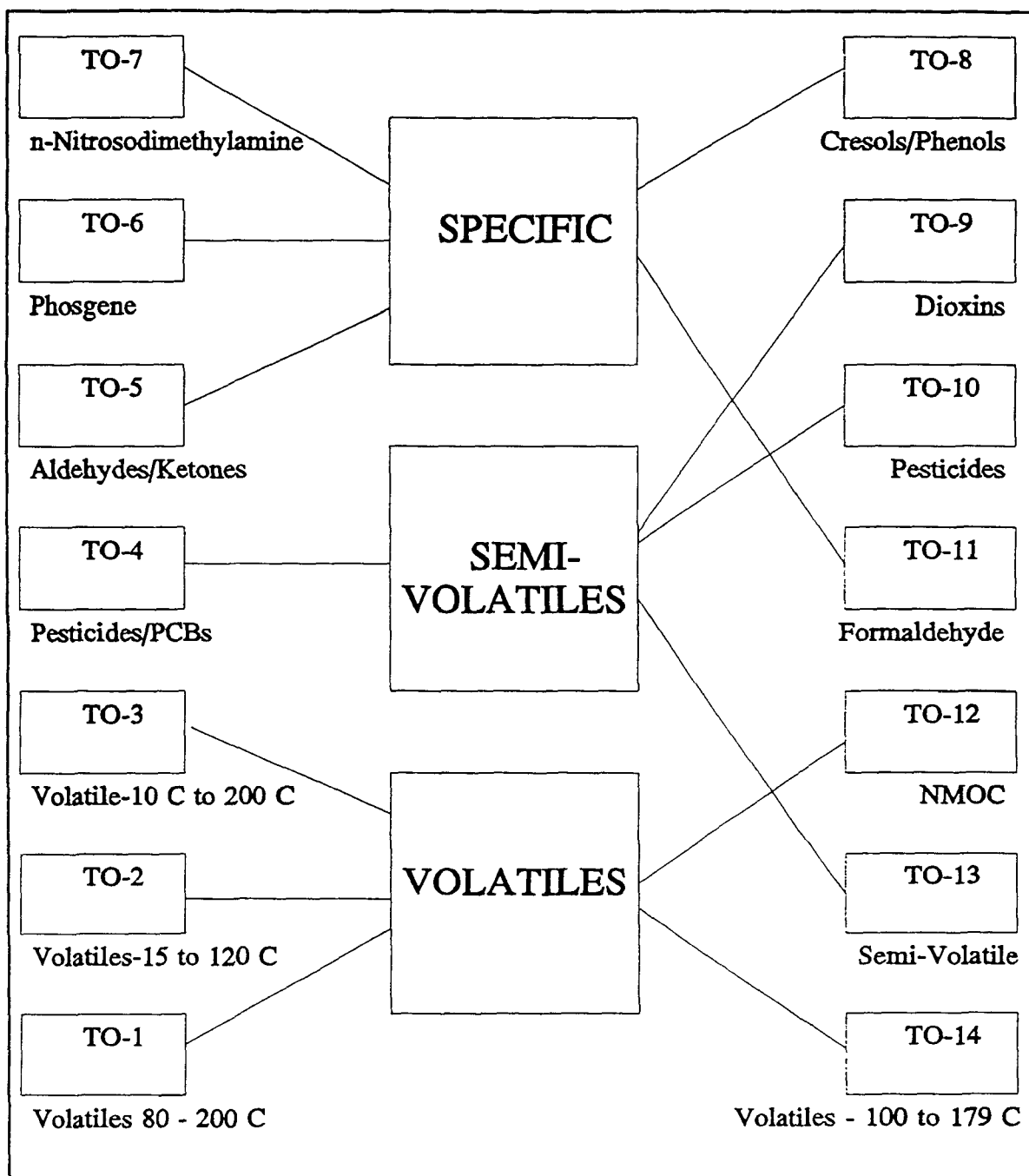


Figure 3-1. Compendium of EPA Toxic Organic Methods (Temperature ranges refer to boiling points).

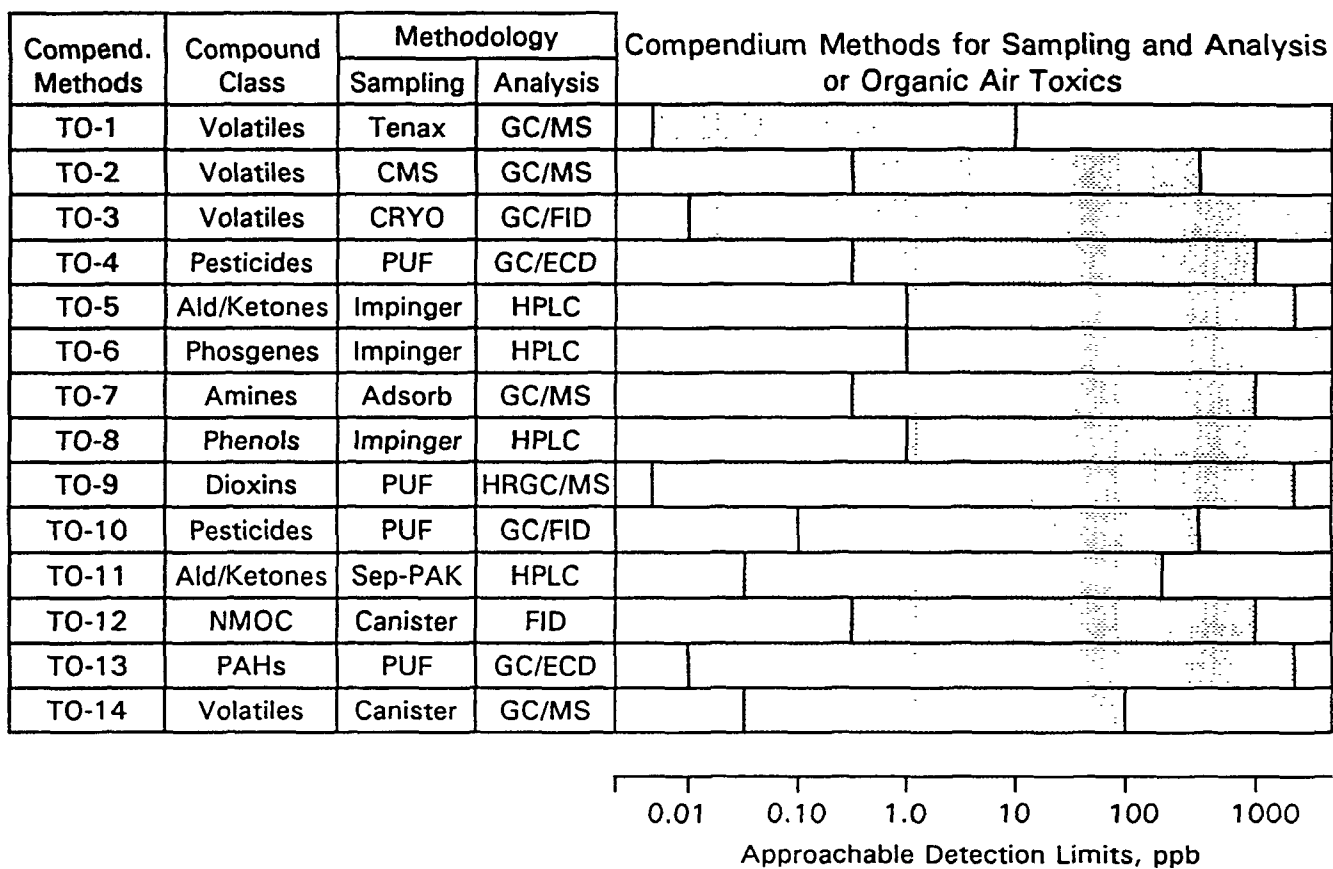


Figure 3-2. Detection Limit and Applicable Range for TO Methods.

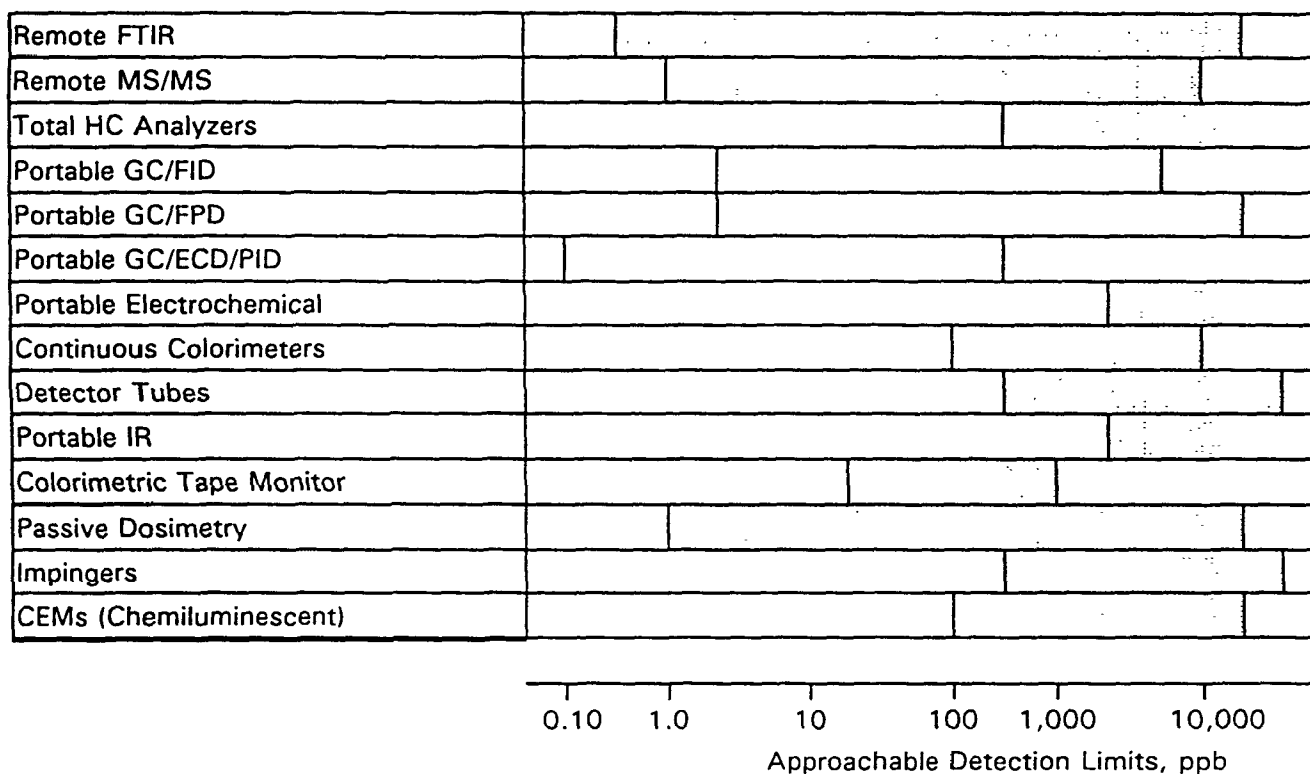


Figure 3-3. Detection Limit and Applicable Range for Various Sampling and Analytical Methods.

The sampling and analytical methods chosen will depend on the number and type of compounds of interest and on the required minimum detection limits. Sampling methods for a number of commonly encountered VOCs are described in Table 3-2. For guidance on compounds or compound types not found in Table 3-1, consult "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air"¹⁰ or the NIOSH Methods Manual.¹²

3.1.2.1 Whole Air Sample Collection

Whole air samples can be collected in glass or steel sample bombs, Tedlar bags, or SUMMA[®] polished stainless steel canisters. The collection and analysis of whole air samples has several advantages over integrated samples collected using sorbent methods. Since the sample is collected whole instead of being adsorbed onto a medium, concerns about collection efficiency or breakthrough are eliminated, as are concerns about desorption efficiency. In addition, there are fewer problems with artifact formation, which can be a problem with sorbent methods. The various whole air sample collection methods are discussed in the following subsection.

SUMMA[®] Polished Stainless Steel Canisters

SUMMA[®] polished stainless steel canisters are specially passivated containers used to collect whole air samples. The interior surfaces of the canisters are coated with pure nickel-chromium oxide (SUMMA[®] polishing process), which renders them inert. Because the entire container is metallic, no photochemical reactions occur after sample collection, and permeation of the compounds in or out of the container does not occur. The samples can leak, however, if the inlet lines, valves, and seals are defective or not used properly. The sample atmosphere can be kept at negative pressure to minimize the effects of water vapor condensation and chemical reactions. Also, the canisters can be reused after a relatively simple cleaning procedure. This is the only suitable whole air collection method if samples must be stored for more than 24 hours before analysis.

Table 3-2.

Summary of VOC Sampling Methods

Compound Types	Sampling and Analytical Methods	Method Description
Aromatic Hydrocarbons		
Aromatic Hydrocarbons, including benzene, toluene, ethylbenzene, xylenes, and many substituted benzene compounds.	EPA Method TO-1	VOCs are trapped on Tenax cartridges. Suitable for nonpolar VOCs with boiling points between 80°-200°C.
	EPA Method TO-2	VOCs are trapped on a carbon molecular sieve cartridge. Suitable for nonpolar VOCs with boiling points between -15°-120°C.
	EPA Method TO-3	VOCs are trapped in a liquid argon or oxygen cooled trap directly interfaced to a GC. After a sufficient volume is collected on the trap, a multiport rotary valve is used to sweep the sample onto the instrument column. Suitable for highly volatile compounds with boiling points between -10°-200°C.
	EPA Method TO-14	VOCs (and some SVOCs) are collected in SUMMA® polished stainless steel canisters. Suitable for most polar and nonpolar VOCs and some SVOCs. The exact target list will depend on the analytical techniques used.
	NIOSH Method 1501	Aromatic hydrocarbons are collected on charcoal sorbent and analyzed by GC-FID. Applicable to BTEX and other similar compounds.
Halogenated Hydrocarbons		
Halogenated Hydrocarbons including Chloroform, Tetrachloroethylene, 1,1,1-Trichloroethane, Methylene Chloride, Trans-1,2-Dichloroethylene, Vinyl Chloride, 1,2-Dichloroethane, Chlorobenzene, 1,1-Dichloroethane, Carbon Tetrachloride, and Trichloroethylene	EPA Method TO-1	VOCs are trapped on Tenax cartridges. Suitable for nonpolar VOCs with boiling points between 80°-200°C. Method has very low retention volume for many of the lighter halogenated hydrocarbons such as 1,1,1-trichloroethane, chloroform, or carbon tetrachloride. This method may not be suitable for vinyl chloride.
	EPA Method TO-2	VOCs are trapped on a carbon molecular sieve cartridge. Suitable for nonpolar VOCs with boiling points between -15°-120°C. Best suited to lighter chlorinated compounds. This method exhibits poor recovery of carbon tetrachloride.
	EPA Method TO-3	VOCs are trapped in a liquid argon or oxygen cooled trap directly interfaced to a GC. After sufficient volume is collected on the trap, a multiport rotary valve is used to sweep the sample onto the instrument column. Suitable for highly volatile compounds with boiling points between -10°-120°C.
	EPA Method TO-14	VOCs (and some SVOCs) are collected in SUMMA® polished stainless steel canisters. Suitable to most polar and nonpolar VOCs and some SVOCs. The exact target list will depend on the analytical techniques used. Generally suitable for the largest target list of any of the TO methods.
Oxygenated Hydrocarbons		
Including acetone, formaldehyde, acetaldehyde, and acrolein.	EPA Method TO-5	Air is drawn through midjet impingers containing 2,4-dinitrophenylhydrazine (DNPH) in 2N HCl and isooctane. Aldehydes and ketones react to form DNPH derivatives, which are more stable than the original compounds. The use of midjet impingers and liquid solutions is cumbersome.
	EPA Method TO-11	Air is drawn through DNPH-coated silica gel tubes. Aldehydes and ketones react to form DNPH derivatives. Similar target compounds to Method TO-5 but sampling generally is easier.
	NIOSH Method 1614	Air is drawn through HBr-coated charcoal tubes. The ETO reacts with the HBr to form a more stable derivative. Samples are analyzed by GC-FID.
Ethylene Oxide		
Phenol and Cresols	EPA Method TO-8	Air is drawn through midjet impingers containing 0.1N NaOH. The samples are then analyzed by HPLC.

Most hydrocarbons and chlorinated hydrocarbons (including BTEX) are stable in SUMMA® canisters for periods of at least 30 days.^{13,14,15} The holding times for some of the light oxygenated compounds such as acetone or methanol, however, are not well documented, but are thought to be two weeks or more.

Samples can be collected in evacuated canisters in one of two ways: under positive pressure or negative pressure (subambient). In subambient pressure sampling, a mass flow controller or vacuum regulator is used to control the flow of sample into the evacuated canister. The difference in pressure between the canister and the ambient environment provides the driving force for collecting the sample. Sampling may continue until the canister is slightly below atmospheric pressure. It is best not to continue sampling until the pressure is equalized, since this makes it difficult to ascertain exactly when sampling ceased and if leakage has occurred. Also, the sample flow rate will typically drop off as the canister nears ambient pressure.

Vacuum regulators are designed to maintain a constant flow as long as the difference in vacuum between the source (in these cases, the canister) and the ambient environment is within a certain range. Vacuum flow regulators usually provide a constant flow until the vacuum inside the canister reaches approximately 8-10" Hg (approximately 5 psig) vacuum. At this point, the flow rate will decrease at an almost linear rate until the canister reaches ambient pressure. Once the flow rate begins to decrease, there is no longer true integrated sampling. A mass flow controller used with a subambient sampling system, on the other hand, can be used to within approximately 1" Hg (0.5 psig) with no change in the flow rate. Therefore, when using subambient (non-pumped) sampling systems, the sampling run should be stopped with 8-10" Hg remaining in the canister when using vacuum flow regulators for controlling the flow and with 1-2" Hg remaining in the canister when using mass flow to control the sampling systems.

The second collection method involves using a pump to fill the canister to above ambient pressure. With this system, canister leakage will not affect sample integrity to the same extent as for subambient systems, since any leakage will be of sample out of the

canister rather than of ambient air into the canister. When sampling with a pump in areas with high humidity, however, water may condense inside the canisters if they are pressurized above 5 psig. This can cause compounds to adsorb into the water droplets and also subsequently cause canister cleaning problems. Another potential drawback of a pump-based canister sampling system is that pumps are more difficult to keep clean because of the teflon or other porous materials typically contained in pump diaphragms or parts. In general, the less material and void volume between the sample inlet and the canister, the better the sample representativeness and integrity.

Glass Sampling Bombs

Glass sampling bombs are generally small (125-ml to 1000-ml) glass containers with a stopcock on each end. These are fairly inexpensive, easy to handle, and are relatively inert. They generally make good containers for grab sampling if the contents will be analyzed within 8 hours of sample collection. They are, however, quite prone to breakage and must be protected from light so photo-induced reactions won't occur. They also are not suitable for integrated sampling.

Stainless Steel Bombs

Stainless steel bombs are another option for collecting grab samples. They are identical to the canisters discussed above, but they are not SUMMA[®] passivated. Since these devices are not passivated, they are not as inert as the SUMMA[®] processed canisters and are therefore more prone to reactions (including corrosion of the interior surface). Stainless steel bombs are usually less than 1 liter in volume and have most of the same attributes as glass bombs, but they are not prone to breakage. They usually have valves on both ends and the sample can be introduced by using the vacuum of an evacuated bomb to pull in ambient air, or by using a pump to force air into the bomb. Samples should not be held for over 24 hours unless the stability of the compounds of interest in these containers has been documented. In general, these vessels should be considered only for grab sampling and on-site analysis.

Gas Sampling Bags

Gas sampling bags are used to collect and store air samples for short periods (less than 8 hours). The sampling bags are known by various trade names such as Tedlar®, Teflon®, Mylar®, and Saran®. These bags are relatively inert but can be prone to leakage or permeation of compounds into and out of the bag. The materials from which these bags are made are somewhat porous and therefore tend to adsorb organic compounds. Consequently, it is difficult to clean gas sampling bags to meet strict background (blank) standards. As a general rule, gas sampling bags are not suitable for collecting samples for the analysis of sub-ppm levels of ambient organic compounds.

3.1.2.2 Sorbent Collection Methods

Solid sorbents are a collection medium used to adsorb and hold VOCs, which are then desorbed from the medium using either thermal or chemical extraction before analysis. Sorbent media are able to concentrate organic analytes from an air stream, thus decreasing the detection limits (DLs) for those analytes over DLs for whole air collection methods used with direct injection analytical methods (whole air samples can be preconcentrated, as with EPA Method TO-14). Sorbent methods have certain general advantages and disadvantages that should be considered before a sampling and analytical method is selected for a given application. In addition, many different sorbents are available, and each has its own specific advantages and disadvantages.

Sorbent sampling techniques tend to be relatively cost effective. The medium itself is inexpensive, readily available from several manufacturers, and available for many specific compounds or compounds classes. Since sample volumes can be adjusted (to a certain extent) according to anticipated ambient levels of the target analyte(s), adequate detection limits for many compounds can be attained.

There is no "universal" sorbent; consequently, sorbent selection should be carefully tailored for the target analyte(s). If the target analyte list contains a variety of compound types, several different sorbents (e.g., multi-bed sorbent tubes) may be needed. Factors to consider when selecting a specific sorbent include sample interferences, ambient moisture (humidity), breakthrough characteristics of the compound(s), the desorption characteristics of the analyte with the particular sorbent, and sample stability.

There are two basic types of sorbent materials: those that adsorb the VOCs onto the sorbent medium and those that chemically react with the target analyte(s) to form a new compound. Chemically-reactive sorbents are typically used to collect compounds that are very unstable or reactive. For example, HBr-coated charcoal tubes can be used to collect ethylene oxide, and dinitrophenylhydrazine (DNPH)-coated silica gel can be used to collect aldehydes and ketones (EPA Method TO-13).

Although many types of sorbent materials are available for sampling VOCs, each sorbent type has certain limitations that must be considered. Many sorbents are affected by high ambient humidity. For these sorbents, moisture coats the sorbent material, effectively "blinding" the medium by filling the active sites with water instead of VOC. The other potential problem with sorbent tubes is breakthrough, as discussed above.

Many of the sorbent tube sampling methods were developed for industrial hygiene (IH) applications. The detection limits needed for work-place exposure estimates are generally orders of magnitude higher than those needed to determine long-term health effects, such as the 1 in 10^6 cancer risk. Problems that can be encountered when attempts are made to adapt IH methods to fence-line ambient monitoring; are:

- Moisture interference from longer sampling periods;
- Breakthrough due to longer sampling periods;
- Sample or compound degradation due to larger air volumes; and
- Insufficient sample detection limits.

All of these considerations need to be evaluated before selecting a sampling method. In some instances, the site investigators should perform a methods development program to determine whether a specific method is adaptable to a given application. The review and input of staff experienced in the sampling and analysis of VOCs is recommended as part of the method selection process.

3.1.2.3 Automated Fixed-Location Continuous Analyzers

The use of fixed-location continuous analyzers has increased in recent years. These instruments are capable of the near real-time analysis of a range of organic compounds, at detection limits in many cases equal to what can be achieved in the laboratory. A few of these techniques include a sample preconcentration system to increase analyte detection limits. A common preconcentration approach is the use of a sorbent with thermal desorption. Information about real-time instruments, including automated continuous analyzers, is summarized in Table 3-3.

These systems offer many advantages, particularly when site remediation is expected to last several years. The systems can be configured many different ways using detectors best suited for the given target analytes. The near real-time (each analysis taking approximately 30 minutes) data collection allows the investigator to make decisions whether ambient levels of pollutants are exceeding action levels and about what action to take, instead of having to rely on less accurate methods (such as OVAs) to determine whether remediation should continue or be curtailed. Also, compliance with the action level(s) for a given compound is known immediately instead of several days after the fact.

The main disadvantages of these methods are high detection limits, expense, maintenance, and siting. Original equipment costs (including shelters) can run as high as \$100,000 per site, depending on the sophistication of the instruments purchased and siting concerns. Also, a network of this type will require highly trained and knowledgeable technicians to keep the equipment functioning properly and to ensure that data collected meet program objectives. Since these units need a clean, climate-controlled shelter, siting

Table 3-3.

