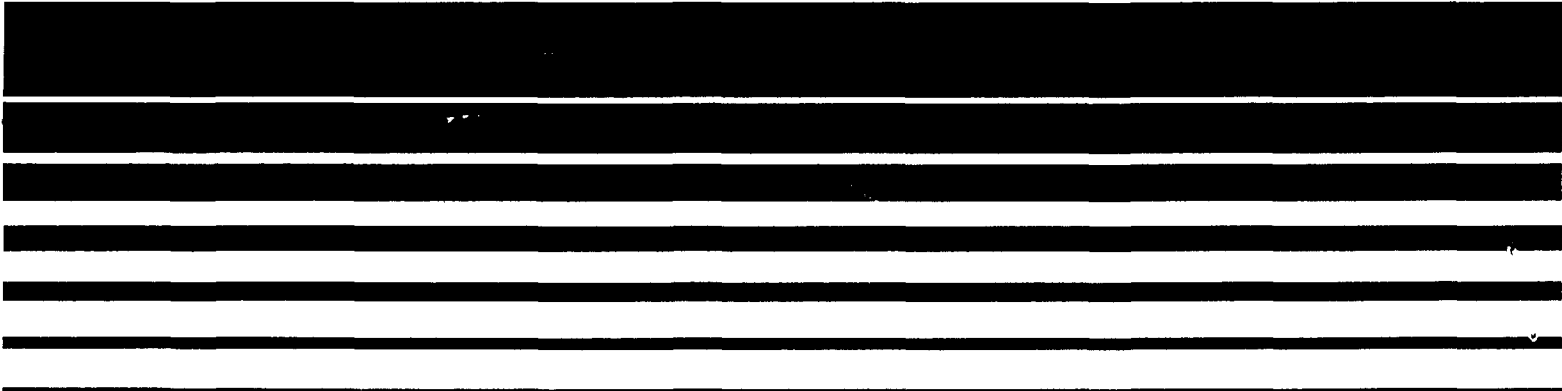

Air/Superfund



AIR/SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES

Applicability of Open Path Monitors for Superfund Site Cleanup



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FOR SUPERFUND SITE CLEAN-UP

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FINAL REPORT

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EXECUTIVE SUMMARY

This document provides guidance on the applicability of Open Path Monitors (OPMs) for ambient air monitoring at Superfund sites. OPMs are a subgroup of Optical Remote Sensors (ORSs) which are a group of spectroscopic techniques that may have application to environmental monitoring. The relatively limited use of these devices for ambient air monitoring has led to many questions concerning their applicability, reliability, and sensitivity for these applications. OPMs are still undergoing development and the instrumentation and associated software are being refined, but there is a current need for guidance to help determine when an OPM may be suitable for Superfund applications.

The actions undertaken during the Superfund clean-up process are divided into three phases: pre-remediation, remediation, and post-remediation. Each phase may consist of several steps. This document discusses the specific ambient air monitoring (AAM) needs during each step. Guidance is provided for the suitability of OPMs for use during each of these steps based on the typical goals, emission levels, data quality objectives, etc.

Information is provided as to the general capabilities of OPMs. More specific information is presented for the three most widely used OPMs for AAM applications: Fourier transform infrared (FTIR) spectrometry, ultraviolet-differential absorbance spectrometry (UV-DOAS), and gas filter correlation (GFC) spectrometry. The compounds that each method is capable of detecting are tabulated. The detection limits of each type of instrument are discussed and compared to the detection limits achievable using conventional AAM techniques such as EPA Method TO-14 as well as to short-term and long-term health-based action levels. The data turnaround time and the ability to resolve temporal variations in emissions are also discussed.

The steps of the Superfund process where OPMs are generally applicable are identified. OPMs are not considered generally applicable for use during the Site Investigation, Remedial Investigation, and Operation and Maintenance steps of the Superfund process. The typical monitoring goals and the baseline emission levels during these steps dictate that more sensitive monitoring methods be employed. OPMs, however, may be well-suited for use during the Emergency Response, Feasibility Study and Remedial Action steps. Emissions are likely to be much higher than baseline levels during these activities. Also, the variability in the emission rate and potential exposure of downwind receptors are usually the dominant concerns and OPMs offer certain advantages over conventional AAM methods with regards to addressing these concerns.

Conventional point monitoring methods and OPMs each have relative advantages and limitations that must be considered when selecting a monitoring approach. No single approach is always going to be the best approach for a given type of site or for activities over the lifetime of a given site. The use of a combination of conventional and open path monitoring techniques may offer the best potential of meeting the monitoring needs for various Superfund applications.