Summary of Information for Selected Classes of Real-Time Instruments^a

Measurement System	Gases Measured	Concentration Range	Relative Accuracy (% full scale)	Typical Cost	Advantages	Limitations
Electrochemical	T, C, O ₂ , THC, H ₂ S, CO	ppm to 100% LEL	± 10%	\$1,500	Inexpensive Lightweight, portable Durable Responds to specific compounds	Detects specific compounds only Limited applications Subject to interferences Sensor lifetime <2 years
Total Hydrocarbon Flame Ionization Detector	THC, VOC, SV	0-100 ppm or 0-100%	± 1%	\$4,000- \$8,000	Responds to most hydrocarbons Wide dynamic range	Requires hydrogen supply Less tolerant of shock Response varies by compound
Photoionization Detector	VOC, SV	0.1-2000 ppm	± 1%	\$5,000	Hydrogen not needed Responds well to aromatic compounds Easy to use	Unresponsive to methane Poor response-chlorinated compounds Response varies by compound
Thermal Detector	THC, H ₂	0-100% LEL	± 2%	\$1,500	Easy to use Lightweight, portable Responds to most hydrocarbons Inexpensive	May be temperature sensitive Largely nonspecific
Solid State	THC, T, C	50-10,000 ppm 50-300 ppm	± 5%	\$2,000	Extremely portable Responds to specific compounds	Relatively inaccurate Limited applications
Colorimetric Solid	VOC, SV, THC, T, C	0-250 ppm	5-25%	\$400	Small, light, inexpensive Safe in all atmospheres Responds to specific compounds Simple to operate	Short-term, non-continuous sampling Temperature sensitive Limited shelf life Subject to interferences
Paper Tape	O ₂ , T, C	0-200 ppm	± 5%	\$5,000- \$10,000	Responds to specific compounds Long-term continuous sampling	Flow rate sensitive Limited reagent shelf life
Liquid	T, Formaldehyde	0-10 ppm	1%	\$6,000	Simple to operate Responds to specific compounds Long-term continuous sampling	Subject to interferences Flow rate sensitive Limited reagent shelf life
Spectrophotometric Nondispersive Infrared	VOC, SV, T, HC	0-10, 100, 1000, 2500, 3000 ppm	± 0.5% to ± 1%	\$7,500	Highly selective Broad measurement range Responds to hundreds of compounds	Subject to interferences May be temperature sensitive Shock & vibration sensitive
Optical Remote Systems	VOC, SV, THC, T, C	ppb to %	1 cm ⁻¹	>\$100,000	Multicomponent analysis Very low detection limits Emission rate measurements	High costs Requires well trained operators Data verification problems Often must be customized

Table 3-3. (Continued)

Measurement System	Gases Measured	Concentration Range	Relative Accuracy (% full scale)	Typical Cost	Advantages	Limitations
Gas Chromatograph	VOC, SV, THC, T, C	0.01-1000 ppm	± 0.5%	\$14,000	Good component identification Good quantitative ability Few interferences	Expensive Requires well trained operators Requires support gases Shock & vibration sensitive.
Gas Chromatograph/ Mass Spectrometer	VOC, SV, THC, T, C	10 ppb-1%	± 0.3%	> \$75,000	Excellent component characterization Few interferences	Very expensive Requires well trained operators Requires support gases Shock & vibration sensitive
Particulate Optical	TSP	0-100 mg/m ³	± 10%	\$8,000	Less operator time required Provides real-time data Data in digital format	Expensive Requires skilled operators
Radiometric	PM ₁₀	0-20 mg/m ³	± 7%	\$14,000	Less operator time required Provides real-time data Data in digital format	Expensive Requires skilled operators Requires shelter

Key:

C	= Combustibles	PM ₁₀	= Particles ≤ 10 microns diameter
cm ⁻¹	= Wave numbers	ppb	= Parts per billion
CO	= Carbon Monoxide	ppm	= Parts per million
HC	= Hydrocarbons	SV	= Semi-Volatile Organic Compounds
H ₂	= Hydrogen	T	= Toxics
H ₂ S	= Hydrogen Sulfide	THC	= Total Hydrocarbons
LEL	= Lower Explosive Limit	TSP	= Total Suspended Particulates
mg/m ³	= Milligrams per cubic meter	VOC	= Volatile Organic Compound
O ₂	= Oxygen	>	= Greater than

*All data given were supplied by vendors. Actual performance in the field for criteria such as relative accuracy may be significantly different than the values shown.

can pose problems. The shelters need electrical service (a minimum of 100 amps to support the heating and cooling equipment), level-protected sites, and telephone lines if data are to be retrieved electronically. Given the cost and logistical constraints, this sampling option is best suited for AAM studies expected to last over one year.

3.1.2.4 Portable Real-Time Analyzers

Portable real-time analyzers are generally used to provide screening or industrial hygiene applications. These analyzers are usually either the general-response type, i.e., they respond to general classes of compounds, or specific-response analyzers which only respond to a specific compound. Most real-time instruments (excluding particulate analyzers and fixed location instruments such as GC, GC/MS, or FTIR) can be separated into three broad categories according to their detection methodology:

- Electrochemical Systems;
- Total Hydrocarbon Systems; and
- Spectrophotometric Systems.

Information about portable real-time analyzers is included in Table 3-3.

A wide selection of electrochemical systems is available for measuring toxic gases. These systems are commonly used in industrial hygiene applications because of their small size, simple operation, and low cost. Electrochemical sensors are designed to be compound specific; they respond to only one compound (i.e., oxygen, carbon monoxide, hydrogen sulfide, hydrogen chloride, sulfur dioxide, etc.) rather than to a broad family of compounds.

Total hydrocarbon monitors are capable of detecting a wide range of hydrocarbons. The most widely-used total hydrocarbon systems are those that use flame ionization detectors (FID) and photoionization detectors (PID). Thermal detection monitors and solid-state detectors are also available. The most commonly used total hydrocarbon analyzers are the OVA, which uses an FID to detect hydrocarbons, and the HNu®, which uses a PID to detect hydrocarbons. Both of these analyzers report a total instrument

response rather than data for individual species. The PID analyzer is less sensitive to aliphatic hydrocarbons than the OVA, but is very sensitive to aromatic hydrocarbons, such as benzene; however, it cannot differentiate one compound from another.

Spectrophotometric analyzers encompass a broad range of widely-used analyzer systems that determine airborne pollutant concentrations by measuring their absorption of radiant energy. In most instrument applications, radiant energy from the ultraviolet, visible, or infrared regions of the electromagnetic spectrum is used. Spectrophotometric systems most applicable to Superfund air monitoring applications include Nondispersive infrared (NDIR) analyzers and Optical Remote Systems (see Section 3.1.2.6).

A more complete discussion of real-time monitoring instruments and their capabilities, along with a current list of the vendors, can be found in Reference 11.

3.1.2.5 Colorimetric Gas Detection Tubes

Colorimetric gas detection tubes produce a color change when exposed to the target compound. These tubes were originally designed for industrial hygiene applications; however, many are capable of measuring contaminants at ambient levels. This technique involves pulling an air sample through the detection tube with either a hand- or battery-operated pump. The tubes are calibrated based on a preset sample volume specific to each tube.

Colorimetric gas detection tubes offer the advantage of being small, portable, and inexpensive; in addition, they provide essentially instantaneous results. Gas detection tubes are also available for a wide array of compounds. Their main disadvantages include lack of specificity (interferences from other compounds that may be present), lack of adequate detection limits for some compounds, and inability to be used for automated sampling. Also, sampling techniques relying on gas detection tubes cannot be readily modified to meet special program demands.

Another type of colorimetric detection system are portable tape instruments. These instruments collect an air sample onto a chemically treated tape whose color changes if the specific compound is present. The color intensity is proportional to the concentration of the compound. These monitors are available for only a small number of compounds. They generally offer good analytical detection limits for those compounds in ambient air.

When considering a colorimetric gas detection tube or portable tape monitor, the vendor literature should be consulted to determine if the particular technique will be sensitive enough for its application, if it is free from interferences, and if it will meet the monitoring goals of the program. These techniques are generally best used for area or personnel monitoring, and are not typically appropriate for fence-line or perimeter monitoring or for evaluating community exposure downwind of the contaminated site.

3.1.2.6 Open Path Monitors

An emerging set of technologies for monitoring ambient air are open path monitors (OPMs).¹⁶ OPMs rely on the interaction of light with matter to yield qualitative and quantitative information about that matter. Since every molecule and atom exhibits a unique spectral pattern as a function of wavelength, the identification of each molecule or atom is possible if enough of the spectral pattern is obtained. Two types of OPM systems are commercially available for ambient air monitoring -- the Ultraviolet-Differential Optical Absorbance Spectrometer (UV-DOAS) and the Fourier Transform Infrared (FTIR) spectrometer. The UV-DOAS is normally configured as an open path monitor (OPM); the FTIR can be used as an OPM or a closed path monitor (CPM). A third OPM system, gas filter correlation (GFC), also is currently ready for use at Superfund sites.

The FTIR and UV-DOAS systems direct a beam of light through the ambient air (the sample), collect the transmitted light, and analyze the change in light intensity at selected wavelengths. The UV-DOAS is capable of path lengths on the order of 3 kilometers; the FTIR is capable of path lengths approaching 1 kilometer. Since the light beam is interacting with molecules along its entire beam path, its output is a path-weighted

concentration with units of concentration times distance such as ppm•meter. The ppm•m value can be converted to a direct concentration by dividing by the path length; however, this will only yield an accurate concentration measurement at a specific point along the path if the compound is homogeneously distributed along the path.

Open path monitors are useful when long perimeter distances need to be monitored, a fast time response is required, or continuous monitoring is required. The OPM output of ppm•m can be used with an inverted dispersion equation to calculate a source term, which is then used in a dispersion model to predict downwind concentrations.⁵ Information on the use of OPM data is given in Section 5.

The FTIR also can be used as a CPM by allowing the sample to flow through an optical cell. The light is multi-passed through the cell; path lengths of 400 meters for cells 3 meters in length are achievable.¹⁷ By design, the CPM is a point sampler. It retains the advantage of fast time response and continuous monitoring but loses the wide area monitoring capabilities. The use of CPM systems versus OPM systems is compared in Table 3-4.

OPM systems are capable of detecting a wide range of compounds as shown in Table 3-5; the ability of canister methods (TO-14) to detect these same compounds is also shown for comparison. Detection limit information for OPM systems is shown in Table 3-6.

3.1.3 Semi-Volatile Compound Sampling Techniques

Semi-volatile compounds (SVOCs) include polynuclear aromatic compounds (PAHs), their halogenated derivatives such as PCBs, organopesticides, and polychlorinated dibenzo(p)dioxins and furans. Depending on the number of fused carbon rings and the vapor pressure of the compound, these compounds will exist in both vapor phase and particulate-bound forms. Therefore, a collection system capable of collecting both phases is needed to collect representative samples. Table 3-7 summarizes the sampling methods used to collect the SVOCs normally encountered at Superfund sites.

Table 3-4.

Comparison of Conventional Point Monitoring and Open Path Monitors

	CPM	OPM
Detection Limits	Lower detection limits than OPMs; usually below the long-term action levels.	Higher detection limits than CPMs on most path lengths; may be above some long-term action levels.
Data Turn Around	For speciated data, at least 1-hour, but generally 24-48 hours; may not be able to warn if short-term action levels are exceeded.	Speciated data for tens of compounds available in minutes. Can warn of short-term health exceedances.
Dispersion Model Inputs	Must be extrapolated from a line of point samplers.	Direct output in one or two dimensions.
Unknowns	More accurately identifies the presence of compounds near the detection limit; accuracy doesn't necessarily improve as concentrations increase.	Less accurate at lowest concentrations observable, but gets better as concentration increases over reasonable range. Easier to identify unknowns at reasonable concentrations.
Guidance	Well documented and accepted.	Little documentation; still not well understood.
Site Layout	Sensitive to areas where sampler can not be placed on the ground; insensitive to hilly or broken site terrain.	Sensitive to line-of-sight obstruction; insensitive to recessed obstacles such as lagoons and pits.

CPM = Conventional Point Monitor

Table 3-5.

Methods for Monitoring Specific Compounds

Compounds	Canister	UV-DOAS	FTIR	GFC
ALKANES				
Ethane	X		X	X
Propane	X		X	X
n-Butane	X		X	X
n-Hexane	X		a	a
Isopentane	X		a	a
Isooctane	X		a	a
Cyclopentane	X		X	X
ALKENES				
Ethene	X		X	X
Propene	X		X	X
1-Butene	X		X	X
1-Hexene	X		X	X
Trans-2-butene	X		X	X
1,3-Butadiene	X		X	X
Isoprene	X		X	X
ALKYNES				
Acetylene	X		X	X
AROMATICS				
Benzene	X	X	X	X
Toluene	X	X	X	X
Ethyl benzene	X	X	X	X
o-Xylene	X	X	X	X
p-Xylene	X	X	X	X
m-Xylene	X	X	X	X
1,3,5-Trimethyl benzene	X	X	X	X
HALOGENATED				
Trichloroethylene	X		X	X
Chloroform	X		X	X
Tetrachloroethylene	X		X	X
1,1,1-Trichloroethane	X		X	X
Methylene chloride	X		X	X
t-1,2-Dichloroethane	X		X	X
Vinyl chloride	X		X	X
1,2-Dichloroethane	X		X	X
Chlorobenzene	X		X	X
1,1-Dichloroethane	X		X	X
Carbon Tetrachloride	X		X	X
PCB's		b	b	b

Table 3-5. (Continued)

Compounds	Canister	UV-DOAS	FTIR	GFC
METALS				
Arsenic				
Cadmium				
Chromium				
Copper				
Lead				
Mercury		X		
Zinc				
OXYGENATES				
Methanol	c		X	X
Ethanol	c		X	X
n-Propyl alcohol	c		X	X
Dimethyl ether	c		X	X
Methyl t-butyl ether	c		X	X
Acetone	c		X	X
Formaldehyde	c	X	X	X
Acetaldehyde	c		X	X
OTHERS				
Hydrogen chloride			X	X
Hydrogen fluoride			X	X
Hydrogen cyanide			X	X
Chlorine		X		
Bromine		X		
Fluorine		X		
Carbon dioxide			X	X
CRITERIA POLLUTANTS				
Ozone		X	X	X
Nitrogen dioxide		X	X	X
Sulfur dioxide		X	X	X
Carbon monoxide			X	X

X = A compound is detectable by this method.

a = These compounds are generally reported as part of the hydrocarbon continuum and not as individual compounds.

b = These techniques have the potential to measure this compound but no detection limit information is available.

c = "Polar" compounds, specifically oxygenates, may not be measured accurately by canisters.

UVDOAS = Ultraviolet-Differential Optical Absorbance Spectrometer

FTIR = Fourier Transform Infrared Spectrometer

GFC = Gas Filter Correlation Spectrometer

Table 3-6.

Detection Limits for OPMs

Compound	FTIR ppm*m	GFG ppm*m	UV-DOAS ppm*m
Trichloroethylene	2.5	NA	ND
Chloroform	3.0	36*	ND
Tetrachloroethylene	0.7	NA	ND
1,1,1-Trichloroethane	2-9*	NA	ND
Methylene chloride	30	NA	ND
t-1,2-dichloroethylene	2-9*	NA	ND
Vinyl chloride	2*-24	42*	ND
1,2-dichloroethane	72	NA	ND
Chlorobenzene	10.6	NA	NA
1,1-dichloroethane	2-9*	20*	ND
Carbon Tetrachloride	2.0	NA	ND
PCBs	a	a	a
Benzene	26	60*	0.75
Toluene	24	60*	0.75
m-Xylene	10	60*	0.75
o-Xylene	15	60*	3.00
p-Xylene	16	60*	0.75
Ethylbenzene	50	60*	1.50*
Phenol	a	a	0.75*
Cyanides	d	d	d
Arsenic Compound	d	d	d
Cadmium Compound	d	d	d
Chromium Compound	d	d	d
Copper Compound	d	d	d
Lead Compound	d	d	d
Mercury Compound	d	d	0.0005 ^c
Zinc Compound	d	d	d

a = potential to detect these compounds

b = compound specific

c = for atomic mercury

d = potential to detect certain compounds

* = provided by vendor

ND = Not detectable

NA = Not available

SOURCE: Reference 5

Table 3-7.

Summary of SVOC Sampling Methods

Compound Types	Sampling and Analytical Methods	Method Description
Polychlorinated Biphenyls and Organopesticides	EPA Method TO-4	PCBs and Organopesticides are collected with a high-volume sampler (200 L/min or higher). The sample is collected on a quartz fiber filter (or equivalent) and polyurethane foam (PUF) plugs. A solid sorbent, such as Florisil, in addition to the PUF should also be used, depending on the molecular weight of the target compounds.
Polychlorinated Dibenzo(p)dioxins and Polychlorinated Dibenzo(p)furans (PCDDs/PCDFs)	EPA Method TO-9	PCDDs/PCDFs are collected using a high volume sampler (200 lpm or better). The sample is collected on a quartz fiber filter (or equivalent) and polyurethane foam (PUF) plugs. Sample volumes of between 800-1200 m ³ should be collected, depending on the analytical technique used.
Organochlorine Pesticides	EPA Method TO-10	A low-volume sampler (1-5 L/min) is used along with PUF plugs to collect the organochlorine pesticides. The low volume helps prevent breakthrough; however, the use of an additional sorbent, such as Florisil, is recommended.
Polynuclear Aromatic Hydrocarbons (PAHs or PNAs)	EPA Method TO-13	A high-volume sampler, along with a quartz fiber filter (or equivalent) and XAD-2 resin, is used to collect the samples. PUF and XAD-2 resin can also be used.

Sampling systems for SVOCs must employ a quartz fiber (or other low background) filter followed by a suitable sorbent media. Also, these systems generally require large air volumes (e.g., the use of a high-volume air sampler) to achieve the necessary detection limits for evaluating health risk or action levels for SVOCs.

Even though these samples are collected on combined filter and sorbent media, it cannot be assumed that separate analyses of the two substrates will yield the relative particulate-borne and vapor-phase constituent concentrations. Some SVOCs will be transferred from the particulate phase to the vapor phase because of the vacuum applied during the sampling process. The phase distribution depends on the temperature and the degree of volatility of the individual compound. Techniques for phase distribution analysis are still being developed. Most of the phase distribution techniques require the use of low-volume sampling techniques and therefore are not appropriate for many compounds that have low health effects levels.

Polychlorinated Biphenyls (PCBs)

PCBs usually are collected using a high-volume PS-1 sampler manufactured by General Metal Works, Village of Cleves, Ohio. Substrates consisting of a quartz fiber filter (or similar low background filter) with a solid sorbent consisting of layers of polyurethane foam (PUF) between a layer of Florisil® resin. Foam plugs alone can be used; however, when using PUF plugs alone, the collection efficiency of mono- and di-chlorinated congeners may decrease.

Sampling duration should be approximately 24 hours, or 200 cubic meters (m^3). Sample volumes significantly less than 200 m^3 may result in diminished detection limits, while sample air volumes in excess of 275 m^3 may result in analyte breakthrough. These sample volumes will generally be adequate for any Superfund site containing PCB-contaminated soils. If the known contamination levels are extremely high, lower sample volumes and/or shorter sampling durations may be used, however, it is probably best to start

with the sampling times and volumes outlined and adjust them accordingly as data becomes available.

A NIOSH method using sorbent tubes for determining PCB concentrations also exists. This method is similar to the high-volume methods described above in terms of sorbent media type and analytical method, but it uses small sorbent tubes and low volumes. This technique was developed to monitor workplace exposure and consequently has detection limits several orders of magnitude higher than those needed to determine action levels for community exposure. The techniques may be appropriate for monitoring worker exposure during remediation, but it should not be used for fence-line monitoring or to determine compliance with health risk action levels.

Polychlorinated Dibenzo(p)dioxins and Polychlorinated Dibenzo(p)furans (PCDDs/PCDFs)

Polychlorinated dibenzo(p)dioxins and polychlorinated dibenzo(p)furans (PCDDs/PCDFs) may be found at Superfund sites either due to their presence in soil from contamination by organopesticides or their production during the on-site incineration of soil or waste containing high levels of chlorinated compounds (such as chlorinated solvents).

PCDDs/PCDFs are toxic to varying degrees, depending on the number of chlorine molecules and the position of those molecules. Generally, only the fifteen 2,3,7,8-substituted isomers of PCDDs/PCDFs are a major health risk concern; 2,3,7,8-tetrachloro-dibenzo(p)dioxin (TCDD) is the greatest risk. Although the octa-chlorinated dioxins and furans are ubiquitous in the environment, they pose little health risk and therefore are seldom quantitated.

Action levels for 2,3,7,8-TCDD may be on the order of 3.0 pg/m³ to 5.5 pg/m³.¹⁸ Action levels are not normally used for the other 2,3,7,8-substituted isomers. To obtain such low detection levels, very large air sample volumes must be sampled (800-1200 m³). Samples should be collected on quartz fiber filters (or equivalent) with a PUF plug solid sorbent using a PS-1 high-volume air sampler. Sample collection duration will be 48-72

hours, depending on the analytical technique used to analyze the samples. Sample breakthrough with PCDDs/PCDFs is not a problem; however, it is important that surrogate compounds be added to each PUF plug before sampling to determine sampling and analytical recoveries. The air volume needed will depend somewhat on the analytical technique used to analyze the samples; the lower value (800 m³) is needed for high resolution gas chromatography/mass spectroscopy (GC/MS), and larger volumes are required for medium or low resolution GC/MS.

Organochlorine Pesticides

Organochlorine pesticides can be collected using a low-volume sampling technique, adsorbing the pesticides on to polyurethane foam (EPA Method TO-10), or they can be collected using a high-volume technique. Care must be taken when using high volume sampling techniques because many of these compounds have low breakthrough volumes with PUF sorbent media. An additional sorbent medium, such as Florisil® resin, should be used in addition to the PUF plugs. When using a high-volume approach, adequate surrogates should be added to help determine the potential for breakthrough.

The advantage of high-volume sampling is the ability to concentrate more ambient air and consequently lower the detection limits. Using the PUF along with Florisil® resin allows for the simultaneous collection of both PCBs and pesticides, with the Florisil resin helping to prevent breakthrough of the lighter molecular weight pesticides.

Polynuclear Aromatic Hydrocarbons (PAHs)

Polynuclear aromatic hydrocarbons (PAHs or PNAs), can be encountered at many sites, especially old "Town Gas" sites. PAH compounds range from three to six aromatic rings and will exist in both the vapor and particulate-borne phases. The percentage of the compound found in each form generally depends on the molecular weight of the compound (i.e., the lower the molecular weight the greater the percentage of compound found in the vapor phase).

Like other semi-volatile compounds, PAHs also must be collected with both a particulate filter and back-up sorbent media. Several sorbents have been used to collect the PAHs, including Tenax GC, XAD-2, and PUF. All these compounds have been found to have a high collection efficiency for benzo(a)pyrene (B[a]P). EPA Method TO-13 specifies the use of either XAD-2 resin or PUF. Other variants include XAD-2 resin sandwiched between two one-inch PUF plugs, or XAD-2 resin supported by a one-inch PUF plug. For the heavier PAHs, any of these techniques should prove satisfactory; however, if lower molecular weight compounds, such as naphthalene, acenaphthylene, or acenaphthene are to be quantitated, XAD-2 resin without any PUF should be used. This is due to high background levels in the PUF material. The XAD-2 resin also has a high background level of naphthalene; however, typical ambient levels should be well above the background level if careful cleaning is performed.

As with most of the semi-volatile compounds, samples usually are collected using PS-1 high-volume samplers. Other low- and medium-volume samplers are also acceptable; however, the lower the total sample volume, the worse the analytical detection limits. In some cases, such as when reliable electrical power is not available, battery-operated, low-volume samplers may be necessary. Sampling periods may need to be extended if low-volume samplers are used.

A NIOSH method exists that uses filter and sorbent tubes for determining PAH concentrations. This method is similar to the high-volume method described above in sorbent media type and analytical method, but it uses small sorbent tubes and low volumes. The technique was developed to monitor workplace exposure; consequently, the detection limits are several orders of magnitude higher than those needed to determine action levels for community exposure. The technique may be appropriate for monitoring worker exposure during remediation but it should not be used for fence line monitoring or determine compliance with health risk action levels.

3.1.4 Particulate Matter

Solid or liquid particulates (aerosols) can be released from Superfund sites into the ambient air. These can include contaminated and noncontaminated soil particles, heavy metal particulates, pesticide dusts, and droplets of organic or inorganic or organic liquids. Particulate matter (PM) is collected to determine the total or size-fractionated particulate matter concentrations, heavy metals concentrations, and/or particulate-borne aerosols/organic compound concentrations in the ambient environment surrounding a site. Table 3-8 summarizes the advantages and disadvantages of certain particulate sampling techniques.

Several different sampling devices can be used to collect the samples including real-time analyzers, low- to high-volume particulate samplers, and sampling systems that only collect a certain size fraction of the particulate matter. Manual collection methods are by far the most commonly used for measuring both total suspended particulate (TSP) matter¹⁹ and particulate matter with an aerodynamic diameter of less than 10 microns (PM_{10}).²⁰ Both methods require the subsequent analysis of collection filters, a process that can take, at the very least, 24 hours.

Two types of high-volume samplers are commonly used to collect particulate matter. The first collects all airborne particulate matter and is referred to as a total suspended particulate (TSP) sampler, while the second collects only particulate matter with an aerodynamic diameter of less than 10 microns (PM_{10}). The PM_{10} particulate matter is important from a health risk perspective, since this size fraction can enter the human respiratory system because it is too small to be filtered out by the body's defense mechanisms. At most sites, PM_{10} will be measured because the results from this analysis can be directly correlated with potential health effects. If environmental impacts being evaluated, TSP samplers may be more appropriate.

Table 3-8.

Summary of Inorganic Compound Sampling Methods

Compound Types	Advantages	Disadvantages
Total Suspended Particulate (TSP) Sampling	Reference Method (40 CFR, Part 50, Appendix B). High-volume method allows analysis of filter for metals. Simple to operate.	Total particulate results may not be able to be used to determine the health effects of respirable particulate matter. Requires 110V, 20-amp electrical service.
Respirable Particulate Matter (PM ₁₀)	Reference Method (40 CFR, Part 50, Appendix J). High-volume method allows analysis of the filter for metals. Capable of collecting only respirable fraction of particulate matter (can be used for health risk assessment). Simple to operate.	Requires 110V, 20-amp electrical service. The sampler is large and bulky, and is not easily moved.
Dichotomous Sampler	Small, easy to handle. Capable of collecting size-fractionated particulate matter. Fairly low power requirements; could be adapted for remote use.	Fairly complicated to operate. Small sample volume, which makes chemical analysis of collected particulate matter difficult.
Beta Gauge Particulate Samplers	Real-time data; can be used for making immediate decisions on continuing or curtailing remediation efforts.	Cannot be used to differentiate or quantitate heavy metals and other particulate matter of concern

Direct reading instruments able to continuously monitor and display ambient air particulate counts have been available for several years and are increasing in use. They fall into two classes: optical devices and radiometric devices.

Optical-based particulate monitors include Transmissometers and Light Scattering devices. A transmissometer consists of a light source and a detector. By comparing the obstruction of a light beam by particulate matter in the sample gas to an unobstructed light path. These types of monitors are also used for in-situ applications, such as across a stack. Radiometric monitors measure particulate matter by a radiation attenuation technique; low-energy beta radiation is normally used. In the typical beta-gauge, a filter tape is slowly moved past a radioactive beta source, and the sample is drawn into the sample inlet of the instrument, where it passes through a tape filter mechanism. The radiometric attenuation of the filter is then measured before collection in the clean state and after collection in the dirty state.

Automated particulate monitors (of either type described above) are able to provide real or near-real time data of ambient air particulate concentrations. They are particularly valuable, therefore, in emergency removal applications, where frequent updates are required. Automated particulate monitors are more expensive than more conventional particulate sampling techniques and, because of their increased complexity, require greater technical skills by the operators responsible for maintaining them. Also, they must be installed in an environmentally controlled shelter, making them less amenable to small or short-term monitoring programs. No information about heavy metal concentrations or other constituents can be discerned from these monitors.

At many sites where the pollutant of interest is particulate borne (e.g., heavy metals), portable analyzers can only be used to estimate the potential exposure from the pollutant by using the particulate value to extrapolate a heavy metal concentration. The action limits set using these analyzers are usually quite conservative and are generally based on historical data from high-volume sampling techniques. Portable real-time PM analyzers are available with detection limits of $1 \mu\text{g}/\text{m}^3$.¹¹

3.1.5 Inorganic Compound Collection Methods

Heavy metals, including lead, arsenic, chromium, cadmium, nickel, and zinc, are a concern at many Superfund Sites. Mercury and such inorganic compounds such as cyanide are also encountered frequently. These elements may have vastly differing effects on human health, depending on the form or compound in which the element exists. An example is the difference between hexavalent chrome (chrome (VI)) and trivalent chrome (chrome (III)).

Methods for determining the different forms or valence states of an element or compound can be labor and time intensive in relation to determining the existence of the base compound. In many instances, an action level will be based on the concentration of the base compound (e.g., total chrome) as if it were all in the more toxic form (i.e., hexavalent chrome). This may hamper remediation efforts if such efforts are curtailed when a "true" health concern does not actually exist. In this instance, performing the more difficult and expensive analysis could remove some undue restraints from the remediation effort. Various methods for collecting the inorganic compounds commonly found at Superfund sites are discussed below.

High-Volume Sampling For Heavy Metals

As the name implies, high-volume collection methods collect large volumes of air. Most metal samples are collected on either quartz or glass fiber filter. While either of these filters can be used, experience has shown that quartz fiber filters provide lower background levels of compounds of interest and less chance of interferences. Since heavy metals are associated with particulate matter in the environment, a decision as to what particulate fraction to collect must be made.

There are two basic types of high volume samplers -- those that filter out all particulate matter in the air sample (TSP) and those that collect a certain size fraction, normally 10 microns and less (PM₁₀). Particles with an aerodynamic diameter of more than 10 microns aren't generally able to enter the human body because they are filtered out by the

body's defense mechanism. Particles smaller than 10 microns are able to enter the body and therefore pose a greater risk to human health. If a health risk action level based on respiratory action is being applied, PM₁₀ particulate matter should be collected. TSP samplers are appropriate where the potential for land deposition and bio-accumulation is of concern.

Medium- and Low-Volume Sampling

Medium- and low-volume particulate sample collection methods are those that collect less than 10 cubic feet-per-minute; some samplers designed to collect only a few liters-per-minute. Samplers included in this class include the Dichotomous sampler, the Battelle-Columbus medium-volume air sampler, and other portable particulate samplers.

These samplers are generally used for specialty applications (i.e., the Dichotomous sampler is used to size fractionate ambient particulate matter) or where large masses of particulate matter are not needed for chemical speciation. Also, there are low-volume solar or battery operated particulate samplers for use in areas where electrical service is not available. As a general rule, if electrical service is available, high-volume methods are generally preferable to low-volume methods when the particulate matter needs to be analyzed.

Mercury

Almost all metals can be collected using a high-volume sampling technique. The one notable exception is mercury. Mercury can exist in several forms, including vapor-phase elemental mercury, which is the most common form in ambient air. Because of the volatility of mercury, high-volume filtration techniques are not appropriate for sampling mercury. From a health effects perspective, the elemental and methylmercury forms are the most serious. Methylmercury forms when mercury is deposited in freshwater lakes and is transformed into methylmercury at the water sediment interface. Therefore, methylmercury should not be of concern at most Superfund sites. Elemental mercury will typically be the

primary form. The best methods for collecting mercury involve amalgamating the mercury with gold. Several researchers, including Gary Glass with the U.S. EPA in Duluth, Minnesota,²⁰ have used the Jerome mercury analyzer with good results. This analyzer can be used to determine real-time mercury concentrations and, by using gold foil dosimeters, can be used to measure time-integrated samples.

Cyanide

The commonly employed methods for determining cyanide involve collecting the cyanide in basic (either NaOH or KOH) impingers. If both the particulate cyanide and gaseous cyanide are to be determined, a teflon filter can be used before the impingers. Potassium hydroxide (KOH) is the recommended impinger solution; however, sodium hydroxide (NaOH) can also be used.

3.2 ANALYTICAL METHODS

An overview of analytical methods is given below, followed by a discussion of specific methods for analyzing VOCs, SVOCs, and PM/Metals.

3.2.1 Overview of Analytical Methods

To a certain extent, the sampling method used to collect the samples will dictate what analytical methods can be used. In some instances, however, several analytical methods will be appropriate and a decision as to what method to use will have to be made. Choosing an analytical method will require a knowledge of the form of the analyte being determined as well as other factors, including:

- Level of quantitation required to meet action levels;
- The sample turnaround time;
- Anticipated form(s) of the analyte present in the sample; and
- Availability and capability of on-site or nearby laboratories.

An example of the trade-offs in choosing among analytical methods is the availability of GC and GC/MS techniques for analyzing both VOCs and SVOCs. For most of the organic compounds discussed in this section, both GC and GC/MS methods are given. As a general rule, GC methods coupled with appropriate detectors are more sensitive, in some cases by several orders of magnitude, than the corresponding GC/MS method. GC methods, however, all suffer from the potential co-elution of peaks, although using multiple detectors can help alleviate some of this problem. GC/MS is much more accurate from a qualitative standpoint, but often is unable to detect compound levels commensurate with pre-set action levels. Determination of the most appropriate analytical method for each target analyte will have to be based on site-specific objectives.

This section briefly describes appropriate analytical methods for many compounds typically encountered at Superfund sites. Real-time monitors, remote sensing instrumentation, and fixed location continuous analyzers are not discussed in this section, since their applications are a combination of simultaneous sampling and analytical functions. A summary of the various analytical methods, along with the advantages and disadvantages of each, is presented in Table 3-9. The various analytical approaches used in the TO methods are shown in Figure 3-4.

3.2.2 Volatile Organic Compound (VOC) Methods

This section discusses VOC samples collected in SUMMA[®] polished stainless steel canisters and those collected on sorbent media. Because of the vast number of sorbents for collecting VOCs, only general guidance for performing sorbent analysis is given.

Canister Methods

Canister sampling techniques are appropriate for a wide range of volatile organic compounds. Likewise the two most commonly used analytical techniques for analyzing canister samples are able to determine a wide range of compounds. These methods are gas chromatography with multiple detectors (GC/MD) or gas chromatography with mass spectroscopy (GC/MS). These two analytical techniques are the basis of EPA Method TO-14.

Table 3-9.

Summary of Analytical Methods for the Various Compound Types

Analyte Type	Method	Advantages	Disadvantages
Volatile Organic Compounds (VOCs) Includes: Aromatics, Halogenates, Oxygenates	Gas Chromatography (GC)	Wide range of detectors available. Relatively inexpensive.	Lack of specificity.
	Gas Chromatography Multiple Detector (GC/MD)	More sensitive than GC/MS. Can analyze polar compounds since the system is less sensitive to water vapor. Can analyze low molecular weight compounds. Detectors can be tailored to analytes present for greatest sensitivity. Generally less expensive capital equipment compared with GC/MS.	Potential for compound co-elution. Less certainty of compound identity since identification is based on retention times and known standards.
	Gas Chromatography Mass Spectroscopy (GC/MS) - Full Scan	Very good qualitative information for a large number of compounds.	Sensitive to water vapor in samples. Poor sensitivity/detection limits. Unable to analyze polar compounds because of sample drying. Difficulty in quantifying low molecular weight compounds.
	Gas Chromatography Mass Spectroscopy (GC/MS) - Selective Ion Monitoring	Good sensitivity for targeted compounds (similar to GC/MD for many compounds). Very good at quantifying individual target compounds.	Sensitive to water vapor in samples. Unable to analyze polar compounds because of sample drying. Difficulty in quantifying low molecular weight compounds.
	High Performance Liquid Chromatography (HPLC)	Very low detection limits for applicable compounds.	Suitable for small number of VOCs (namely TO-11 analytes). Potential for co-elution of peaks.
Semivolatile Organic Compounds			
PCBs	Gas Chromatography/Electron Capture Detection (GC/ECD)	Relatively inexpensive. Highly sensitive (low detection limits).	Cannot be used if PCBs have been altered by heat (e.g., such as through incineration). Recognizes individual Arochlor patterns instead of individual PCB congeners.
	Gas Chromatography Mass Spectroscopy (GC/MS)	Can detect individual PCB congeners. High accuracy in compound identification.	Less sensitive than GC/ECD. More expensive an analysis.

Table 3-9. (Continued)

Analyte Type	Method	Advantages	Disadvantages
PCDDs/PCDFs	Low/medium resolution GC/MS	Instrumentation is more available than HRGC/HRMS	Marginally suitable for ambient levels. Significantly higher detection limits. Must collect significantly larger air samples for analysis (~30% more).
	High resolution GC/MS (HRGC/HRMS)	High degree of accuracy. Detection limits of pg/sample.	Instrumentation expensive and not widely available.
	Gas Chromatography/Electron Capture Detection (GC/ECD)	Relatively inexpensive. Highly sensitive (low detection limits).	Identification based on peak retention times, possible co-elution.
	Gas Chromatography Mass Spectroscopy (GC/MS)	Higher degree of certainty in compound identification.	Much less sensitive, average detection limits may exceed normal ambient levels.
PAHs	High Performance Liquid Chromatography (HPLC)	Highly sensitive, especially when using combination detectors. Relatively inexpensive analysis.	Potential for co-elution of compounds.
	Gas Chromatography Mass Spectroscopy (GC/MS)	Higher degree of certainty in compound identification than HPLC.	Higher cost for analysis than HPLC. Higher detection limits, many compounds may be below normal GC/MS detection limits.
Inorganic Compound Analysis			
Heavy Metals	Inductively Coupled Argon Plasma Emission Spectroscopy (ICAPES)	Can analyze multiple elements simultaneously.	Instrumentation is expensive. Has low sensitivity to some common elements such as lead and arsenic.
	Atomic Absorption Spectroscopy (AAS)	Relatively inexpensive. Readily available. Can easily be performed on site. Good sensitivity for for most metals.	Can only do one element at a time. Not well suited to some common elements such as lead and arsenic.
	Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)	Very good sensitivity to certain common elements such as lead and arsenic.	Only able to determine one element at a time.
	Ion Specific Electrode (ISE)	Simple Analysis. Capital equipment costs are low.	Several potential interferences.
Cyanides	Colorimetric Procedure	Simple Analysis. Capital equipment costs are low. Suited to low concentration levels.	Several interferences.
	Titration with Silver Nitrate	Simple Analysis. Capital equipment costs are low.	Not suited to low ambient levels.

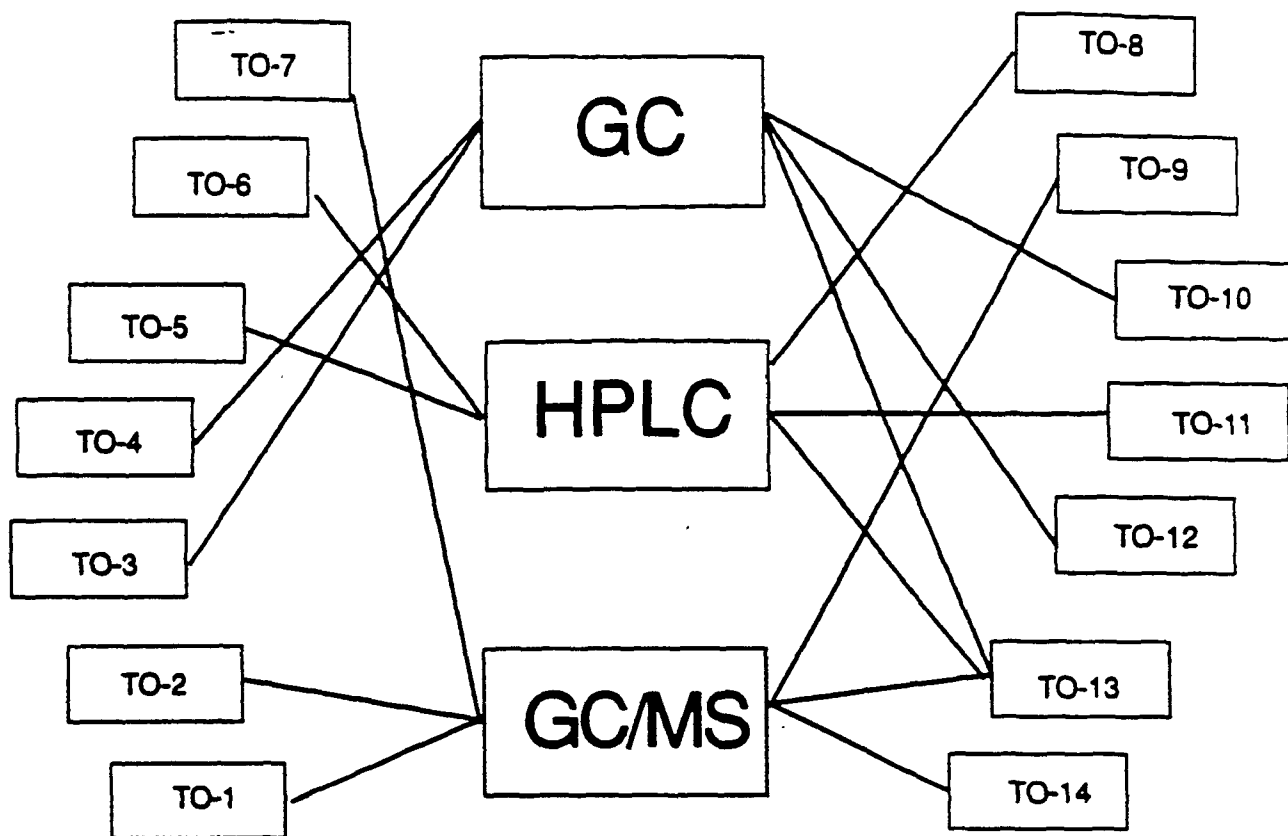


Figure 3-4. Compendium of TO Analytical Methods

GC/MD uses several analytical detectors either in series or in parallel. Since selection of the detectors can be based on the compounds present at the site, lower detection limits or greater specificity for certain compounds can be achieved. An example of this is the use of a Hall Electroconductivity Detector (HECD) for detecting halogenated compounds. This detector is capable of detecting many halogenated compounds at ambient concentrations of 10-100 parts-per-trillion with good precision and accuracy. With either method, some type of sample preconcentration is required. Normally cryogenic preconcentration is used; however, sorbent preconcentration with thermal desorption can also be used.

Selecting GC/MD or GC/MS will depend on several factors, including:

- The physical characteristics of the compounds to be analyzed;
- The number of compounds quantitated; and
- The detection levels required (usually driven by health risk criteria).

There are several types of GC/MS systems, and the specific operating mode will affect the choice of analytical techniques. All GC/MS techniques involve separating a gas sample using capillary chromatography and basing the identification of compounds on the compounds mass fractionation. In general, however, all GC/MS techniques suffer for similar problems. They include:

- Sensitivity to water vapor; the samples must be thoroughly dry before analysis;
- Difficulty in determining low molecular weight compounds; and
- Generally less sensitivity than GC only methods.

GC/MS instruments are typically operated in either full scan mode or in selective ion monitoring (SIM) mode. SIM is used when a small target list (usually less than 15 target compounds) of compounds are being quantitated. SIM has the advantage of being significantly more sensitive than the full-scan mode for most compounds, but cannot detect ions from other compounds that are not on the target list. Full-scan monitoring provides more qualitative information, but may not be sensitive enough to determine the health risk potential of many ambient compounds.

Because of the number of different detectors available, GC/MD may be preferable in some instances. GC/MD systems are not as sensitive to water vapor as GC/MS systems; therefore, they can be used to analyze samples containing polar compounds, which would typically be removed in the sample drying process. A GC/MD will normally be capable of detecting significantly lower ambient concentrations than a GC/MS, although SIM may achieve similar analytical detection limits. When using SIM, however, the ability to detect a large number of compounds will be jeopardized. GC/MD relies primarily on chromatographic retention time to determine compound identity. Co-elution of compounds may cause interference; however, the compound identity can many times be confirmed by the relative responses for that compound from the different detectors.

Both GC/MD and GC/MS are excellent analytical methods, and each has certain advantages and disadvantages for specific applications; however, the overall differences between the two methods are fairly minor. The choice of GC/MD or GC/MS should be made by an experienced chemist, based on the compounds present at the site, the potential uses of the data, the project needs, and the necessary detection limits required.

Sorbent Methods

Because of the number of sorbent methods for collecting and analyzing volatile organic compounds, this section will only deal with general cautions and concerns with sorbent sampling in general. Sorbent media analysis may involve many techniques, including gas chromatography with a variety of different detectors and high-performance liquid chromatography (HPLC). Regardless of the exact analytical technique, all sorbent sampling has common steps involved in collecting and analyzing the samples. They include:

- Drawing ambient air through the medium and adsorbing the analyte(s) of interest onto the medium;
- Preservation of the collected species until analysis can be performed;
- Desorption of the analytes of interest from the medium; and
- Separation and detection of the target analytes.

Precautions that need to be taken while VOCs are being collected on the sorbent medium are discussed in Section 3.1; therefore, sampling precautions are not discussed further here. Once the sample is collected, two main factors affect the reliable quantitation of the target species -- media artifacts and the desorption characteristics of the medium and analytes.

Media artifacts or background compound levels must be known to adequately characterize the analytes being sampled. If the background level is large in relation to ambient concentrations of target compounds, adequately characterizing the target compounds will be difficult. Also, media artifacts can form during sampling that may co-elute with the analytes, thereby masking the true analyte concentration. For any sorbent tube sampling, adequate media blanks must be analyzed to ensure that background levels of the analytes of interest will not interfere with the method.

Spiked media samples should also be analyzed to ensure that media artifact peaks are not occurring during sampling. This is done by spiking one sorbent tube with the analytes of interest and collecting an ambient sample with this tube side-by-side with an unspiked tube. The spike recovery will be determined by the difference between the unspiked sample concentration and the spiked sample concentration minus the spike value. In addition to helping to determine the formation of possible interference compounds during sampling, this technique also helps to evaluate overall sample collection, desorption, and analysis procedures.

The other test that must be done on all sorbent tubes is a desorption study. Regardless of the desorption technique (e.g., solvent extraction, or thermal desorption), the efficiency of removing the target analytes from the sorbent media needs to be ascertained. One potential drawback of some sorbents is that they "hang on" to the compounds too tightly, and removing the targets from the media is difficult. Because of the generally rapid turnaround required for Superfund monitoring this may not be a problem; however, if samples are collected and archived, this may need to be considered.

Desorption studies should be performed by spiking the sorbent medium with the target analytes and leaving the spike on the medium the same length of time that ambient samples are on the medium. Then the spikes are handled in the same way as the field samples. If the data indicate a consistent bias due to desorption efficiency, either internal standards can be added before sampling to adjust the data, or a factor can be used to correct for the bias caused by incomplete desorption.

3.2.3 Semi-Volatile Compounds (SVOC) Methods

This section discusses the general methods used to analyze ambient air samples for classes of semi-volatile compounds that may be encountered at Superfund sites. The sampling methods for these compounds have been discussed in Section 3.1.2. In some instances, only a single method is suited for the analysis of the compounds, in others, two or more methods may be appropriate. In these instances, the differences in the methods will be discussed, as will the relative advantages of each method.

Polychlorinated Biphenyls (PCBs)

There are two generally accepted methods for determining the quantity of PCBs collected on PUF or on combined PUF/solid sorbent media, gas chromatography with electron capture detection (GC/ECD) or gas chromatography/mass spectroscopy (GC/MS). GC/ECD is the analytical method outlined in EPA Method TO-4. This method detects PCBs by their Aroclor pattern. An Aroclor is a mixture of compounds that make up a commonly used product. Since various PCBs have historically been used for a variety of purposes, the individual arochlor can be identified. GC/ECD analysis has the advantage of being fairly simple and relatively inexpensive to perform. The major drawback of this analysis is the inability to detect the compounds when such things as incineration or thermal destruction have degraded the individual Aroclors.

If PCBs are being remediated at a site using incineration (or some other high-temperature treatment) on-site, GC/MS must be used to determine if PCBs are present. This is necessary if the Aroclors are being incompletely combusted, the Aroclor pattern is destroyed and the GC/ECD analysis would not be able to recognize the characteristic pattern.

**Polychlorinated Dibenzo(p)dioxins/Polychlorinated Dibenzo(p)furans
(PCDDs/PCDFs)**

PCDDs/PCDFs or dioxins and furans have very low health risk action levels (NOEL of 5.5 pg/m³ for 2,3,7,8-TCDD);¹⁸ therefore, the collection and analysis of these compounds is quite difficult and expensive. It is generally accepted that at least 800 m³ of air sample be collected for analysis. Analyses should be performed using high resolution gas chromatography/high resolution mass spectroscopy (HRGC/HRMS); however, if the air volume is increased to approximately 1200 m³, medium resolution GC/MS may be used.

Dioxins and furans are very heavy compounds and, depending on the molecular structure of the congener, they can be quite difficult to remove from the PUF medium used to collect them. It is very important when monitoring for PCDDs/PCDFs that the laboratory personnel be experienced in this analysis. Because of the very low levels found, laboratory contamination is a serious problem, especially if the same laboratory is also handling high-level samples such as those found in contaminated soils.

Because of the risk of losing or of not being able to remove these compounds from the various media used to collect and clean the samples during the sample collection and analysis processes, many surrogate compounds must be added at various steps along the sample collection/sample analysis process. Surrogate compounds are isotopically labeled compounds that will act similarly to the native compounds but that can be differentiated from the native compounds because of the mass difference of the isotope. It is not uncommon for up to 13 surrogate compounds to be added to each sample. The surrogates are used to correct sample concentrations due to losses from incomplete desorption of the targets and losses during sample "clean-up."

Because of the complexity of the sampling and analysis of PCDD/PCDF compounds and the extremely high level of quality control needed, the sampling and analysis should only be performed by individuals experienced in this area. Also, care must always be exercised to prevent contamination or other bias in the sample collection and analysis.

Organochloride Pesticides

The two primary analytical methods for determining concentrations of organochlorine pesticides in air samples, gas chromatography with electron capture detection (GC/ECD) and gas chromatography/mass spectroscopy (GC/MS). GC/ECD is by far the preferred method because of its lower cost and greater sensitivity. GC/ECD has an order of magnitude, or greater, sensitivity than GC/MS. Compound identification by GC/ECD is accomplished by using characteristic retention times, compound standards, and second detector confirmation. Therefore, GC/MS offers greater confidence in compound identification because of the mass spectra produced during analysis; however, many sample concentrations will be below what is detectable by GC/MS.

Polynuclear Aromatic Hydrocarbons (PAHs)

Polynuclear Aromatic Hydrocarbons (PAHs) are generally analyzed by either high-performance liquid chromatography (HPLC) or gas chromatography/mass spectroscopy (GC/MS). HPLC methods involve using high-pressure liquid chromatography coupled to either a fluorescence detector or a combination of a fluorescence and ultraviolet detectors. Because of the second detector confirmation, this latter method renders highly accurate results. Also, many fluorescence detectors are capable of being programmed to scan certain wavelengths for additional confirmation and lower detection limits.

Like the other method comparisons described above, GC/MS is capable of accurate identification; however, its sensitivity is generally less by an order of magnitude or more. GC/MS is also more costly than HPLC. Depending on what ambient levels are detected,

identification of a few samples by GC/MS will help confirm identifications made by the HPLC analysis.

3.2.4 Inorganic Compound Methods

The inorganic compounds normally found at Superfund sites include heavy metals, including mercury, and cyanide salts. These analytical methods are discussed in this section.

Heavy Metal Analytical Methods

Filter samples from high-volume samplers are digested in acid and analyzed by one of several methods. The potential methods include atomic absorption spectroscopy (AAS), inductively coupled argon plasma emission spectroscopy (ICAPES), and graphite furnace atomic absorption spectroscopy (GFAAS). These three methods are similar in their analytical theory, the differences being primarily in the exact technique. The merits of these methods are discussed below.

Atomic absorption spectroscopy (AAS) involves aspirating an acid-digested filter sample into a flame, which vaporizes the element of interest. Light of known intensity characteristic of the element is directed through the metal vapor where it is absorbed. The absorption is proportional to the concentration over a certain range. This technique is relatively inexpensive, readily available, and quite sensitive for most heavy metals. Its major drawback is that only one element at a time can be determined.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) uses a very high-temperature argon plasma flame to excite the atoms. ICAPES can be used to detect up to 40 elements simultaneously, which makes it very cost effective for analyzing samples of several elements. While these instruments are widely available in laboratories, they are expensive and may not be suitable for an on-site laboratory because of their cost.

There are several commonly occurring metals found at Superfund sites that are not amenable to either AAS or ICAPES. They include notably lead and arsenic. For these compounds, GFAAS should be used. Although they can be detected by the other two methods, the sensitivity is significantly better on GFAAS. For instance, the typical laboratory detection limit for lead by ICAPES is approximately 50 $\mu\text{g/L}$, while for GFAAS, the laboratory detection limit is approximately 5 $\mu\text{g/L}$. If very high lead concentrations are always found, the ICAPES could be used as a more cost effective way (since it could be done simultaneously with other metals) to determine lead; however, if greater sensitivity is desired, GFAAS should be used.

Mercury was discussed in the metals sampling section. Although there are other methods for collecting mercury, the most accurate methods involve amalgamating the mercury with gold. As mentioned earlier, the Jerome analyzer (which uses gold foil techniques) can be used quite successfully for sampling and analyzing mercury. Another technique (which also involves collecting the mercury on gold) uses cold vapor atomic absorption spectroscopy to quantitate the mercury concentration. This technique measures the mercury concentration "cold" without using flame or a high-temperature furnace. The Jerome analyzer flashes the mercury off the gold dosimeter and measures the difference in conductance before and after flashing.

Cyanide

Cyanide generally refers to all the CN groups in a compound that can be determined as the CN^- ion. Cyanide compounds may be classified as being either simple, in which the CN group is present as either CN^- or HCN, or complex, where the CN group is complexed, typically to a heavy metal. Generally, simple cyanides are more toxic than the complex, due to the greater availability of HCN.

It is possible, by selective preparation methods, to differentiate between the simple and complex forms of cyanide. Simple cyanides may usually be brought into solution by aqueous dissolution, as in an impinger. Complex cyanides require a more rigorous digestion,

such as in acid and with a catalyst, to liberate CN^- for analysis. After the appropriate preparation of a collected sample, all solutions may be analyzed for CN^- by the methods described below.

Three commonly used analytical techniques are used to measure cyanide concentrations. They include:

- Cyanide ion-specific electrodes;
- Colorimetric procedures using spectrophotometric techniques; and
- A titration technique using silver nitrate.

The major drawbacks of the ion-specific electrode include potential interferences, many of which could easily be present, along with cyanide contamination, at a site. The interferences include sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron, and mercury.

The colorimetric method converts the cyanide to cyanogen chloride, complexing the cyanogen chloride with a pyridine-barbituric acid reagent to form the color, and measuring the absorbance. This method is fairly sensitive, with a detection limit of approximately 0.02 mg/L. The major interferences include thiocyanates, sulfide, and high concentrations of cadmium.

The third method involves titrating the impinger solutions with a solution of silver nitrate in the presence of a silver-sensitive indicator. This method is best suited to higher levels of cyanide (i.e., more than 1 mg/L in the solution). Sulfides are the major interferant.

The analytical method chosen for cyanide will depend on what other compounds are also present at the site, since all three analytical methods have interferences. The various analytical methods are also sensitive to concentration. To get the best mix of sampling time or volume, along with the appropriate analytical technique, may require some methods development and trial and error. Again, the review and input of staff experienced in this type of sampling is recommended as part of the method selection process.

SECTION 4

QUALITY ASSURANCE AND QUALITY CONTROL

EPA requires that a quality assurance project plan (QAPP) be prepared and implemented for all environmental measurement programs mandated or supported by the agency through regulations, grants, contracts, or other formalized means. The main purpose of the QAPP is to specify the minimum procedures that must be used to ensure that the accuracy, precision, completeness, and representativeness of the resulting measurement data are known, documented, and sufficient to achieve the overall goals of the measurement program. The information for ambient air monitoring (AAM) programs at Superfund sites may be incorporated into other documents, such as the site Health & Safety Plan or Remedial Design Documents, rather than as a stand-alone document. For sites where AAM will be conducted on a long-term basis, however, a separate QAPP for the AAM program is recommended.

The general principles of quality assurance and quality control are described in Section 4.1 of this document. Specific guidelines for preparing and implementing QAPPs for Superfund Air Pathway Assessment Programs appear in Section 4.2.

4.1 GENERAL PRINCIPLES OF QUALITY ASSURANCE AND QUALITY CONTROL

In the context of this document, as in other EPA reports, the term **quality assurance** refers to the entire system of activities, planned or taken, to ensure that the measurement data are of sufficient quality to meet the overall goals of the program. In this context, quality assurance includes such things as: quality planning, personnel training, standardization of procedures, documentation, data validation, and data quality evaluations. The term **quality control** relates more specifically to the operational techniques and activities used to sustain acceptable levels of data quality. Such things as routine instrument checks, flow rate checks, duplicate samples, blanks, calibration checks, etc., are part of quality control.

Detailed guidelines and procedures for achieving quality assurance and quality control in air pollution measurement systems are given in EPA's five-volume series, "Quality Assurance Handbook for Air Pollution Measurement Systems".²¹⁻²⁵ Although the series deals primarily with routine air monitoring for criteria air pollutants (SO₂, NO₂, O₃, CO, PM₁₀ and Pb), the principles of quality assurance given in Volume I of this QA Handbook form an appropriate basis for designing a quality assurance program for air pathway assessment activities. Other useful references are EPA's "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air"²⁶ and "Preparing Perfect Project Plans".²⁷ Much of the information that follows is drawn from these documents.

The QA handbook and TAD both describe several different elements of quality assurance that together make up a comprehensive QA program. The individual QA elements, listed in Table 4-1, are grouped into separate functional units that relate to the organizational level to which responsibility is normally assigned. These functional units are: (1) quality assurance management, (2) sampling quality assurance, (3) analytical quality assurance, and (4) data management quality assurance. The Quality Assurance Project Plan should address each specific feature of sampling, analytical, and data management quality assurance. Specific guidance for addressing each of these topics in a QAPP is given in Section 4.2. QA management deals with the underlying QA principles and structure used to design and implement the QAPP. A brief discussion of QA management is given below.

4.1.1 Quality Assurance Management

To be effective, a quality assurance program must be thoroughly integrated with the overall monitoring effort. A prerequisite to achieving this goal is establishment of a QA policy, objectives, and organizational structure to support the QA program. All members of the project team must be familiar with the goals and underlying principles on which the QA program is based. In the most general terms, the objectives of the QA program should be to ensure that the measurement data are (1) technically sound and defensible and (2) of sufficient quality to achieve the specific goals of the air pathway assessment. Whenever practical, one person within the organization should be responsible

for coordinating all of the quality assurance activities for the measurement program and for determining whether the objectives of the QA program are being met. To maintain objectivity, however, the QA coordinator should not be responsible for directly implementing the specific QA activities associated with data collection and management (i.e., the specific elements of sampling QA, analytical QA, or data management QA). These responsibilities should be assigned to other qualified personnel.

After establishing the QA policy, objectives, and organizational structure, a QA project plan should be developed. The main purpose of the QA project plan is to specify in advance the actions that will be taken to accomplish the QA objectives. Specific guidelines and specifications for preparing QA project plans were previously established by EPA and are discussed with specific regard to the AAM program in Section 4.2. The structural format of the QAPP (as well as that of all other formal documentation of procedures, plans, and specifications) should include a system of document control for managing the organization and distribution of document revisions.

In addition to the QA items described above, QA management also involves such things as training personnel, evaluating data, conducting quality assurance audits, preparing quality assurance reports, and taking corrective action. EPA offers an extensive list of self instructional and other training courses pertaining to QA/QC through their Air Pollution Training Institute (APTI). For a list of courses or other related information, write to:

Registrar
Air Pollution Training Institute (MD-20)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711
(919) 541-2401

The remaining aspects of QA management are the key elements of a QAPP, these are discussed at length in Section 4.2.

4.2 QUALITY ASSURANCE PROJECT PLAN

Guidelines and specifications promulgated by EPA require that 16 essential QA elements be addressed by the QAPP.²⁸ The first two of these elements, title page and table of contents, pertain only to the structure and format of the QAPP; others provide background information, such as project objectives and measurement approaches, so that individuals not already familiar with the project can be appropriately informed. Most of the QAPP elements, however, describe the specific actions that will be taken to ensure that the data are of known, defensible, and sufficient quality. The 16 essential elements of a QAPP are described below. Wherever appropriate, guidance is given on how to address these elements with specific regard to an air pathway assessment (for some topics, specific guidance is given in other sections of this document--e.g., site selection and measurement methods are described in Sections 2.0 and 3.0, respectively). The QA/QC elements of a long-term AAM program are illustrated for a "typical" Superfund scenario in Appendix D.

4.2.1 Title Page

In addition to the obvious information, the title page should indicate that the QAPP has been approved by the project manager, quality assurance coordinator, and either the remedial project manager or on-site coordinator. Approvals should be shown at the bottom of the title page by the signatures of the appropriate personnel.

4.2.2 Table of Contents

As part of the system of document control, the QAPP Table of Contents should specify the number of pages, revision number, and date of last revision for each of the QAPP sections. A distribution list, indicating all official recipients of the QAPP should be included at the end of the Table of Contents.

4.2.3 Project Description

A general description of the measurement program should be included to provide background information for persons responsible for reviewing the QAPP. The project description should include: (1) a description of the site and the status of any remedial activities, (2) the purpose of the measurement program, (3) target analytes and a brief description of the measurement approach, (4) specific uses of the measurement data, and (5) scheduled start-up and ending dates of the measurement program.

4.2.4 Project Organization and Responsibility

The QAPP should include an organization chart identifying all of the key individuals involved in the technical, QA/QC, and managerial aspects of the measurement program. The specific responsibilities and authorities assigned to each key individual and, in some cases, their qualifications should also be described. In some cases, it might also be desirable to indicate the telephone numbers and office or lab locations of key individuals.

4.2.5 Data Quality Objectives

Data quality objectives, in terms of precision, accuracy, and completeness, must be specified for each primary measurement parameter. These objectives must be defined in terms of project requirements (not based on the capabilities of the measurement methods used) as discussed in Section 2.3 of this document. Qualitative objectives pertaining to the representativeness and comparability of the measurement data should also be addressed. In addition, a discussion of the ramifications of not meeting the stated DQOs should be included in the QAPP.

4.2.6 Site Selection and Sampling Procedures

The QAPP must document the proposed monitoring site locations, and the rationale for their selection. Whenever practical, site maps and schematic diagrams should be used to identify specific locations and monitoring configurations. Photographs taken from each monitoring site showing the ground cover and fields of view in all directions from the monitoring site, as well as a closeup view of the actual site location, are also recommended.

The QAPP must also include a description of the sampling equipment and procedures used for each primary measurement parameter. Whenever practical, conventional EPA sampling protocols such as those described in the various TO Methods should be employed. If standard methods are used, it is enough to simply reference the method. However, if standard methods are modified or if alternate methods are used, a description of the method and the rationale for its selection should be given. The description of sampling procedures should include any specifications for: (1) preparation, cleaning and certification of sampling equipment; (2) sample preservation, transport, and storage; and (3) sample holding times before extraction and analysis.

4.2.7 Sample Custody

A description of all sample custody procedures, forms, documentation, and personnel responsibilities pertaining to both field and laboratory operations must be included in the QAPP. Specific items that must be addressed in this regard are: (1) documentation of procedures for preparing of reagents or other supplies that become an integral part of the sample (e.g., filters, sorbent media, or reagents); (2) procedures and forms for documenting the dates, times, locations, and other relevant data pertaining to sample collection and analysis; (3) documentation of sample custodians in the field and laboratory; (4) documentation of sample preservation methods; (5) sample labels and custody seals; (6) field and laboratory sample tracking mechanisms; and (7) procedures for sample handling, storage, and final disposition.

The level at which these items should be addressed depends on the specific scope and objectives of the air pathway assessment. If the results of the air pathway assessment will be used in litigation, strict chain-of-custody measures, as defined by EPA's Office of Enforcement, can be required. In other cases, the goals of sample custody can simply be to maintain the scientific credibility and integrity of the measurement data.

Detailed guidelines for establishing sample custody procedures are given in Volume II of EPA's QA Handbook for Air Pollution Measurement Systems.²² Key points in this regard are: (1) all samples must be uniquely identified to ensure positive identification throughout the test and analysis procedures; (2) all samples must be handled in a manner suitable to ensuring that there is no contamination or other breach of sample integrity that might otherwise be caused by leakage, reactive decay, accidental destruction, or tampering; (3) chain-of-custody forms must accompany all samples from the field to the laboratory or intermediate storage points, and the chain-of-custody forms should be signed by all persons who handle the samples along the way; (4) samples should be shipped only by registered mail or other forms of registered service, and they should be addressed to the specific person authorized to receive them; and (5) all field notes, laboratory notes, and original calculations should be saved.

4.2.8 Calibration Procedures and Frequency

The QAPP must include a description of the calibration procedures and the recalibration frequencies for each measurement parameter and measurement system. If standard, documented methods are used, simply referring to the method is sufficient. Otherwise, a complete description of the calibration approach should be given. The description of calibration procedures should address: (1) the maximum allowable time between calibrations and calibration checks, (2) the quality and source of calibration standards (as a general rule, calibration standards should be certified to between four and ten times the accuracy of the equipment being calibrated), (3) the traceability of standards to NIST Standard Reference Materials or equivalent Commercial Certified Reference Materials, (4) the documentation of calibration results, and (5) a statement of the appropriate

environmental conditions needed to ensure that the equipment is not adversely affected by its surroundings (e.g., adverse temperatures, humidity, vibration, lighting, chemical emissions, radio frequency interferences, or electrical voltage fluctuations).

The frequency of calibration should be in accord with any applicable regulatory requirements or recommendations of the equipment manufacturer. In the absence any such guidance, an initial calibration interval should be determined, based on the inherent stability, precision, bias, and degree of use of the equipment. The time interval may then be shortened or lengthened, depending on the consistency of results obtained from successive calibrations.

4.2.9 Analytical Equipment and Procedures

Officially approved EPA analytical procedures should be used whenever they suit the particular scope and objectives of the air pathway assessment. In these situations, the applicable method should be referenced in the QAPP. Section 3.0 contains a list of standard methods that might apply to the air pathway assessment. If standard methods are modified or alternative methods employed, the modifications or alternate methods must be described and the rationales must be given for their selection. Whenever modified or nonstandard methods are used, they must first be validated to demonstrate their performance characteristics in terms of accuracy, precision, detection limit, and specificity. Procedures and acceptance terms for the method validation study should be described in the QAPP.

4.2.10 Data Reduction, Validation, and Reporting

A description of the data reduction, validation, and reporting procedures for each primary measurement parameter must be included in the QAPP. These procedures should specify: (1) all equations and statistical approaches used to reduce the measurement data, (2) the method for treating blanks during data reduction, (3) the method for treating cases of undetected compounds in the statistical calculations, (4) the methods used to identify and treat outliers, (5) the criteria for flagging and validating data, and (6) the units for

reporting results. A flow chart is sometimes helpful for depicting the series of specific steps taken from initial data collection, on through data reduction, validation, reporting, and final storage. Specific guidance for reducing, validating and reporting measurement data is given in Section 5.0.

4.2.11 Internal Quality Control

Internal quality control checks should be performed on all sampling and analytical systems to verify and document whether such systems are operating within control limits or require corrective action. The procedures, control limits, corrective actions, and frequencies with which QC checks should be performed should be specified in the QAPP. Items to be considered as part of internal quality control for field sampling systems include: flow rate checks; leak checks; timer checks; and visual inspections of sample lines and inlets for cracks, moisture, or debris. Whenever practical, these checks should be conducted immediately before and after each sample collection period. The procedures for conducting QC checks are likely to be instrument-specific. Equipment manuals or EPA-approved Standard Operating Procedures (e.g., TO Methods) should be consulted for specific guidance on designing internal QC procedures.

Examples of items to be considered as part of analytical internal quality control are: system blanks, replicate analyses, surrogate samples, spiked samples, reagent checks, and calibration checks. A listing of QA/QC samples is given in Table 4-1. These checks can be used to provide immediate feedback for identifying whether the analytical systems are operating within pre-established control limits. If control limits are exceeded, corrective actions should be implemented before additional samples are analyzed. Analytical control checks should be performed at least once a day, or after every 10 samples are analyzed.

Table 4-1.

Types of QA/QC Samples

QA/QC Sample Type	QA/QC Objective	Suggested Minimum Frequency	Responsible Party	Application
Field Blank	QA2	Method dependent, typically not less than 5%.	Field Crew	Used to detect contamination during field operations and shipping.
Trip Blank	QA2	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	QA2, QA3	5% or minimum of 1 per sampling event.	Field Crew	Used to determine variation due to sample collection and/or ambient conditions.
Breakthrough Sample	QA2	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	QA2, QA3	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	QA2, QA3	1 per week when user requires more stringent QC controls.	Field Crew	Used to evaluate laboratory capability. In addition, a blank spike evaluates air matrix and sorbent, if used for sampling.
Lot Blank	QA2, QA3	1 per event per lot, 3-6 whenever new lot of adsorbent acquired.	Laboratory	Used whenever manufacturers supply a lot of samplers or when a fresh lot of sampling media is cleaned.
Reagent/Method Blank	QA2	1 per reagent blank per batch.	Laboratory	Used for impinger samples and for solvent desorbed sorbent media.
Surrogate Spike	QA2, QA3	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	QA2, QA3	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.

In addition to sampling and analytical control checks, quality control samples should also be collected and analyzed to evaluate the overall performance of the measurement system. Types of quality control samples include: field blanks, field duplicates, and field matrix spikes. Note that these types of samples differ from the analytical control samples described above in that they originate at the field site and therefore reflect the combined performance of both sampling and analytical systems. Field QC samples therefore provide a more representative way to evaluate overall data quality, but because of lag times between collection and analysis they are not as effective as analytical control checks for identifying the need for corrective action. The recommended frequency for collecting each type of field QC sample is one per sampling event. Less frequent sample collection is sometimes acceptable, but the total number obtained during any given period should be at least 5% of the total number of ambient samples.

Whenever appropriate, control charts should be used to depict trends in the QC data, distinguish patterns of random variation from variations of assignable causes, and identify when the measurement system is out of control.^{ref} Determinations of appropriate control limits should be based on either the performance characteristics of the measurement system or on the specified requirements of the measurement procedure. Common practice sets control limits at ± 3 standard deviations (excluding outliers) from the mean of previous measurements. Appendix H of The QA Handbook, Volume I, gives detailed guidelines for control charting QC data.²¹

4.2.12 Performance and System Audits

Performance and system audits are the primary method to determine if the QA goals and objectives have been met. The scope and schedule for auditing each primary measurement system or parameter, as well as the personnel conducting the audits, must be specified in the QAPP. Performance audits are used to quantitatively evaluate the accuracy of the data being generated, typically by evaluating the recovery of certified reference materials through the sampling and analytical systems. System audits address, in qualitative

terms, the capabilities of the measurement system for generating data that meet QA objectives for representativeness and comparability. Such things as adherence to established sampling and analytical procedures, sample custody, and equipment maintenance should be addressed in a system audit.

To maintain objectivity, performance and system audits should be conducted by the project's QA Coordinator or other individuals who are not responsible for the operational aspects of the air pathway assessment. All materials and supplies used in the audit should also be different from those used during routine operation and calibration of equipment. Performance audits should be conducted at least once every three months for long-term AAM networks; however, a more frequent schedule is recommended if results are highly variable from one audit to the next. A system audit should be conducted before or shortly after the system becomes operational and should be repeated regularly thereafter (e.g., quarterly or semi-annually).

4.2.13 Preventive Maintenance

The following types of preventive maintenance should be considered part of the quality assurance program and addressed in the QAPP: (1) a schedule of important preventive maintenance tasks that must be carried out to minimize instrument downtime, and (2) a list of any critical spare parts that should be on hand to minimize instrument downtime. Preventive maintenance tasks and spare parts are instrument-specific. Equipment manuals and EPA-approved SOPs should be consulted for guidance on establishing specific procedures and schedules.

4.2.14 Procedures Used to Evaluate Data Precision, Accuracy and Completeness

Specific procedures used to evaluate data quality in terms of the precision, accuracy, and completeness of all primary measurement parameters must be described in the QAPP. These procedures should specify the methods used to gather data for evaluating the precision and accuracy and all equations used in subsequent calculations. Specific

requirements for evaluating the quality of the data generated by criteria air pollutant measurement systems are given in the Code of Federal Regulations and other EPA guidance documents.^{9,30} These methods are not always adaptable to air toxics measurement systems, but whenever practical they should be applied. These and alternative procedures for evaluating data quality are described below. Note that data quality must always be determined in a manner compatible with established data quality objectives.

Recommended procedures for determining precision and accuracy depend on whether the measurement method involves automated on-site analysis or requires integrated sampling subsequent analysis off site. For automated on-site analytical systems, precision data should be obtained by periodically (e.g., daily or weekly) challenging the analyzer with a gas standard of known concentration and observing the analyzer's response. Calculation procedures given in the Federal Register (Part 58, Appendix B) are used to express precision in terms of the upper and lower probability limits of the percent differences between the known and observed concentration values. Although EPA requires these procedures for certain types of criteria air pollutant monitoring systems, no specific requirements exist for air pathway assessments. An alternative expression for precision, in this case, is the relative standard deviation (i.e., standard deviation divided by the mean, expressed as a percentage) of successive precision check results.

Procedures for determining the accuracy of automated on-site analytical systems should be similar to those for determining precision, except that the assessment must be performed by someone other than the operator or analyst who conducts the routine monitoring and must be performed using gases made from different working standards. Accuracy should be expressed as the percentage difference between the known and observed concentration values. Alternatively, accuracy can be expressed as the percent of the known concentration recovered through the analytical system (i.e., the observed concentration divided by the known concentration, expressed as a percentage).

For measurement methods that require integrated sampling and off-site analysis (these methods are sometimes referred to as **manual methods**), duplicate (collocated) sample results should be used for determining data precision. To obtain precision data, collocated samplers should be located at the site with the highest expected concentration levels of target analytes. Duplicate samples can be also obtained at alternating sites if portable or multi-channel samplers are used. Equations for expressing precision in terms of the upper and lower probability limits of the percent difference of duplicate sample results are given in the Federal Register (Part 58, Appendix B). Alternatively, precision can be expressed as the relative percent difference of duplicate sample results, or pooled standard deviation.^{ref}

Accuracy determinations for manual methods should be performed by spiking sampling media with known quantities of target analytes and measuring their recovery through the extraction and analytical systems. Media spikes should be prepared by the QA Coordinator or another individual not involved in the operational activities associated with sample collection or analysis. The accuracy of the measurement data should be expressed as the percentage of the spiked amount recovered in the analysis.

Data completeness for both automated and manual methods should be expressed as the percentage of valid data relative to the amount of data that was expected to be obtained under correct normal conditions.

4.2.15 Corrective Action

A plan for initiating and implementing corrective actions must be included in the QAPP. The plan should specify: (1) conditions that will automatically require corrective actions; (2) personnel responsible for initiating, approving, implementing, and evaluating the resolution of corrective actions; and (3) specific corrective action procedures used when predetermined control limits are exceeded. Corrective actions are usually instrument-specific. Equipment manuals and EPA-approved standard operating procedures should be consulted for guidance on establishing specific corrective action procedures.

4.2.16 Quality Assurance Reports to Management

The QAPP should define a mechanism for periodically reporting to management on the performance of the measurement systems and data quality. At a minimum, QA reports should include: (1) assessments of measurement data accuracy, precision, and completeness; (2) performance and system audit results; and (3) significant QA problems and recommended solutions.

SECTION 5

DATA MANAGEMENT

The goal of ambient air monitoring (AAM) programs at Superfund sites is to generate accurate, verifiable reports on ambient concentrations of air pollutants in the area of concern. These data are usually applied to evaluations of the risk to on-site personnel and the surrounding community. The data used in these evaluations must be defensible and must meet the criteria established in the Quality Assurance Project Plan (QAPP) or AAM Plan for accuracy, precision, completeness, and representativeness. Therefore, establishing sound data management procedures and objectives early in the program can be critical to its success.

Long-term AAM programs may generate tremendous amounts of data. In most cases, AAM data are reviewed regularly (e.g., daily) and compared with action levels to see if any exceedances have occurred. The AAM data are then stored in hard-copy form, entered into databases, or summarized in word processing software. Frequently, problems arise when, at some future date, someone needs to review or use the data. In too many cases, the data record is incomplete, the data are stored in a variety of formats, or they have not been consistently validated. It may then be expensive or impossible to reconstruct a complete set of validated data; therefore, a data management program should be established before any long-term AAM program begins. Much of the information in this section also applies to short-term AAM programs.

The key elements of data management for AAM programs include: data management planning, data acquisition, data reduction, data validation, and data reporting. These elements are discussed in the following sections.

5.1 DATA MANAGEMENT PLANNING

Collecting and maintaining unnecessary or redundant data can create needless data management costs, while insufficient, improperly formatted, or poorly managed data can prove equally costly to the program. To maximize the efficiency of the data management process, data collection methods and standards should be developed early in the program with the end use of the data in mind. Specific information management objectives may require the comparison of data with chemical-specific health criteria, state or local air toxics guidelines, ambient air standards, or other compliance requirements. Monitoring results may be applied to health risk assessment models to calculate the individual or community health risks associated with ambient air pollutants, or they may be used to validate predictive software models.

The QAPP or the AAM plan should provide a management framework to coordinate and evaluate data management program activities. Data management procedures should be contained or referenced in these documents to ensure that sampling and analytical data are captured, stored, and maintained in an efficient and secure environment and that the quality of the measurement data is high enough to meet the goals of the program. Program-specific information for documentation and recordkeeping requirements, data quality objectives, and data storage, transfer, and manipulation should be specifically addressed.

Documentation and Recordkeeping

The sampling plan or the QAPP should specify the data recording procedures for the AAM program. Data must be collected and supporting documentation maintained for:

- Periodic readings of meteorological conditions at appropriate time intervals;
- Temperature, flow rates, volumes and other measured parameters at specified time intervals;
- Instrument operating variables;

- Upset conditions, such as emergency releases;
- Calibration or maintenance procedures; and
- Sample tracking and analytical results.

A logbook should be maintained for the entire sampling program to document sampling descriptions, meteorological data and upset conditions. Logbooks should be maintained for each instrument to record calibration and maintenance activities. Data sheets and forms should be designed to support raw data collection and chain-of-custody information. Documentation of analytical procedures and results must also be developed and maintained throughout the life of the program. Responsibility for maintaining and storing program documents should be clearly specified to facilitate the rapid retrieval of information.

Data Quality Objectives

Data quality objectives (DQOs) and procedures for evaluating data quality are specified in the QAPP to ensure the representativeness, completeness and comparability of measurement data. Acceptance criteria for accuracy, precision, and completeness must be specified for each primary parameter. Corrective action methods for addressing measurements not meeting stated DQOs should be addressed, as well as standard statistical and analytical procedures for manipulating the measurement data.

Data Transfer, Storage and Reporting

Data management procedures for the typical AAM program are characterized by the need to store and integrate large volumes of data derived from a variety of data sources. Because these data may be collected over a long period of time by different parties, developing an integrated data management system for the transfer, storage, and manipulation of data to create final reports is an essential program planning activity.

The integration and management of AAM program data are typically supported by a central, integrated database system. The design and structure of the supporting software should be compatible with program objectives and, at a minimum, should offer:

- Storage for all required data;
- Interfaces for accessing or entering field and laboratory information;
- The ability to retrieve data in the form of standard or user-specified reports.

In most cases, the database system must be developed or modified from an existing system to support the unique needs of the program. Table 5-1 summarizes the topics of concern when developing databases for AAM programs.

5.2 DATA ACQUISITION

Figure 5-1 depicts a data flow diagram for a typical AAM program. Field-based data acquisition systems and sampling methods are predefined in the QAPP or sampling plan. In a well-structured data acquisition environment, automatic interfaces with the central database are present to reduce data handling costs. In current AAM programs, monitoring systems may be linked to the central database via modem or another electronic interface. Sampling information and analytical results are often keyed into the system from hard-copy data sheets. In some cases, raw or analytical data may also be transferred via diskette or other electronic medium, and the data are electronically imported into the central database.

The efficiency of the data acquisition process depends directly on the compatibility of sample numbering schemes, data element definitions, data formats, and units of measure for each priority parameter. Standardization of these items facilitates data transfer, reduces data acquisition costs, simplifies data reduction and validation activities, and ensures the defensibility of the final reports.

Table 5-1.

Database Development Issues

Topic	Possible Results	Potential Pitfalls
Data Volume	Data volume exceeds expectations	<ul style="list-style-type: none"> • unacceptable response times • excessive resource utilization (update time, disk space)
Data Structures	Incorrect design	<ul style="list-style-type: none"> • inflexibility • poor performance • increased storage • update problems • false interferences
Data Relationships/ Indexes	Design not optimized for program data	<ul style="list-style-type: none"> • inefficient updates • complex reporting • poor interactive response
Data Redundancy	Existence of duplicate data	<ul style="list-style-type: none"> • inefficient data retrieval • error-prone reports • complex updates • increased data volume • increased maintenance costs
Data Formatting	Data inconsistency	<ul style="list-style-type: none"> • impedes data transfer • inefficient data comparison/manipulation • error-prone reports
Meaning of Fields	Fields incorrectly defined or having multiple definitions	<ul style="list-style-type: none"> • loss of data integrity • incorrect interferences • programming errors • poor program communication
Documentation	Inadequate/poorly maintained	<ul style="list-style-type: none"> • vulnerable to staff turnover • miscommunication between staff • programming errors • expensive maintenance

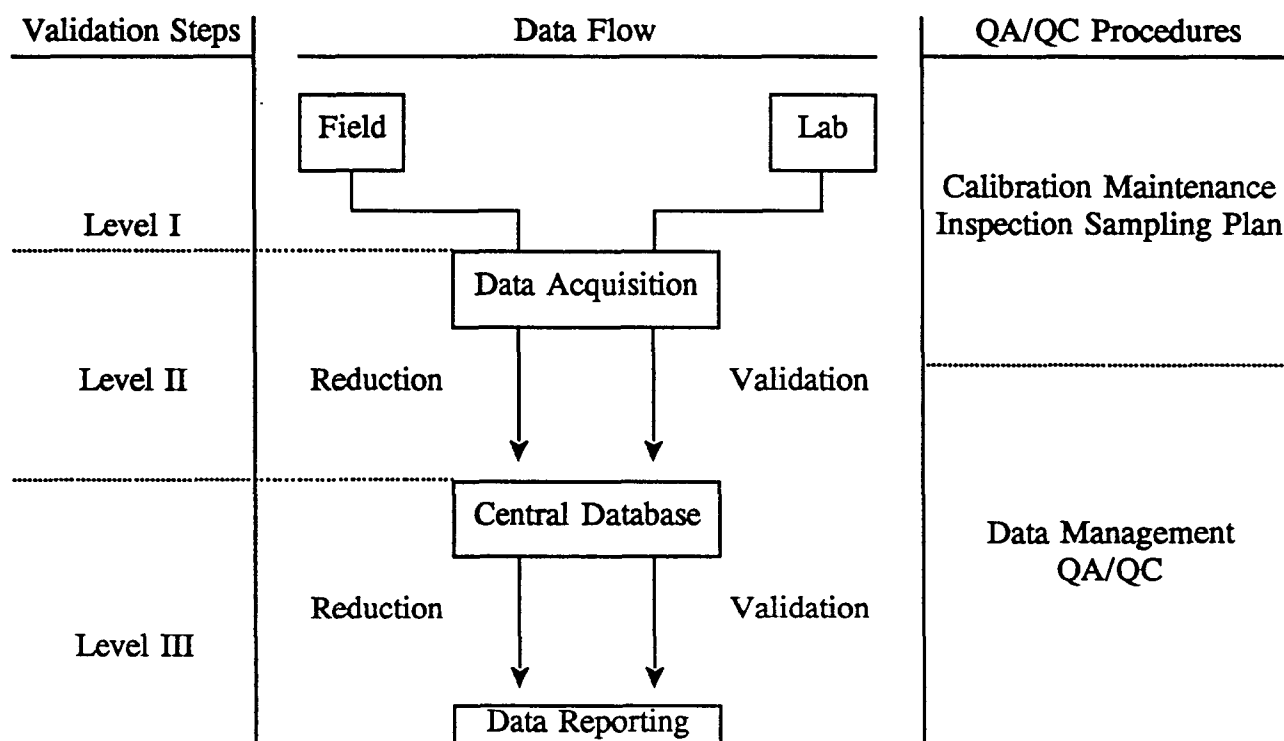


Figure 5-1. Simplified Data Flow Diagram for AAM Programs at Superfund Sites.

5.3

DATA REDUCTION

Data reduction is the manipulation of raw data, by averaging, integration, and statistical methods, to create intermediate products for analytical applications and assessment reporting. Each phase of data reduction is accompanied by a parallel data validation step to ensure the early detection and resolution of data anomalies.

In AAM programs, data reduction is an ongoing process that begins with the field instrumentation and supporting data processors that automatically average measurement parameters for specified time intervals. Laboratory methods for analyzing samples generate individual sample data (e.g., the integration of a chromatographic peak) by manual analysis or the use of supporting software tools. These type of data reduction activities are validated by QA/QC activities for instrument calibration and maintenance and program-specified laboratory methodologies (see Figure 5-1).

Loading field and laboratory data into the central database may require additional data treatment to meet database requirements for units, data formats, etc. Data compatibility issues can be resolved with preprogrammed conversion routines. These activities begin what is typically viewed as the 'data management' portion of the project and are integrated with field and lab QA/QC activities specified for the program, as shown in Figure 5-1.

Once loaded into the central database, raw data should be stored for the life of the program. For long-term AAM programs, raw data may be periodically archived for database maintenance. In all cases, the maintenance of raw data files should be supported by regular backup procedures. These data, once validated, are further reduced to create data summaries (intermediate data) and final reports.

Data reduction procedures involve the application of standard statistical methods for averaging, establishing minimum and maximum values, generating standard deviations, etc. Statistical calculations for determining ambient concentrations of air pollutants are complicated by the limitations of existing measurement methods, which operate within detection limits above those of actual concentration values. For samples characterized as "not detected" the conventional practice is to substitute such value with a value one-half the detection limit. This may, however, result in erroneous or unacceptably high estimates of risk if a number of toxic or carcinogenic compounds are among the target analytes. This effect is exacerbated if the number of "not detected" values make up a significant portion of the data set.

5.4 DATA VALIDATION

Data validation is the systematic review of measurement data for outlier identification or error detection. Suspect values are deleted or flagged by manual or automated data validation methods. The term "validation" typically implies those activities performed upon collected data. Validation is distinguished from the quality control activities that prevent bad data from being collected.

There are three general levels of validation in AAM programs:

- Level I validation -- involves validity checks of raw monitoring data;
- Level II validation -- the independent evaluation of analytical results by a qualified person; and
- Level III -- a review to identify data outliers and anomalies.

Level I validation activities involve reviewing chain-of-custody forms to detect any problems with sampling equipment, canister leakage, etc. that might have contributed to nonstandard sampling intervals, insufficient sample volume, or other problems that may negate the sampling event or create questionable results. For monitoring systems, validation of the raw data is inherent in quality control procedures for calibration and maintenance.

Level II validations verify preliminary compound identifications, confirm that analytical systems are operating within acceptance criteria, and identify anomalies associated with any analysis that might undermine compound results. These activities are performed by a qualified chemist or air specialist and are designed to ensure that the data criteria for each analyte are met. Suspect data are deleted or flagged for resolution; measurement bias, system contamination, or the lack of reproducibility of measurement data may be reasons to judge the data invalid.

In Level III validation, the data are screened for outliers, concentrations inconsistent with historical measurement trends, or measurements that are incompatible with prevailing wind conditions. The validation activities should attempt to correlate any data anomalies with treatment process conditions or on-site activities. Level III validation typically occurs with data stored and reduced in the central database system and is supported by manual review or automated data validation routines.

Acceptance Criteria

The process of data validation ensures that the DQOs for each measured parameter are met. A key acceptance criterion is the data recovery rate, which expresses the number of valid observations as a percentage of total possible observations. Data recovery rates are typically 80% for air quality data and 90% for meteorological data, based on 1990 EPA recovery standards established for permitting purposes.

Section 1.4.17.2.1 of Volume I of the Quality Assurance Handbook for Air Pollution Measurement Systems,²¹ contains detailed information on data validation and screening procedures. In this document, data validation procedures are subdivided into four general categories:

- Routine check and review procedures;
- Tests for internal consistency of data;

- Tests of consistency of data sets with previously analyzed data sets (historical or temporal comparisons);
- Tests of consistency with data sets collected at the same time or under similar conditions.

Table 5-2 summarizes the specific criteria for screening meteorological data, extracted from "On-Site Meteorological Program Guidance for Regulatory Modeling Applications,"²⁸

Air monitoring data validation should include evaluating collocated station results and audit results to determine data precision and accuracy, as described below.

- The percent difference between the air concentrations measured at collocated samplers is:

$$d_i = \frac{Y_i - X_i}{\frac{(Y_i + X_i)}{2}} \times 100$$

where: d_i = the percent difference between the concentration of air toxic constituents Y_i measured by the collocated monitoring station and the concentration of air toxic constituent X_i , measured by the monitoring station reporting the air quality.

- The average percent difference d_j for the monitoring period is:

$$d_j = \frac{1}{n} \sum_{i=1}^n d_i$$

where: d_i = percent difference defined above, and
 n = number of samples collected during the monitoring period.

- The standard deviation S_j for the percent differences is:

$$S_j = \frac{1}{n-1} \left[\sum_{i=1}^n d_i^2 - \frac{1}{n} \left(\sum_{i=1}^n d_i \right)^2 \right]^{1/2}$$

Table 5-2.

Suggested Meteorological Data Screening Criteria^a

Meteorological Variable	Screening Criteria ^a
Wind Speed	<ul style="list-style-type: none"> • Is less than zero or greater than 25 m/s; • Does not vary by more than 0.1 m/s for 3 consecutive hours; and • Does not vary by more than 0.5 m/s for 12 consecutive hours.
Wind Direction	<ul style="list-style-type: none"> • Is less than zero or greater than 360°; • Does not vary by more than 1° for more than three consecutive hours; and • Does not vary by more than 10° for 18 consecutive hours.
Temperature	<ul style="list-style-type: none"> • Is greater than the local record high; • Is less than the local record low; (The above limits could be applied on a monthly basis.) • Is greater than a 5° change from the previous hour; • Does not vary by more than 0.5°C for 12 consecutive hours.
Temperature Difference	<ul style="list-style-type: none"> • Is greater than 0.1°C/m during the daytime; • Is less than -0.1°C/m during the nighttime; and • Is greater than 5.0°C/m or less than -3.0°C/m.
Dew Point Temperature	<ul style="list-style-type: none"> • Is greater than the ambient temperature for the given time period; • Is greater than a 5°C change for the previous hour; • Does not vary by more than 0.5°C for 12 consecutive hours; and • Equals the ambient temperature for 12 consecutive hours.
Precipitation	<ul style="list-style-type: none"> • Is greater than 25 mm in one hour; • Is greater than 100 mm in 24-hours; and • Is less than 50 mm in three months. <p>(The above values can be adjusted base on local climate.)</p>
Pressure	<ul style="list-style-type: none"> • Is greater than 1,060 mb (sea level); • Is less than 940 mb (sea level); and <p>(The above values can be adjusted for elevations other than sea level.)</p> <ul style="list-style-type: none"> • Change by more than 6 mb in three hours.

^aSome criteria may have to be changed for a given location.

SOURCE: Reference 28

- The 95-percent probability limits for precision are:

$$\text{Upper 95 \% Probability Limit} = d_j + 1.96 \frac{S_j}{\sqrt{2}}$$

$$\text{Lower 95\% Probability Limit} = d_j - 1.96 \frac{S_j}{\sqrt{2}}$$

- The accuracy is calculated for the monitoring period by calculating the percent difference d_i between the indicated parameter from the audit (concentration, flow rate, etc.) and the known parameter, as follows:

$$d_i = \frac{Y_i - X_i}{X_i} \times 100$$

where: Y_i = monitor's indicated parameter from the i^{th} audit check; and
 X_i = known parameter used for the i^{th} audit check.

These results should then be compared with the QA/QC criteria stipulated in the monitoring plan to determine the validity of the data.

Resolution of Data Concerns

To support the resolution of data anomalies, records should be maintained to track raw data as it is reduced and validated to create intermediate data sets and reporting summaries. At any stage in this process, data flags may be appended to a measurement. The specific methods for flagging data may be manual or automatic; they depend on the program design and the sophistication of supporting software tools. Flags appended to data during validation may be reclassified or removed after the specific issues for that data point have been resolved in accordance with the corrective action procedures established for the program.

5.5

DATA REPORTING

Meteorological and air monitoring data summaries are prepared from validated database files. These reports summarize data for airborne pollutant concentrations at sample locations and facilitate the determination of exposure potentials.

Meteorological Data Summaries

Meteorological data summaries should contain at least the following information:

- Hourly averages for all meteorological parameters for the sampling period;
- Summary wind roses, including daytime and nighttime wind roses (for coastal or complex terrains);
- Data recovery summaries for each measured parameter;
- Summary of dispersion conditions for the sampling period;
- Tabular summaries of means and extremes for temperature and other parameters.

It is recommended that sequential hourly data be derived for the summary reports to keep data volumes down and avoid undue complications in evaluating the data. A one-hour time frame is enough to account for temporal variabilities in the measured parameters. For multistation sites, it may be useful to format the data in adjacent columns to facilitate manual comparisons. Data recovery target standards are 90% for meteorological parameters and are an initial reflection of data completeness and representativeness.

Statistical summaries by month, year, season, and for the monitoring period can be derived from the meteorological data summaries. Figure 5-2 depicts a useful format for representing wind rose summary data. For sites with diurnal wind patterns, separate wind rose summaries for daytime and nighttime conditions are recommended.

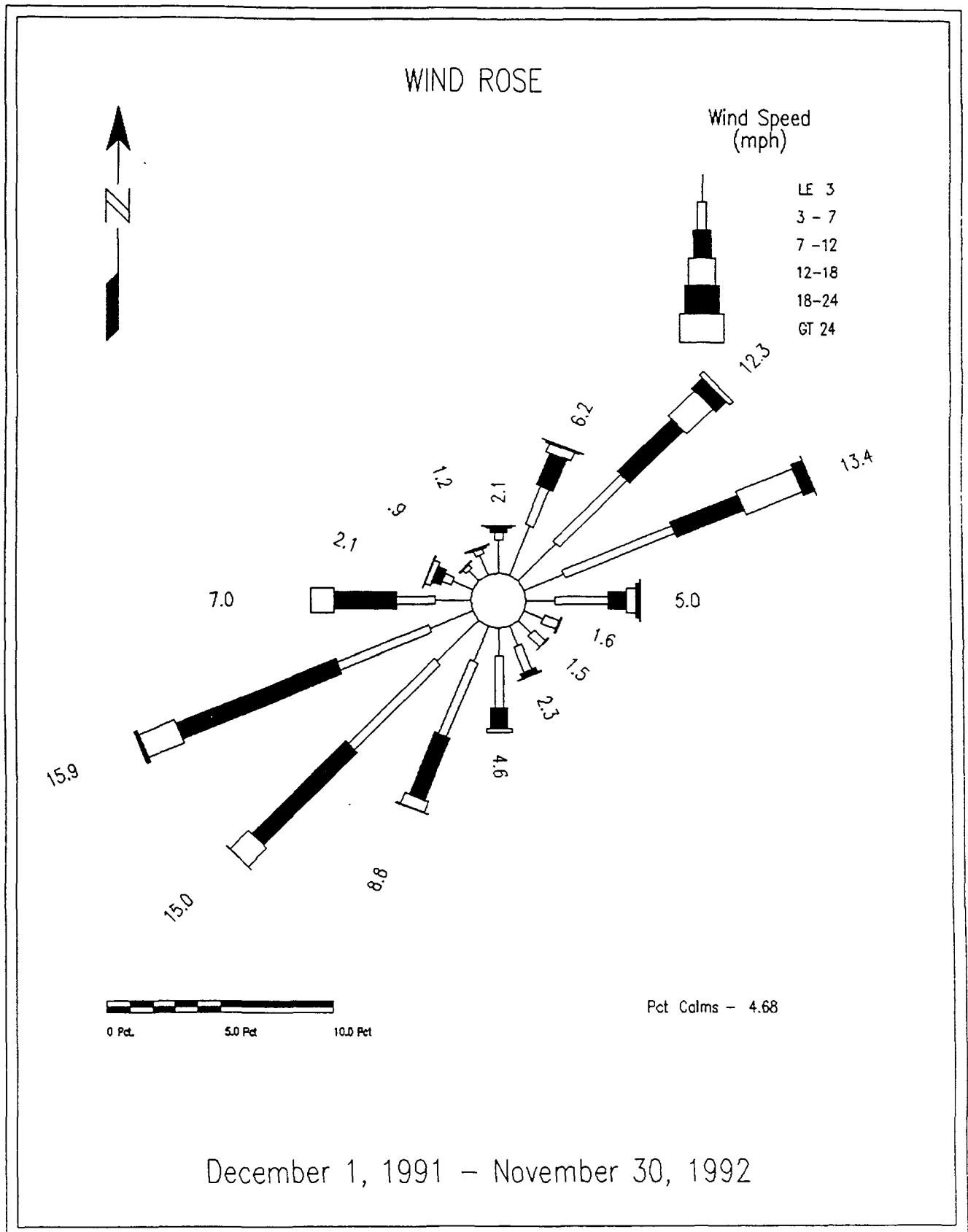


Figure 5-2. Sample Wind Rose Diagram

Air Data Summaries

Air data summaries list the concentrations of all monitored constituents by station and monitoring/sampling period. The summarized data should include method detection limits, undetected compounds, and upwind/downwind exposure classifications. Operational data for monitoring stations, such as sample flow rates, station numbers, and sampling duration should also be reported.

For each measured constituent at each monitoring station, the following data should be presented:

- Total number of samples;
- Data recoveries (target 80%);
- Mean, median, minimum, and maximum concentrations;
- Detection limits;
- Frequency above and below detection limits;
- Number of exceedances for QAPP-selected values; and
- Upwind and downwind exposure summaries.

The standard unit of measure for reporting air concentrations is micrograms per cubic meter, or parts per billion (ppb). It is also useful to include raw data used to derive concentration values, such as the duration of sampling event (unit time); the volume of sampled air (cubic meters); the temperature (degrees Fahrenheit); the pressure (mm Hg); and constituent content in the sample (micrograms). Upwind and downwind summaries, such as those shown in Figures 5-3 and 5-4, should be included for each monitoring station to support data interpretation. Upwind conditions are applied to background characterization, and concentrations measured downwind are applied to source-specific exposure assessments.

Further analyses or statistical treatment of these basic data are carried out to derive information for sample event and results summaries; relationships between sample events, unit operating efficiencies and meteorological conditions; and comparisons with background levels and other air emission sources. The air monitoring data summary typically includes a narrative discussion of sampling results and conclusions about the quality of the data set according to established data quality objectives.

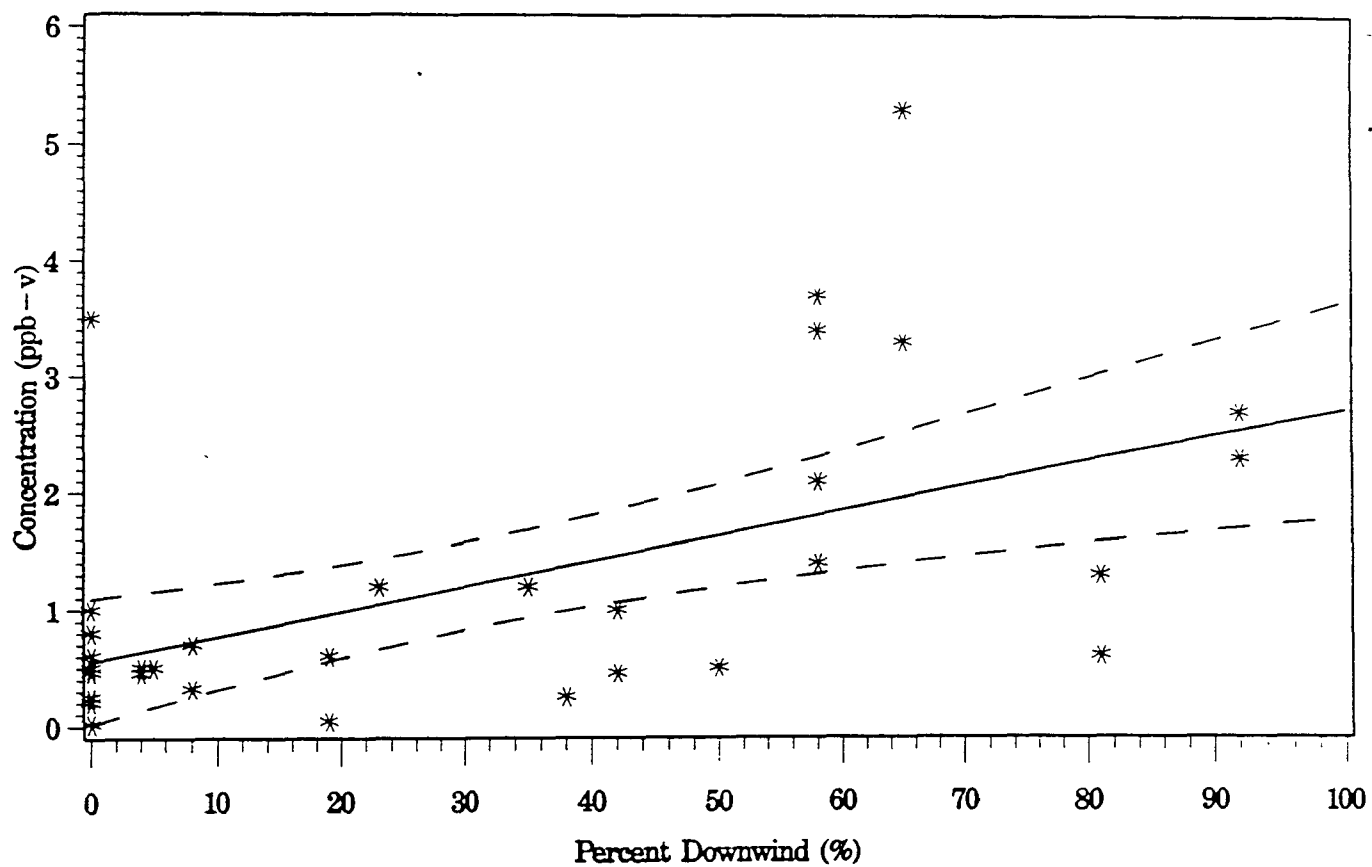


Figure 5-3. Regression Equation of Concentration versus Percent Downwind Overlayed with 95% Confidence intervals for the Mean

Reports

Data summaries are further reduced and validated to present statistical reports for the monitoring period and for monthly, seasonal, and annual ambient conditions. The information in final reports is used to support data interpretation and program decision-making. Concentration means and extremes, exceedances of health and safety criteria and other selected compliance thresholds, and data quality summaries are typically included in annual or final reports. These reports should be reviewed by knowledgeable individuals to validate the summary conclusions and to ensure that the data are accurately represented to avoid the possible misinterpretation of reported results

Data from AAM reports are often used to augment and validate air dispersion models, which aide in the interpretation and extrapolation of ambient concentration data to unmonitored on and off site locations. These data can be applied to health risk assessment models to determine the risk of exposure of site personnel and the surrounding community.

5.6 DATA USAGE

Ambient air monitoring data may be generated from a variety of sampling locations at Superfund sites, including personal (IH) samplers, and samplers situated at the work zone, site perimeter (fenceline), and off-site near sensitive receptors. These data may have several uses. The most common usage is to compare the measured air concentrations with short- or long-term action levels. Comparisons with short-term action levels can be done directly with individual data points. Any exceedance of short-term action levels may indicate that adverse exposures have occurred. Comparisons with long-term action levels can be done with individual data points, but more meaningful comparisons are made using data averages developed from weeks or months of data. Any exceedances may not necessarily indicate a problem, because long-term action levels typically are based on lifetime exposures. If the data trends show a consistent pattern of exceeding the long-term action levels, then some remedial action may be warranted.

Ambient air monitoring data frequently are used in conjunction with dispersion modeling results. The AAM data can be used to validate the model outputs for the specific site of interest. This is done by comparing measured ambient air concentrations to the concentrations predicted by an atmospheric dispersion model that uses the actual meteorological conditions present during the monitoring. Dispersion models are inherently conservative, so the model output will usually overpredict ambient concentrations. The degree to which the model over (or under) predicts will depend on site-specific factors. The degree of overprediction observed for the short-term dispersion modeling may be used, with limitations, as a correction factor when interpreting long-term dispersion modeling results. All of the above discussion, of course, assumes that the source term (i.e., emission rate) for the site is known.

AAM data can, under ideal conditions, be used to generate a source term for a site. This is done by modelling a unit emission rate (i.e., 1 g/sec) and ratioing the estimated downwind concentrations to the actual measured concentrations (measured/estimated). This ratio can then multiplied by the unit emission rate to yield a source term. If multiple sets of AAM data versus model output show a consistent ratio, then the estimated source term can be assumed to have less uncertainty than a ratio derived from a single data set. It may be difficult or impossible to estimate a source term using AAM data if multiple emission sources exist at the site, if the emission rate varies over timeframes that are shorter than the AAM duration, or if there are upwind emission sources.

AAM data obtained from OPM systems usually are in path-weighted units of ppm*meter or ug/m² and, therefore, are not directly comparable to typical action levels or health standards that are given in units of ug/m³ or ppm. This does not mean that the OPM data are not usable, only that the OPM data may require further data reduction before comparisons can be made. The most common data treatment is to divide the OPM data by pathlength to yield a path-averaged concentration (in ppm or ug/m³) along the path that is monitored. This average concentration is analogous to an average obtained from a line of point samplers. The OPM data, however, can not be used directly to determine if the mass of emissions was equally distributed along the beam path or if there were localized "hot

spots" of relatively high air concentrations. Such information can be obtained only if multiple OPM configurations are used; for example, different path lengths could be used and the measured concentrations compared to identify when contributions from any hot spots are observed.

OPM data also can be used to back-calculate a source term using one of several methods. If the emission plume is fully contained within the beam path, one need only determine the vertical dispersion to calculate the source term (see Reference 5). The vertical dispersion can be evaluated using a vertical array of point samplers, or it may be extrapolated from measurement of the wind direction standard deviation (σ_θ) by using Pasquill-Gifford stability classes and the associated dispersion curves. A second method is to use a tracer gas on the site. The tracer gas is released at a controlled rate. The path-weighted concentration of the tracer is measured at a downwind line. The simplest method of calculating a source term using a tracer gas is to ratio the measured concentrations of the tracer gas and the compound of interest and use this as a multiplier to the known emission rate of the tracer gas to obtain the emission rate of the compound of interest. This approach is limited by the degree to which the tracer release approximates the emission source and, in some cases, by differences in atmospheric transport between the tracer gas and the compound(s) of interest.

SECTION 6

ESTIMATION OF PROGRAM COSTS

The costs associated with conducting ambient air monitoring (AAM) at Superfund sites will depend on a number of issues, including:

- Objectives of the monitoring program;
- Target analyte list;
- Frequency of monitoring; and
- Duration of the AAM program.

The objectives of the AAM program will dictate the costs. Usually, monitoring objectives will involve some combination of documenting community exposure to ensure the protection of the surrounding community and documenting the exposure of on-site workers (industrial hygiene). Since these two primary objectives may involve significant differences in the sampling approach taken and in the type of equipment, as well as differences in analytical methodology, the differences in costs can be substantial. The air action levels (AALs) set for community exposure are normally much lower than equivalent AALs for on-site workers, since on-site workers can use personal protective equipment. Therefore, the evaluation of community exposure generally requires more sensitive monitoring and analytical methods, thus increasing the costs of this type of monitoring.

The number and type of target analytes selected will influence the types of analytical methods used and the detection limits that must be achieved; therefore, they may have a significant impact on program costs. Depending on the analyte and associated analytical method, analytical costs may run from as little as \$25 for the determination of lead on a high-volume filter to over \$2000 per PUF sample for dioxins and furans. Savings in analytical and data management costs can be achieved by selecting an appropriate subset of the compounds present at the site as target analytes, instead of monitoring for an extensive list of compounds.

The frequency of sample collection will have a significant effect on program costs. For long-term programs, these costs may easily out-weigh all other monitoring costs,

including capital equipment and operation costs. Depending on the estimated duration of the program, it may be more cost-effective to use automated real-time monitoring or to set-up an on-site laboratory than to use a more traditional approach of sending discrete samples to an off-site analytical laboratory. Data turnaround and laboratory responsiveness should also be factors in such a decision.

The duration of the monitoring program may influence the selection or implementation of sampling and analytical methods. For example, a more labor-intensive sampling approach might be considered for a three-week program than for a two-year program. In general, the longer the program the more cost-effective automated real-time monitoring becomes.

The cost estimates given in this section are based on the assumption that all capital equipment for a given application would be acquired for the program, regardless of the sampling duration. Although some ambient equipment can be leased (especially portable real-time monitors), many monitors are not readily available or, if they are, they have short recovery costs, such as 3-6 months.

Tables 6-1 through 6-3 present the estimated costs of an AAM program for volatile, semi-volatile, and inorganic compounds. Whenever possible, costs are provided on a per-unit or per-sample basis, both for equipment and analytical work. Other expenses, such as labor requirements for network operation and data management and reporting are given as estimated number of hours. The unit cost for labor and the actual labor hours themselves may vary significantly, depending on the level of personnel involved and the charge rates of the individuals or organizations actually performing the work. Therefore, these estimates are, at best, general guidelines.

Program costs will of course vary considerably depending on the area of the country, the availability of equipment manufacturers and suppliers, analytical laboratories and contractors. These estimates should only be used to try to estimate "ballpark" costs that may be associated with the start-up and execution of an ambient monitoring program. Of course,

RPMs/OSCs or their designates should get detailed price quotes to determine actual program costs before initiating or committing to an ambient monitoring program.

Site preparation costs also can vary considerably from site to site. These costs will depend on the distances involved and the complexity of providing electrical service to the monitoring location, on whether, and to what extent, site security needs to be provided for each monitoring location, and on what other types of preparation the site needs.

Normally, the acquisition of electrical power will be the most costly item associated with site preparation; therefore, if utility service is readily available, site preparation costs should be in the low range of the estimates given.

The costs of real-time analyzers can vary over more than an order of magnitude. The typical costs of selected categories of real-time monitoring equipment are given in Table 6-4.

Table 6-1
Estimated Costs for Implementing a VOC Air Monitoring Program

Cost Type	Cost Elements	Unit Costs (\$)
Capital Cost	Option 1 - Time-integrated whole-air canister sampling	
	Canister samplers	4000-12,000
	6-liter SUMMA® Canisters	500-800
	Packing crates for shipping canisters	100-300
	Option 2 - Time-integrated sorbent tube sampling	
	Sorbent tube samplers	500-10,000
	Sorbent tubes (per box)	50-250
	Option 3 - Automated fixed-location continuous analyzers	
	Analytical equipment	2,000-150,000
	Climate controlled shelters	8,000-15,000
	Spare parts (per location/station)	2,000-5,000
	Option 4 - Remote sensing systems (FTIR/UV-DOAS)	
	Analytical Equipment	> 100,000
	Climate Controlled Shelter	8,000-15,000
Start-up Costs	Develop Monitoring Plan	200-400 hours
	Equipment set-up/installation - includes utilities, site pad, manpower, etc. (per site)	2,000-15,000
	Operator Training	80-160 hours
Operational Costs	Option 1 - SUMMA® canister analysis	350-600
	Option 2 - Sorbent tube analysis	80-200
	Option 3 - Calibration supplies/expendables	3,000-5,000
	Quarterly field QA/QC audits (options 1, 2, & 3)	4,000-5,000
	Laboratory audit (options 1 & 2)	1,500-2,500
Data Management and Reporting	Data validation (per site/month)	20-40 hours
	Database processing and maintenance (per site/month)	20-40 hours
	Data interpretation and reporting (per site/month)	40-80 hours

Table 6-2
Estimated Costs for Implementing a SVOC Air Monitoring Program

Cost Type	Cost Elements	Unit Costs (\$)
Capital Costs	General Metal Works, PS-1 high-volume sampler	2000-2500
	PS-1 calibration kit	700-800
	Spare parts (per sampler)	150-250
	Glass Sampling Cartridges (need approximately 6/sampler)	75-100
Start-up Costs	Monitoring Plan Development	200-400 hours
	Equipment set-up/installation - includes utilities, site preparation (if required), and manpower (per site)	1,000-5,000
	Operator Training	40-80 hours
Operational Costs	Sampling media (including PUFs, sorbents, and filters) per cartridge includes preparation	100-250
	Analysis Costs (PCBs by GC/ECD)	150-250
	Analysis Costs (PCBs by GC/MS)	250-500
	Analysis costs (PCDDs/PCDFs by HRGC/HRMS)	1,800-2,400
	Analysis costs (PCDDs/PCDFs by medium resolution GC/MS)	800-1,00
	Analysis costs (organochloride pesticides by ECD)	150-250
	Analysis costs (organochloride pesticides by GC/MS)	250-500
	Analysis Costs (PAHs by HPLC)	150-250
	Analysis Costs (PAHs by GC/MS)	250-500
	Quarterly field QA/QC audit	4,000-5,000
	Quarterly laboratory audit	1,500-2,500
Data Management and Reporting	Data validation (per site)	20-40 hours
	Database processing and maintenance (per site/month)	20-40 hours
	Data interpretation and reporting (per site/month)	40-80 hours

Table 6-3
Estimated Costs for Implementing an Inorganic Compound
Air Monitoring Program

Cost Type	Cost Elements	Unit Costs (\$)
Capital Costs	High-volume air sampler (TSP)	1,800-2,500
	High-volume PM ₁₀ air sampler	4,000-4,500
	Spare parts (per sampler)	150-250
	Low/medium-volume air samplers	2,000-4,000
	Hardware for impinger sampling (CN)	500-1000
Start-up Costs	Monitoring Plan Development	200-400 hours
	Equipment set-up/installation - includes utilities, site preparation (if required), and manpower (per site)	1,000-5,000
	Operator Training	40-80 hours
Operational Costs	Sampling media - quartz or glass fiber filters	1-5
	Filter preparation/weighing	0.25-0.50 hours
	Filter digestion/analysis preparation	20-40
	Analysis Costs - ICP-AES analysis - depending on number of elements per scan	45-250
	Analysis Costs - AAS - per element	20-40
	Analysis costs - GFAAS - per element	20-40
	Analysis costs cyanide	40-100
	Quarterly field QA/QC audit	4,000-5,000
	Quarterly laboratory audit	1,500-2,500
Data Management and Reporting	Data validation (per site)	20-40 hours
	Database processing and maintenance (per site/month)	20-40 hours
	Data interpretation and reporting (per site/month)	40-80 hours

Table 6-4.
Summary of Information for Selected Classes of Real-Time Instruments

Measurement System	Gases Measured	Typical Cost
Electrochemical	T, C, O ₂ , THC, H ₂ S, CO	\$1,500
Total Hydrocarbon		
<i>Flame Ionization Detector</i>	THC, VOC, SVOC	\$4,000 - \$8,000
<i>Photoionization Detector</i>	VOC, SVOC	\$5,000
<i>Thermal Detector</i>	THC, H ₂	\$1,500
<i>Solid State</i>	THC, T, C	\$2,000
Colorimetric		
<i>Solid</i>	VOC, SVOC, THC, T, C	\$400
<i>Paper Tape</i>	O ₂ , T, C	\$5,000 - \$10,000
<i>Liquid</i>	T, Formaldehyde	\$6,000
Spectrophotometric		
<i>Nondispersive Infrared</i>	VOC, SVOC, T, HC	\$7,500
<i>Optical Remote Systems</i>	VOC, SVOC, THC, T, C	>\$100,000
Gas Chromatograph	VOC, SVOC, THC, T, C	\$14,000
Gas Chromatograph/Mass Spectrometer	VOC, SVOC, THC, T, C	>\$75,000
Particulate		
<i>Optical</i>	TSP	\$8,000
<i>Radiometric</i>	PM ₁₀	\$14,000

KEY:

C = Combustibles
 CO = Carbon Monoxide
 HC = Hydrocarbons
 H₂S = Hydrogen Sulfide
 O₂ = Oxygen
 PM₁₀ = Particles ≤ 10 microns diameter

SVOC = Semi-Volatile Organic Carbon
 T = Toxic Compounds
 THC = Total Hydrocarbons
 TSP = Total Suspended Particulates
 VOC = Volatile Organic Compounds

SECTION 7

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APPENDIX A

BIBLIOGRAPHY OF NTGS DOCUMENTS

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APPENDIX B

USEFUL CONTACTS AND TELEPHONE NUMBERS

APPENDIX B

USEFUL CONTACTS AND TELEPHONE NUMBERS

1. EPA Regional Offices

Each EPA regional office has the following staff positions:

- Air/Superfund Coordinator;
- ARARs Coordinator; and
- Air Toxics Coordinator.

The Air/Superfund coordinator is the best single point of contact for air issues related to Superfund Sites. The individuals in the staff positions listed above can be reached through the office switchboards at the following numbers:

Region	Location	Telephone Number
I	Boston	(617) 565-3420
II	New York	(212) 264-2657*
III	Philadelphia	(215) 597-9800
IV	Atlanta	(404) 347-3004
V	Chicago	(312) 353-2000
VI	Dallas	(214) 655-6444
VII	Kansas City	(913) 551-7000
VIII	Denver	(303) 293-1603
IX	San Francisco	(415) 744-1305
X	Seattle	(206) 442-1200

*Air Programs Branch x-2517

2. Air/Superfund Program Contact

The primary contact for the Air/Superfund program is Mr. Joseph Padgett of EPA's Office of Air Quality Planning and Standards at (919) 541-5589.

3. Document Ordering Information

Documents can be obtained through the National Technical Information Service (NTIS) at (703) 487-4650. Information of Air/Superfund reports that are not yet in the NTIS system can be obtained from Environmental Quality Management at (919) 489-5299.

Other sources of documents include:

- EPA's Control Technology Center (CTC) at (919) 541-0800;
- EPA's Center for Environmental Research Information (CERI) at (513) 569-7562; and
- U.S. Government Printing Office (USGPO) at (202) 783-3238.

4. Other Useful Contacts

Air and Waste Management Associates (412) 232-3444.

5. Hotlines

OAQPS TTN Modem # (919) 541-5742

The OAQPS TTN consists of the following:

Bulletin Board	Contact	Phone Number
AMTIC	Joe Elkins	(919) 541-5653
APTI	Betty Abramson	(919) 541-2371
CHIEF	Michael Hamlin	(919) 541-5232
CTC	Joe Steigerwald	(919) 541-2736
EMTIC	Dan Bivins	(919) 541-5244
OAQPS	Herschel Rorex	(919) 541-5637
SCRAM	Russ Lee	(919) 541-5638

AIRS Database	Andrea Kelsey	(919) 541-5549
BLIS Database (RACT/BACT/LAER)	Joe Steigerwald	(919) 541-2736
NATICH Database	Vasu Kilaru	(919) 541-0850
TOXNET	Information	(301) 496-6531
IRIS	User Support	(513) 569-7254

APPENDIX C

LIST OF VENDORS FOR ANALYTICAL AND SAMPLING EQUIPMENT

Electrochemical Systems

Vendor	Instrument	Gases Measured		
		THC	Toxics	Combustibles
AIM USA	Model 1100		Yes	Yes
AIM USA	Model 2000		Yes	
Bacharach Inc.	Sentinel 4			Yes
Bacharach Inc.	TLV Sniffer	Yes		
Bacharach Inc.	Model 505		Yes	Yes
Bacharach Inc.	Gas Pointer II			Yes
Bacharach Inc.	Sentinel 44		Yes	Yes
Bacharach Inc.	Sniffer 302			Yes
Bacharach Inc.	Sniffer 303			Yes
Biosystems, Inc.	Cannonball 2	Yes	Yes	Yes
CEA Instruments Inc.	TG-BA		Yes	
CEA Instruments Inc.	TG-KA		Yes	
Capital Controls Co. Inc.	Multipoint Gas Detector 1660		Yes	
Gas Tech Inc.	GX-86		Yes	Yes
Gas Tech Inc.	GX-91		Yes	Yes
Gas Tech Inc.	HS-91			Yes
Gas Tech Inc.	HS-91		Yes	Yes
Industrial Scientific Corp.	HS 560		Yes	
Industrial Scientific Corp.	CL 266		Yes	
Industrial Scientific Corp.	MX 251			Yes
Industrial Scientific Corp.	TMX 410		Yes	Yes
International Sensor Tech	Remote Link System III	Yes	Yes	Yes
Lumidor Safety Prod/ESP Inc.	Model MPU-16		Yes	Yes
Lumidor Safety Prod/ESP Inc.	Model MPU-44		Yes	Yes
Lumidor Safety Prod/ESP Inc.	Gas Pro SGM-1000		Yes	Yes
Lumidor Safety Prod/ESP Inc.	MPU-220 (Pump)		Yes	Yes
Lumidor Safety Prod/ESP Inc.	MPU-220 (Remote)		Yes	Yes
Metrosonics Inc.	PM-7000		Yes	
Sensidyne Inc.	SS-2000		Yes	

Abbreviations:

THC = Total Hydrocarbon
 O₂ = Oxygen

Total Hydrocarbon Systems: Flame Ionization Detectors

Vendor	Instrument	Gases Measured			
		VOC	S-VOC	THC	n-CH ₄
CSI	HC 5002C			Yes	
CSI	HC 5002C			Yes	
Eagle Monitoring	EM7000	Yes	Yes	Yes	
Eagle Monitoring	EM700	Yes	Yes	Yes	
Eagle Monitoring	EM7000	Yes	Yes	Yes	
Eagle Monitoring	EM700	Yes	Yes	Yes	
Foxboro Company	OVA-108	Yes	Yes	Yes	
Foxboro Company	OVA-88	Yes	Yes	Yes	
GOW-MAC Instrument Company	Model 23-500	Yes		Yes	
GOW-MAC Instrument Company	Model 23-500	Yes		Yes	
GOW-MAC Instrument Company	23500 TH Analyzer			Yes	
GOW-MAC Instrument Company	23500 TH Analyzer			Yes	
Heath Consultants	DP-III	Yes		Yes	
Heath Consultants	DP-IIM	Yes		Yes	
Heath Consultants	PF-II	Yes		Yes	
MSA Instrument Division	Model 1015A	Yes		Yes	
MSA Instrument Division	Model 1015H	Yes		Yes	
MSA Instrument Division	Gas Corder - FID	Yes		Yes	
MSA Instrument Division	Model 1015H	Yes		Yes	
MSA Instrument Division	Model 1015A	Yes		Yes	
Pace Environmental	JUM 109A			Yes	Yes
Pace Environmental	JUM - VE7			Yes	
Pace Environmental	JUM 3-100			Yes	
Pace Environmental	JUM 3-100			Yes	
Pace Environmental	JUM 3-300			Yes	
Pace Environmental	JUM 5-100			Yes	
Pace Environmental	JUM - VE7			Yes	
Pace Environmental	JUM 5-100			Yes	
Pace Environmental	JUM 3-300			Yes	
Pace Environmental	JUM 109A			Yes	Yes
Rosemount Analytical	400A			Yes	
Rosemount Analytical	404A			Yes	
Rosemount Analytical	402			Yes	
Rosemount Analytical	404A			Yes	
Rosemount Analytical	400A			Yes	
Rosemount Analytical	402			Yes	
Sensidyne Inc.	Portable FID	Yes			
Thermo Environmental	Model 51			Yes	
Thermo Environmental	Model 51			Yes	

Abbreviations:

VOC = Volatile Organic Compounds
S-VOC = Semi-Volatile Organic Compounds

THC = Total Hydrocarbons
n-CH₄ = Non-Methane Hydrocarbons

Total Hydrocarbon Systems: Photoionization Detectors

Vendor	Instrument	Gases Measured			
		VOC	S-VOC	THC	n-CH4
HNU Systems	DL-101	Yes	Yes	Yes	
HNU Systems	HNU 201	Yes	Yes	Yes	
HNU Systems	HNU 201-250	Yes			
HNU Systems	HNU 201	Yes	Yes	Yes	
HNU Systems	HW-101	Yes	Yes		
HNU Systems	PI-101	Yes	Yes		
HNU Systems	HNU 201-250	Yes			
HNU Systems	IS-101	Yes	Yes		
MSA Instrument Division	Model 1015C	Yes	Yes		
MSA Instrument Division	R-Photon PID	Yes		Yes	Yes
MSA Instrument Division	Model 1015C	Yes	Yes		
MSA Instrument Division	Gas Corder - PID	Yes	Yes	Yes	Yes
Photovac Inc.	Microtip	Yes	Yes	Yes	
Sentex Systems	Scentogun	Yes		Yes	
Thermo Environmental	Model 52	Yes	Yes		
Thermo Environmental	Model 580S	Yes	Yes	Yes	Yes
Thermo Environmental	Model 52	Yes	Yes		
Thermo Environmental	Model 580 B	Yes	Yes		

Abbreviations:

VOC = Volatile Organic Compounds
 S-VOC = Semi-Volatile Organic Compounds
 THC = Total Hydrocarbons

Total Hydrocarbon Systems: Others

Vendor	Instrument	Detector	Gases Measured				
			VOC	S-VOC	THC	Toxics	Combustibles
AIM USA	Model 1200	TD			Yes		
Bacharach Inc.	TLV Sniffer	EC, CB			Yes		
International Sensor Tech.	Remote Link System III	EC, SS			Yes	Yes	Yes
Matheson Gas Products	Model 805A	SS, TC, Plat	Yes	Yes	Yes	Yes	Yes
Matheson Gas Products	Custom Gas Det. Sys.	SS	Yes	Yes	Yes	Yes	Yes

Abbreviations:

VOC	=	Volatile Organic Compounds
S-VOC	=	Semi-Volatile Organic Compounds
THC	=	Total Hydrocarbons
TD	=	Tin Dioxide
EC	=	Electrochemical
SS	=	Solid State
TC	=	Thermal Conductivity
Plat	=	Platinum

Spectrophotometric Systems

Vendor	Instrument	Detector	Gases Measured					
			VOC	S-VOC	THC	Toxics	Combustibles	Others
CEA Instruments Inc.	RI-411A	NDIR						Yes
MSA Instrument Division	LIRA-3000	NDIR			Yes	Yes		
Milton Roy	Model 3300A	NDIR				Yes	Yes	
Rosemount Analytical Inc.	880A	NDIR			Yes	Yes		
Foxboro Company	MIRAN 203	IR	Yes	Yes				
Foxboro Company	MIRAN 1B-X	IR	Yes	Yes				
ABB Environmental	ER 130	UV	Yes	Yes		Yes	Yes	
ABB Environmental	ER 110	UV	Yes	Yes		Yes	Yes	
AIM USA	OPM	GFC	Yes	Yes		Yes	Yes	Yes
Anarad Inc.	AR9000	FTIR	Yes	Yes	Yes	Yes	Yes	
MDA Scientific Inc.	FTIR Remote Sensor	FTIR	Yes	Yes	Yes	Yes	Yes	
MIDAC Corporation	FTIR	FTIR	Yes	Yes	Yes	Yes	Yes	
Mattson Instruments Inc.	REA-FTIR	FTIR	Yes	Yes	Yes	Yes	Yes	
Nicolet Instrument Corp.	FTIR OPM	FTIR	Yes	Yes	Yes	Yes	Yes	
Brueel & Kjaer	Type 1302	IPA	Yes	Yes	Yes			

Abbreviations:

VOC	=	Volatile Organic Compounds
S-VOC	=	Semi-Volatile Organic Compounds
THC	=	Total Hydrocarbon
CO ₂	=	Carbon Dioxide
NDIR	=	Non-dispersive Infrared
IR	=	Infrared
UV	=	Ultraviolet
GFC	=	Gas Filter Correlation
FTIR	=	Fourier-Transform Infrared
IPA	=	Infrared Photoacoustic Absorption

Colorimetric Systems

Vendor	Instrument	Detector	Gases Measured					
			VOC	S-VOC	THC	Toxics	Combustibles	Others
CEA Instruments Inc.	TGM-555	Liquid				Yes		Yes
MDA Scientific Inc.	Portable 7100	Tape				Yes	Yes	Yes
MDA Scientific Inc.	TLD-1	Tape				Yes		
MSA Instrument Division	Detector Tubes	Solid	Yes	Yes		Yes	Yes	
Matheson Gas Products	Matheson-Kitagawa	Solid	Yes	Yes	Yes	Yes	Yes	
National Draeger Inc.	Detector Tubes	Solid	Yes	Yes	Yes	Yes	Yes	
Sensidyne Inc.	Detector Tubes	Solid	Yes	Yes	Yes	Yes	Yes	

Abbreviations:

VOC = Volatile Organic Compounds
 S-VOC = Semi-Volatile Organic Compounds
 THC = Total Hydrocarbon

Gas Chromatograph/Mass Spectrograph Systems

Vendor	Instrument	Detector(s)	Gases Measured				
			VOC	S-VOC	THC	Toxics	Combustibles
CMS Research Corporation	2000 Minicams Sys	FID,PID,FP	Yes				
Foxboro Company	OVA-128	FID	Yes	Yes	Yes		
HNU Systems Inc.	HNU 301-DP	FID,PID,UV,ECD	Yes	Yes	Yes		
HNU Systems Inc.	HNU Model 311 GC	PID,UV,ECD	Yes	Yes	Yes		
MSA Instrument Division	Model 8550	FID,PID,TCD,HID,ECD	Yes	Yes	Yes	Yes	
MSA Instrument Division	Model 1030A	FID			Yes		
MTI Analytical Instruments	Quad 400 gas analyzer	SS	Yes	Yes	Yes	Yes	Yes
MTI Analytical Instruments	P 200 Microgas Analyzr.	SS	Yes	Yes	Yes	Yes	Yes
MTI Analytical Instruments	M200 Microgas GC	SS	Yes	Yes	Yes	Yes	Yes
Microsensor Systems	MSI-301A	TCD	Yes				
Microsensor Systems	MSI-301E	TCD	Yes				
Microsensor Systems	MSI-301B	TCD	Yes				
Microsensor Systems	MSI-301	TCD	Yes				
Photovac Inc.	10-S Plus	PID	Yes	Yes	Yes		
Photovac Inc.	10-S Plus	PID	Yes	Yes	Yes		
Photovac Inc.	Snapshot	PID	Yes	Yes	Yes		
SRI Instruments Inc.	Model 8610 GC	FID,PID,FP,ECD,ELCD	Yes	Yes	Yes	Yes	Yes
Sentex Systems Inc.	Scentograph	PID,TCD,AID,ECD	Yes	Yes	Yes		
ABB Process Analytics	EnviroSpec 3000	MS	Yes	Yes	Yes	Yes	Yes
Extreal Corporation	Questor II Process MS	MS	Yes	Yes	Yes		
ELI Eco-Logic	Sims 500	MS	Yes	Yes			
Viking Instruments	2400-700	MS	Yes	Yes		Yes	Yes

Abbreviations:

VOC	=	Volatile Organic Compounds
S-VOC	=	Semi-Volatile Organic Compounds
THC	=	Total Hydrocarbons
FID	=	Flame Ionization Detector
PID	=	Photoionization Detector
FP	=	Flame Photometric
UV	=	Ultraviolet
ECD	=	Electron Capture Detector
TCD	=	Thermal Conductivity Detector
HID	=	Helium Ionization Detector
SS	=	Solid State
ELCD	=	Electrolytic Conductivity Detector
AID	=	Argon Ionization Detector
MS	=	Mass Spectrograph

Particulate Samplers

Vendor	Instrument	Detector
Anderson Samplers Inc.	FH 61 I-N Beta	Radiation-based Particulate Monitor
Climet Instrument Company	CI-4224	Opacity-based Particulate Monitor
Climet Instrument Company	CI-4120	Opacity-based Particulate Monitor
Climet Instrument Company	CI-7350	Opacity-based Particulate Monitor
Climet Instrument Company	CI-4124	Opacity-based Particulate Monitor
Climet Instrument Company	CI-4220	Opacity-based Particulate Monitor
Climet Instrument Company	CI-7300	Opacity-based Particulate Monitor
Climet Instrument Company	CI-7400	Opacity-based Particulate Monitor
Climet Instrument Company	CI-4100	Opacity-based Particulate Monitor
Climet Instrument Company	CI-4200	Opacity-based Particulate Monitor
Climet Instrument Company	CI-7600	Opacity-based Particulate Monitor
Climet Instrument Company	CI-7200	Opacity-based Particulate Monitor
Dasibi Environmental Corp.	PM-10 Beta Gauge	Radiation-based Particulate Monitor
MIE Inc.	FM-7400	Laser Fiber Detection
MIE Inc.	PDM - 3	Opacity-based Particulate Monitor
MIE Inc.	RAS-2	Opacity-based Particulate Monitor
MIE Inc.	RAS 3Ex	Opacity-based Particulate Monitor
MIE Inc.	RAM-1	Opacity-based Particulate Monitor
MIE Inc.	RAM-5	Opacity-based Particulate Monitor
Sensidyne Inc.	LD-1	Laser Light Scattering
Wedding & Associates	PM-10 Beta Gauge	Radiation-based Particulate Monitor

APPENDIX D

CASE EXAMPLE

NOTE: This case example is a slightly modified version of a case example originally published in "Guidance on Applying the Data Quality Objectives Process for Ambient Air Monitoring Around Superfund Sites (Stage III)".

D.1 BACKGROUND

This hypothetical Superfund site, located on the outskirts of an urban area, consists of approximately 180 acres. The fenced-in site property is mostly flat, covered by weeds and brushes 1 to 2 meters in height. Also, there is a continuous row of both deciduous and nondeciduous trees ranging from 18 to 23 meters in height, just inside the boundary fence. Figure 1 is a scaled map of the site.

Site records indicate that approximately 20,000 drums containing waste from local industries were buried here from 1959 until 1980. Most of the drums were buried in a single layer at a depth of about 2 meters. The 3-acre area marked "A" in Figure 1 designates where the drums were buried. The drums contain mainly spent solvents representing RCRA waste codes F001 through F006.

Some of the drums have leaked and contamination of soil and ground water is possible. This potential problem led to a Remedial Investigation/Feasibility Study (RI/FS) for the site. The remedial action selected following the RI/FS was to dig up the buried drums, pack them into larger drums labeled as containing hazardous waste, and transport them to a nearby hazardous waste facility. This remediation effort is expected to take 12 months of on-site activity based on an 8-hour, 5-day-a-week work schedule.

During the RI/FS, drums were disturbed and an unusual odor was detected at the house identified as receptor R1 in Figure 1. A measurement made with a total VOC instrument indicated that VOCs had been released into the air; therefore, monitoring will be necessary to detect any subsequent releases to the ambient air which would pose a threat to public health during remediation.

A State-operated meteorological monitoring station has been operating for a number of years outside the fenceline of this site (see Figure 1). Its location adjacent to the site is coincidental, but historical meteorological data such as wind speed, wind direction, rainfall, and temperature will be useful in designing the monitoring network. In addition, data from the nearest National Weather Service station could be used to provide supplementary information.

D.2 WASTE CHARACTERIZATION

There are no compound-specific air monitoring data available for this site. Therefore, to gain an understanding of which VOCs may be released to the atmosphere during remediation, it was necessary to determine the composition of the buried waste. The first step was to review the site records, which showed that the site contained waste codes F001 through F006. A list of VOCs contained within each waste code was obtained from 40 CFR, Part 261 (subpart D, paragraph 261.31 of Table 1). Physical property data were then used to rank the compounds according to their volatility (vapor pressure or Henry's Law constant) and their toxicity (carcinogen or noncarcinogen) to select target compounds.

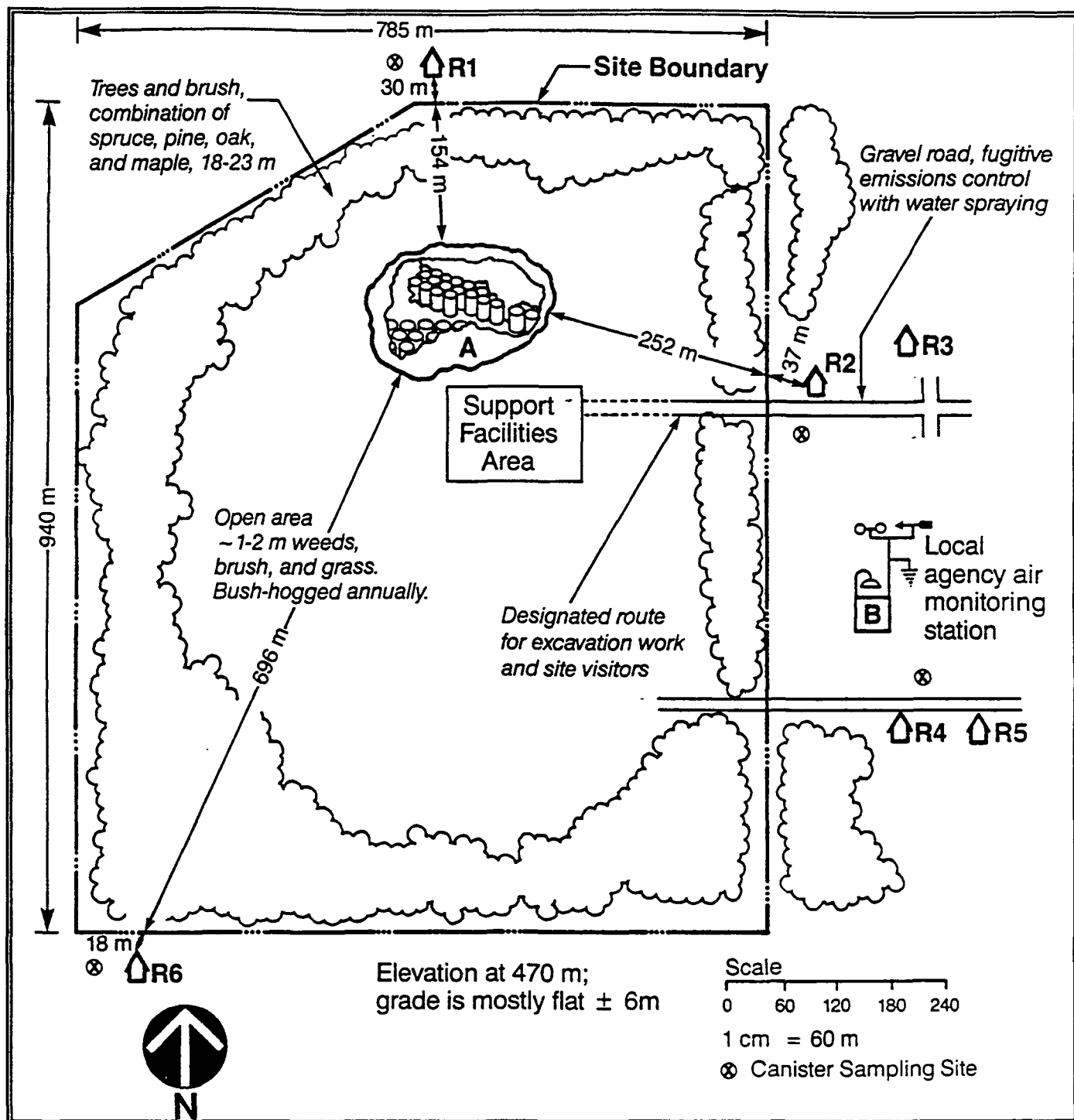


Figure 1. Hypothetical Superfund Site with Location of Buried Drums.

D.3 OVERVIEW OF AAM PROGRAM

The measurement system design consists of three monitoring strategies. First, modeling data indicated that in the absence of open pools of liquid waste, the probability of the residents at the receptor sites being exposed to VOC concentration levels of concern was very small. Thus, a single screening strategy was designed to provide the RPM/OSC with real-time information on total VOC concentrations near and downwind of the work site to allow timely initiation of emission control procedures when necessary.

The second element selected for the monitoring system design was a refined screening strategy. This strategy will be employed if the results from the screening work show that a preset criterion has been exceeded. The reason for implementing the refined screening strategy is to provide the RPM/OSC with real-time or near real-time concentrations of the six indicator compounds near and downwind of the work site. Since the concentration level of concern is different for each VOC, a knowledge of the individual VOC concentrations provides the RPM/OSC with more information to assess the risk of not initiating emission control actions than is available from the screening results. Also, this refined screening strategy provides total VOC concentrations at the impacted receptor site in real-time to allow for timely initiation of emission control actions and provide information on short-term exposure levels.

When on-site measurements from the screening and/or refined screening strategies exceed preset criteria (i.e., action levels), a third element of the monitoring system, a quantitative assessment strategy will be employed to provide the RPM/OSC with 8-hour average concentrations of individual VOCs at the receptor sites for that work day. The monitoring methods that are selected should have detection levels equal to or lower than the applicable action levels.

Procedures for selecting monitoring instrumentation for each of the three monitoring strategies are discussed separately by strategy in the following subsections. The selection process starts with a description of the performance and operational requirements of the monitoring instrument. This is followed by an overview of the commercially available instruments considered for this application. Finally, the instrument and associated apparatus selected for this application are discussed.

D.4 INSTRUMENT SELECTION

Instrument Selection for Screening Strategy

The primary function of the monitoring instrument for the screening strategy is to provide a continuous, real-time indication of VOC concentrations near and downwind of the work site. There are several commercially available VOC monitors that provide real-time data for total VOC concentrations.

The operational requirements and performance capabilities of an instrument for this application are as follows:

- Operate outside year-round.

- Operate continuously over an 8-hour work day without external electrical power.
- Be portable, easily carried by one person.
- Respond to all six indicator compounds.
- Have a detection limit of better than 1 ppm for isobutylene (the calibration gas).
- Be capable of recording the total VOC data over an 8-hour period.
- Not respond to interferences common to Superfund sites including methane, water, carbon dioxide, nitrogen, and oxygen.
- Be capable of visual or audible alarms at preset total VOC concentration levels.

There are a number of manufacturers marketing total VOC monitors. Each manufacturer usually specializes in a monitor with one of two possible detectors: a flame ionization detector (FID) and a photoionization detector (PID). Thus, the first decision in the instrument selection process was to decide on the appropriate detection technique. The PID responds to all six compounds with detection limits below the respective levels of concern (0.1 of the OSHA Permissible Exposure Limit). The FID does not respond to carbon disulfide. Also, a total VOC monitor equipped with a PID does not require a source of hydrogen gas as does a monitor equipped with an FID. The FID hydrogen-burning system requires more controls and a more complicated pneumatic system.

The instrument chosen for this task was a total VOC-PID monitor with the following capabilities:

- Designed to operate outside in the extremes of weather.
- Designed to operate continuously throughout the 8-hour work day with the use of an additional battery.
- Is portable, easily carried by one person, and easy to operate and maintain.
- Responds to all six indicator compounds at concentration below the respective levels of concern.
- Shows a detection limit of 0.1 ppm for the calibration gas, isobutylene.
- Incorporates advanced microprocessor technology for real-time digital or graphic data assessment and built-in data logging capability for storing data, including concentration with time and location.

- Does not respond to methane, water, carbon dioxide, nitrogen, and oxygen.
- Programmed to sound an alarm at predetermined total VOC concentrations.

Instrument Selection for Refined Screening Strategy

The refined screening strategy provides the RPM/OSC with near real-time concentrations of the six high-risk indicator compounds near the work site and total VOC concentrations at the impacted receptor site. Also, the refined screening strategy will provide information on the appropriateness of the six high-risk compounds selected as indicators. This strategy will provide tentative identification of unknown compounds released from the work site, serve to determine when to implement the quantitative assessment strategy, and provide guidance on when to submit the quantitative assessment sample for analysis by GC/MS to identify unknown compounds. This information is used to assess the seriousness of the emissions from the work site.

The instrument for providing total VOC concentrations at the receptor is a total VOC-PID. It was selected for the same reasons discussed in the screening strategy.

The operational requirements and performance capabilities of an instrument for providing near real-time concentrations of at least the six indicator compounds near the work site are as follows:

- Operate outside year-round.
- Operate continuously over an 8-hour work day without external electrical power.
- Be portable, easily carried by one person.
- Respond to all six indicator compounds.
- Have a detection limit of better than 1 ppm for benzene.
- Be capable of recording the total VOC data over an 8-hour period.
- Have a precision, expressed as a relative standard deviation, of 20% or better for each of the six indicator compounds at their respective levels of concern, and have a negligible bias.

There are a number of manufacturing marketing portable GCs which are equipped with one or more detectors. The four available detection techniques are argon ionization detector (AID), photoionization detector (PID), flame ionization detector (FID), and electron capture detector (ECD). The PID and AID respond to all six indicator compounds with detection limits below the respective levels of concern (0.1 PEL). The AID and PID provide similar responses for four of the six compounds with the AID having

superior sensitivity for the two remaining compounds. At least one of the six compounds result in minimal or no response using the FID and ECD detection techniques.

The detection technique chosen for this application is the AID because of its ability to respond to all six indicators. Once the detection technique was selected, recommendations were solicited from individuals with experience using the portable GC-AID in the field. One GC-AID monitor possessing all the required capabilities was reviewed and selected for this application. The instrument chosen was a portable GC-AID monitor with the following features:

- Designed to operate outside in the extremes of weather.
- Designed to operate on batteries and continue throughout the 8-hour work day.
- Is portable, easily carried by one person, and easy to operate and maintain.
- Responds to all six indicator compounds at concentrations below the respective levels of concern.
- Shows a detection limit of better than 0.1 ppm for benzene.
- Incorporates advanced microprocessor technology for near real-time data output. Data can be retrieved by either reviewing on a computer screen or connecting the GC-AID to a printer. The computer program provides peak identification of up to at least 9 peaks, calibration information, and concentrations of the 9 peaks.

Instrument Selection for Quantitative Assessment Strategy

The purpose of the quantitative assessment strategy is to document the ambient air 8-hour average concentrations that occurred at the receptors during the work day. Note that the total VOC-PID monitor described in the refined screening strategy provides real-time total VOC concentrations at the receptor site.

The operational requirements and performance capabilities of an instrument for this application include the following:

- It must collect a representative 8-hour sample year-round.
- It must provide data of sufficient quality (precision and bias) for meeting the DQOs.
- It must provide concentration results within one week of sampling.
- It must provide speciation of all VOC compounds identified in the liquid waste.

Sample collection can be conducted using either a sorbent or a stainless steel canister. Summa canisters and adsorbent tubes have both been successfully used for ambient air monitoring at Superfund sites. Both methods have their strengths, their applications, and their problems. Experienced users of both methods believe that they are capable of producing data of sufficient quality to satisfy the DQOs. For actual application, the selection would probably be based on the personal preference of the user. For this illustration, canister samplers serve as the selected method of collection 8-hour VOC samples.

To provide data of sufficient quality to satisfy the DQO, a laboratory GC is required for analysis of the canister samples. A GC with one or more of three detectors or a GC with mass spectrometry will provide the quality of data necessary. The three detectors generally available are PID, FID, and ECD; many times, more than one detector would be operated on the same GC (note the AID has lower detection limits but may not, at this time, be available in most laboratories). The PID responds to all six indicator compounds with detection limits below the respective levels of concern. For this application, the low detection limits are important since most of the VOC concentrations will be below the levels of concern. At least one of the six compounds provide minimal or no response using the FID or ECD detection techniques.

Since both systems GC/MS and GC-PID with confirmation by FID will reportably produce data of sufficient quality to satisfy the DQOs and have similar costs the selection is based on convenience. Because of a local laboratory equipped with and experienced in the use of GC-PID/FID, this becomes the method of choice for this application.

The selected system will use evacuated canisters to collect an ambient air sample and use GC-PID with confirmation by FID to analyze the ambient air sample. Ten percent of the samples will be subjected to GC/MS for qualitative confirmation. The primary criterion for subjecting a sample to analysis by GC/MS is an indication by the on-site portable GC-AID monitor that unknown compounds were released from the work site during that work day. These GC/MS analyses will be performed by a laboratory that does not use a perma-pure drier in the GC/MS sampling line because of the potential sample losses of methyl ethyl ketone and carbon disulfide. The canister will begin and end sampling under a vacuum (not using a sample pump) to minimize the potential of contamination. The canister analysis will be conducted by a laboratory with demonstrated experience. Demonstrated experience was documented by participating successfully in the EPA's audit cylinder repository program. Prior to initiating the remediation activities, the laboratory chose to analyze the canisters will demonstrate capabilities for analysis of at least the six indicator compounds.

The sampling system selected for this application will provide the following:

- A representative 8-hour sample;
- Detection limits of sufficient sensitivity;
- A precision of 20% RSD (relative standard deviation) with no overall bias to satisfy the DQOs; and

- Specification of all compounds expected to be emitted from the Superfund site.

D.5 MONITORING SYSTEM DESIGN

One function of this monitoring system is to provide the RPM and/or on-site coordinator (OSC) with data of sufficient quantity and quality to allow for timely initiation of emission control actions. These emission control actions should preclude exposing the subject population to VOC concentrations greater than the levels of concern. This function of the monitoring system will be partially accomplished by a screening strategy that employs a total VOC-PID monitor at the work site to provide real-time data on emissions from the site. In addition, if the screening strategy results show that total VOC concentrations exceed a preset level, a refined screening strategy is initiated. The refined screening strategy employs two instruments, a portable GC-AID near the work site to provide near real-time concentration values for the six high risk indicator compounds and a total VOC-PID at the receptor site to provide real-time total VOC concentrations. This limited speciation by the portable GC-AID will reveal the presence or absence of the high risk compounds. The presence of one or more of these compounds at preset concentration levels will be reason to alert the RPM/OSC to initiate emission control actions, and, under certain conditions, to shut down the remediation activity. The total VOC concentrations measured at the receptor site will also be used to alert the RPM/OSC if predetermined concentrations are exceeded.

Another important function of the monitoring system is to generate data necessary to preclude the RPM/OSC from unnecessarily slowing or stopping the remediation. This function is also fulfilled by using the refined screening strategy. As part of the refined screening strategy, the portable GC-AID is deployed to provide compound-specific data on the high risk compounds. For example, if the total VOC-PID monitor at the work site indicates a VOC concentration of 100 ppm, the RPM/OSC may be inclined to stop the remediation activity if, for example, the portable GC-AID indicates that the total 100 ppm is benzene, which has a PEL of 1 ppm. Conversely, the RPM/OSC would not be as concerned if the total 100 ppm was, for example, methyl ethyl ketone (which has a PEL of 200 ppm). Thus, this function of the monitoring system could be very important in the overall efficiency of the remediation program. Also, results from the portable GC-AID can be used to provide tentative identification of unknown compounds by comparing the observed relative retention time of an unknown peak against relative retention times that had been obtained for the more volatile, non-indicator compounds. The other part of the refined screening strategy involves deploying a total VOC-PID monitor at the nearest impacted receptor site. This total VOC-PID monitor at the receptor site will be used to inform the RPM/OSC that VOCs emitted at the work site are reaching the receptor site.

A third function of the monitoring system is to provide information of sufficient quantity and quality to assure the RPM/OSC, decision maker, and residents at the receptor sites that the DQOs were met. This function is fulfilled by the quantitative assessment strategy consisting of an evacuated canister that collects an 8-hour sample at the subject receptor site for subsequent analysis by laboratory GC-PID with FID confirmation. The precision, bias, and speciation capabilities of this procedure indicate that the DQOs will be satisfied for the compounds of interest for this Superfund site. Since real-time will not be available, the action levels should be reasonably conservative. There is conflicting data on

the stability of methyl ethyl ketone and carbon disulfide in canisters. For this illustration it is assumed that they are stable. Recent evaluation tests indicate that at least methyl ethyl ketone can be successfully collected in canisters.

A special characteristic of this site that has influenced the monitoring system design is that the fenceline around the site is lined with a row of full-grown trees, invalidating the customary procedure of monitoring at the fenceline. This factor, plus the closeness of the receptor sites to the fenceline, means that the sample must be collected at or adjacent to the receptor to be representative of the air at the receptor.

Based on the modeling data and to fulfill the three functions described above, three different monitoring strategies are being employed for this project.

- Screening at the work site for total VOC concentrations in real-time.
- Refined screening at the work site for near real-time concentrations of the six indicator compounds and at the receptor site for real-time concentrations of total VOCs.
- Quantitative assessment at the receptor site for integrated 8-hour averages of individual VOCs.

These monitoring strategies will be used together to guide the on-site personnel in applying emission control actions and to document off-site concentrations at the receptor sites.

Design for Screening Measurements

Screening is the least costly monitoring strategy, but provides the least amount of information. It does provide real-time data, however, allowing for a quick response to a problem should one occur. Screening is to be employed at the beginning of the project and/or work day and will continue until emissions from the work site result in a measured VOC concentration that exceeds a preset level. The monitoring system selected for screening is a total VOC-PID monitor. This monitor will serve dual roles. It will provide health and safety data and screening data for the potential off-site migration of VOCs emitted from the work site.

For the screening strategy, when not in conflict with health and safety monitoring, the total VOC-PID monitor will be positioned on a stable tripod 30 meters downwind of the work site and operated for the 8-hour work day. The monitor will be repositioned at least once an hour if necessary to remain in the plume center directly downwind of the work site. An on-site meteorological station will be used to gauge the direction of the emission plume from its source. In addition, wind socks will be located near major emission sources. (As needed, or when operation in the refined screening level, the total VOC-PID monitor can be used to evaluate upwind concentrations and/or to help the on-site personnel locate the exact emission source at the work site.)

Based on modeling data, the probability of experiencing VOC concentration levels of concern at any of the receptor sites is very low. Thus, this simple screening measurements may prove to be the only air monitoring required during the remediation program.

Screening results are available in real-time and are used to alert the on-site personnel to potential problems. Specifically, results from the total VOC-PID monitor based on preset criteria are used to:

- Alert the RPM/OSC that there is an emission source, allowing the source to be located and controlled if necessary;
- Alert the RPM/OSC to check the proper protective clothing is being worn;
- Direct the monitoring crew to initiate refined screening; and
- Direct the RPM/OSC to initiate emission control actions.

Design for Refined Screening Measurements

Refined screening is employed when a potential problem is indicated by the total VOC-PID response. Refined screening is more costly than screening, but it provides some compound-specific information, allowing the RPM/OSC to better evaluate the seriousness of the problem. The portable GC-AID monitor selected for refined screening can be programmed to identify and quantify at least nine compounds. The nine programmed compounds can be changed if unexpected compounds posing high risk to the resident population are identified during the clean-up process. Initially, the portable GC-AID monitor will be programmed to identify and quantify responses for the six indicator compounds. The total VOC-PID monitor for this strategy is in addition to the one used in the screening strategy. It provides the RPM/OSC real-time data on total VOC concentration at the impacted receptor site.

Refined screening is conducted with the portable GC-AID monitor positioned 30 meters downwind of the work site. The instrument must be calibrated and ready for operation at any time during the 8-hour work day. It should be capable of being placed on-site and generating data within 15 minutes. The portable GC-AID monitor will be repositioned as necessary, but at least once an hour (while refined screening is in effect) to stay in the plume center-line, directly downwind of the work site. An alternative approach to be considered is to set-up the portable GC-AID in the on-site laboratory and take syringe samples in the field for analysis in the laboratory.

The total VOC-PID will be located at the receptor site with the highest probability of being affected should a spill occur. This monitor will be used during the work day and after work hours on evenings when meteorological conditions indicate that there could be an atmospheric temperature inversion.

Concentration values for up to nine compounds are provided by the portable GC-AID approximately once every 10 minutes. These compound-specific data help the RPM/OSC know when to take action and the proper action to take.

Results from the portable GC-AID monitor based on preset criteria are used to:

- Notify the monitoring crew to go to the quantitative assessment strategy, or
- Notify the RPM/OSC to initiate emission control actions.

Design for Quantitative Assessment Measurements

Quantitative assessment strategy provides more compound-specific information than does refined screening. Results from the quantitative assessment strategy are directly applicable to the receptor site. The monitoring system selected for this level of monitoring includes the use of an evacuated canister to collect the sample and a laboratory GC-PID with FID confirmation for analysis. Also, at least 10% of the canister samples analyzed will be subjected to GC/MS for qualitative confirmation. Specifically, the downwind canister sample(s) collected on days that the portable GC-AID results indicate that unknown compounds were released from the work site will be subjected to GC/MS analysis to identify the unknown compounds.

For quantitative assessment, one or two receptor areas identified as having the greatest probability of being impacted (i.e., being downwind of the work site) will be instrumented with an evacuated canister sampling system. Meteorological information will be used to identify the site(s). In areas where two or more receptors are located, a sampling site will be selected so as to be representative of all these clustered receptors. Also, an upwind or parallel site will be selected and instrumented. On a predetermined schedule a co-located sampler will be placed at the receptor site most likely to be impacted as part of the QA program. The samplers must be in place and operating over the 8-hour work day. Results from the portable GC-AID and/or total VOC-PID, combined with meteorological data, will be used to determine if the collected sample will be forwarded to the off-site laboratory for analysis.

Results from analysis of quantitative assessment samples are not available until about two days after sample collection. Thus, the data will be used to develop a data base documenting VOC concentration levels experienced at one or more of the receptor sites for various work-site situations. For example, values for the ratio of the concentrations of an indicator compound at the work site and the receptor site for known meteorological and work site conditions (for example, multiple accidental spills) will be calculated. This information will assist the RPM/OSC in making decisions about the need for emission control actions under similar future work site conditions.

Results of quantitative assessment strategy based on preset criteria will be used to:

- Notify the RPM/OSC that remediation procedures must be changed to reduce emissions if levels of concern are regularly approached or frequently exceeded at one or more receptor sites.
- Notify the RPM/OSC that certain receptor sites must be evacuated before continuing remediation if the levels of concern are regularly exceeded in spite of attempted emission control procedures.
- Provide the RPM/OSC with accurate measures of VOC concentration levels experienced at receptor sites.

D.6 CRITERIA FOR EMPLOYING A MONITORING STRATEGY

The criteria for moving from one strategy to another is based on measured VOC concentrations. In the absence of VOC ambient air measurement data, the criteria are purposely set to error on the side of safety. These criteria will be re-evaluated and changed if necessary as monitoring data become available. The criteria are discussed for each strategy in the following subsections.

The screening strategy is to be employed at the beginning of each work day, unless experience has shown that the remedial activity will result in emission levels that trigger the need for refined screening. The criterion for moving up to the refined screening strategy is any time the total VOC response exceeds 5 ppm for 10 consecutive minutes. This is also the safety criterion for changing from Level C to Level B dress for on-site workers.

Moving from the refined screening strategy back to the screening strategy is accomplished by simply discontinuing the use of the portable GC-AID. The criterion for this move is when the total VOC-PID response has been below 5 ppm for two consecutive hours after the incident that triggered the need for refined screening.

The rationale for the criterion of 5 ppm VOC for 10 consecutive minutes (in addition to it being the safety criterion) follows: benzene, identified as posing the highest risk from the list of compounds in the buried waste, has a PEL of 1 ppm. If, for example, the refined screening results showed the 5 ppm VOC measurement to be 5 ppm benzene, then the RPM/OSC will be notified to initiate emission control actions. Likewise, if the 5 ppm VOC was shown to be 5 ppm methyl ethyl ketone, which has a PEL of 200 ppm, the remediation activity could proceed unimpeded.

The refined screening strategy is employed whenever the total VOC-PID response has exceeded 5 ppm for more than 10 consecutive minutes, or at the beginning of the work day if experience indicates a high probability that initiation of remediation will result in screening results greater than 5 ppm.

The quantitative assessment strategy is implemented in the event that results from either the on-site portable GC-AID or the total VOC-PID monitor located at the receptor site exceed preset values. The quantitative assessment strategy is then initiated (that is, one or both of the downwind canister samples (plus the upwind, co-located and trip blank samples) is forwarded to the laboratory for analysis at the end of the 8-hour work day) if the calculated E_m is greater than 1 for 30 minutes or more during the work day.

A second criterion, independent of the portable GC-AID result, is based on total VOC measurements at the receptor site. The quantitative assessment strategy is initiated if the refined screening strategy results show total VOC concentrations greater than 0.5 ppm for 30 minutes or more during the work day.

These criteria are subjective; however, compound concentrations giving an equivalent exposure value greater than 1 occurring 30 meters downwind of the work site may result in measurable levels at the impacted receptor site(s). Also, a total VOC concentration of 0.5 ppm, corrected for background levels, signal the need for application of emissions control actions at the work site.

The reason for having two criteria, one based on total VOC and one on compound-specific results, is that the total VOC concentration may represent compounds other than the six indicator compounds. The quantitative assessment strategy would identify and quantify all VOCs present at or above detection limit concentrations at the receptor site.

Criteria for taking actions based on screening strategy results follow:

- If the total VOC-PID response is 5 ppm or greater for 10 successive minutes, alert the RPM/OSC that there is an emission source so that the source may be located and controlled as necessary.
- If the total VOC-PID response is 5 ppm or greater for 10 successive minutes, alert the RPM/OSC to check that proper protective clothing is being worn.
- If the total VOC-PID response is 200 ppm or greater for 10 successive minutes, alert the RPM/OSC that emissions must be reduced within the next 30 minutes or halt the remediation activity. (This applies only if the monitoring staff for some reason has been unable to initiate the refined screening strategy in this time period.)

The rationale for the criterion of 5 ppm total VOC is that benzene could account for the major portion of the VOC measurement. Benzene has a short-term exposure limit (STEL) of 5 ppm; thus, the on-site workers would be alerted to wear the proper protective clothing. Also, a potential 5 ppm concentration of benzene 30 meters downwind of the work site may result in a concentration near the level of concern (100 ppb) at one of the receptor sites.

The rationale for the criterion of 200 ppm for 10 successive minutes is that on-site VOC concentrations at this level will probably result in measurable VOC concentrations off-site.

The compound-specific information provided by the portable GC-AID monitor is used to guard against allowing one or more of the high risk compounds to reach the receptor site at concentration levels near one tenth of their respective PELs.

There are two criteria for initiating emissions control actions based on refined screening data. The two should be evaluated separately, that is action must be taken should either one be exceeded. The criterion for emission control actions follows:

- The RPM/OSC is notified that emissions must be reduced within 30 minutes or remediation will have to be halted if the portable GC-AID monitor response results in a calculated E_m greater than 1 for 10 successive minutes.
- The RPM/OSC is notified that emissions must be reduced within 30 minutes or remediation will have to be halted if the total VOC-PID monitor at the receptor site shows a concentration of 0.5 ppm or greater for 10 successive minutes.

The rationale for the criterion of $E_m \geq 1$ for 10 successive minutes is that one or more of the six indicator compounds could be present at concentrations near their respective PEL which could result in receptor site concentrations near the levels of concern. A total VOC concentration of 0.5 ppm at the receptor site is one tenth of the work site criterion of 5 ppm for moving from Level C to Level B protective clothing. This is the same rationale used for establishing the level of concern at one tenth of the PEL.

Quantitative assessment results directly estimate the health risks experienced by residents at the receptor sites. Thus, these results are used by the RPM/OSC to assess when the remediation process being used needs to be changed so that emissions are reduced.

Criteria for taking action based on quantitative assessment strategy results follow:

- The RPM/OSC is notified that remediation procedures must be changed to reduce emissions if any compound identified routinely approaches or exceeds 0.1 PEL, or that the remediation activity must be halted.
- The RPM/OSC is notified that a certain receptor site must be evacuated during the 8-hour work day when meteorological information indicates that it will be in the plume's path and if results have shown one or more compounds to exceed 0.2 PEL under similar meteorological conditions. Otherwise, the remediation activity must be halted.

These above criteria of 0.1 PEL and 0.2 PEL are used here because they are the concentration levels of concern (0.1 PEL) and the concentration level at which the decision maker stated that the monitoring system should be such that the probability of a false negative is no greater than 1 percent.

D.7 ESTIMATED TOTAL LABOR AND COST

In Stage I of the DQO, the following resources were made available for this ambient air monitoring effort:

- A mobile laboratory to be placed on-site for the duration of the clean-up operation.
- Equipment necessary for cleaning the SUMMA® canisters in the on-site laboratory.
- Two monitoring technicians to be dedicated to this air monitoring effort (i.e., 2 FTEs).

The monitoring effort is estimated to require a total work force of 3 FTEs. Thus, one FTE will be required in addition to the two provided by the ESD. It is important to not over-commit the on-site workers because concentrated monitoring activities could occur at any time and the monitoring staff needs to be prepared. The three monitoring personnel will probably have to stagger their shifts in order to fully service the three monitoring systems before and after the work day. That is, the two total VOC-PID monitors and the portable GC-AID must be calibrated before and after each work day. Also the canisters must be deployed and the samplers set to take a sample spanning the 8-hour work day. Costs have been estimated for each monitoring strategy and are based on the assumption that the refined screening and quantitative assessment strategies will be required infrequently.

Individual costs estimates listed below are only for illustrating the process. The individual item costs are believed to be reasonable but they do not represent actual quotes from manufacturers or contractors nor is the listing presented as a comprehensive list.

<u>Project Planning</u>	
<ul style="list-style-type: none"> • DQO Package - Sampling and analysis plan - Quality assurance project plan - Summary work plan 	\$ 75,000
Subtotal:	\$75,000
<u>Manpower</u>	
<ul style="list-style-type: none"> • One technician (1 FTE) (estimated at \$2,500 per week for 52 weeks this includes per diem, overtime, etc.) 	\$130,000
Subtotal:	\$130,000
<u>Screening Strategy Costs</u>	
<ul style="list-style-type: none"> • Purchase price of total VOC-PID monitor • Supplementary field kit • Supplementary battery • Replacement battery • Replacement lamp • Inlet filters (5) • Calibration standard 	\$ 4,500 600 300 300 215 25 500
Subtotal:	\$ 6,440
<u>Refined Screening Strategy Costs</u>	
<ul style="list-style-type: none"> • Purchase price of portable GC-AID monitor • Spare parts and filters • Calibration standard and carrier gas for portable GC-AID • Purchase price of total VOC-PID monitor and needed supplies 	\$ 20,500 525 3,100 6,440
Subtotal:	\$30,565
<u>Quantitative Assessment Strategy Costs</u>	
<ul style="list-style-type: none"> • Purchase price of canister sampler (4) • Purchase price of 34 canisters • Canister analysis by GC-PID/FID at \$500 per sample (130) • Canister analysis by GC/MS at \$1,000 each (5 assumed) 	\$ 20,000 25,000 65,000 5,000
Subtotal:	\$115,000
GRAND TOTAL:	
\$357,005	

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16. ABSTRACT <p>This report presents the results of an EPA-sponsored study to develop guidance for designing and conducting ambient air monitoring at Superfund sites. By law, all exposure pathways - including the air pathway - must be evaluated for every Superfund site; therefore, some level of ambient air monitoring usually is necessary at each site.</p> <p>This document offers technical guidance for use by a diverse audience, including EPA Air and Superfund Regional and Headquarters staff, State Air and Superfund staff, federal and state remedial and removal contractors, and potentially responsible parties. This manual is written to serve the needs of individuals with various levels of scientific training and experience in selecting and using ambient air monitoring methods in support of air pathway assessments.</p> <p>There is no universal approach to conducting an ambient air monitoring program that would satisfy the needs of every air pathway assessment. Instead, each program should be designed to match the specific program needs and available resources. A framework for designing an effective ambient air monitoring is presented in the document. The framework parallels earlier EPA guidance on applying the Data Quality Objectives Process for ambient air monitoring around Superfund sites.</p>					
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