ACRONYMS LIST

AAM	Ambient Air Monitoring
APA	Air Pathway Assessment
BTXE	Benzene/Toluene/Xylene/Ethylbenzene
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CF ₄	Carbon Tetrafluoride
CPM	Conventional Path Monitor
DQO	Data Quality Objective
DIAL	Differential Absorbance LIDAR
DL	Detection Limit
ECD	Electroconductivity Detector
EM	Electromagnetic Spectrum
EPA	Environmental Protection Agency
ER	Emergency Response
FGC	Field Gas Chromatographs
FID	Flame Ionization Detector
FS	Feasibility Study
FTIR	Fourier Transform Infrared Spectrometry
GC	Gas Chromatography
GC/MD	Gas Chromatography-multiple Detectors
GC/MD-MS	Gas Chromatograph/multiple Detectors-mass Spectroscopy
GC/MS	Gas Chromatography-mass Spectroscopy
GFC	Gas Filter Correlation Spectrometry
HRS	Hazardous Ranking System
IR	Infrared
LC	Liquid Chromatography
LIDAR	Light Detection and Ranging
LIF	Laser Induced Fluorescence
LOQ	Limit of Quantitation
MDL	Method Detection Limit
MS	Mass Spectrometry
NPL	National Priorities List
NTG	National Technical Guidance
O&M	Operations and Maintenance
OAQPS	Office of Air Quality Planning and Standards
OP-FTIR	Open Path-FTIR
OPMs	Open Paths Monitors
ORSs	Optical Remote Sensors
OVA	Organic Vapor Analyzers
PA	Preliminary Assessment
PAH's	Polycyclic Aromatic Hydrocarbons
PCB's	Polychlorinated Biphenyls
PICs	Products of Incomplete Combustion
PID	Photoionization detector
PM	Particulate matter

ACRONYMS LIST
(Continued)

RA	Remedial Action
RD	Remedial Design
RI	Remedial Investigation
ROD	Record of Decision
RPMs	Remedial Project Managers
SARA	Superfund Amendment and Reauthorization Act
SI	Site Investigation
SITE	Superfund Innovative Technology Evaluation
SODAR	Sound Detection and Ranging
SVOC	Semi-Volatile Organic Compounds
THC	Total Hydrocarbon
UV	Ultraviolet
UV-DOAS	Ultraviolet Differential Absorbance Spectrometry
VOC	Volatile Organic Compounds

SECTION 1

INTRODUCTION

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 impacts 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 that relate to the Air/Superfund program, including preparation of national technical guidance (NTG) documents. Since the Air/Superfund program was initiated in 1987, a number of NTG documents have been prepared, including a four-volume set of guidance documents¹⁻⁴. Volume IV of this set provides information about air monitoring at Superfund sites. Since preparation of that document, however, the use of spectroscopic methods for air monitoring has undergone rapid development, and these methods are not adequately described in the guidance documents.

Open Path Monitors (OPMs), are a group of spectroscopic techniques that apply to environmental monitoring. Specifically, OPMs are spectroscopic instruments configured to monitor the open air over extended paths (e.g., paths on the order of hundreds of meters). They rely on the interaction of light with matter to obtain information about that matter. Since most OPMs are incapable of determining the location of species along the path, the data obtained are of a path-weighted variety. For example, measurements are reported as concentration*path length (or ppm*meter). While these units may at first appear odd, they provide information that is at least as useful as data from conventional point samplers or monitors.

The relatively limited use of these devices in the past for monitoring ambient air has led to many questions about their applicability, reliability, and sensitivity for these applications. Open path monitoring is still undergoing development and the

instrumentation and associated software are being refined, but there is a current need for guidance to help Superfund Remedial Project Managers (RPMs) and other decision-makers determine when an OPM may be suitable for Superfund applications^{5,6}.

For the Superfund Program, the potential advantages of OPMs compared with more conventional air monitoring approaches are several: 1) There is rapid, essentially real-time data analysis that can be used to determine action-level exceedences on site; 2) no sample collection is required in the normal sense of the term; and 3) data are path-weighted concentrations rather than concentrations for specific sampling points, which allows source terms to be directly determined. These advantages will be discussed in detail later in this document.

This document discusses the capabilities of OPMs and compares them with conventional point monitoring approaches, such as sorbent tube samplers and evacuated canisters. Continuous, total hydrocarbon (THC) ambient air monitoring (AAM) methods are considered to be less applicable to Superfund sites; therefore, their relative advantages and limitations compared to OPMs are not discussed. The use of OPM and conventional AAM methods for the simultaneous detection of multiple VOC and SVOC compounds is stressed, since information about the ambient concentrations of individual compounds is needed for risk assessment purposes.

The goals of this document are twofold. The first is to provide guidance on the appropriate use of OPMs. This is accomplished by explaining their operational characteristics and describing the relative strengths and weaknesses of various OPMs. The second goal is to provide information on the types of OPMs (e.g., FTIR, UV-DOAS) that are best suited for a specific application. This is primarily accomplished by presenting expected field detection limits for various OPMs and compounds of potential interest.

A related document is being prepared that provides guidance on structuring an Open Path-FTIR (OP-FTIR) monitoring program⁷. Similar documents for other types of OPMs will be prepared in the future if needed.

It is assumed that the reader has only a limited knowledge of spectroscopy in general, and open path monitoring in particular. It is also assumed that the reader is conversant with the major issues related to ambient air monitoring (AAM) using conventional approaches, meteorological monitoring, dispersion modeling, and the assessment of AAM and meteorological data. Volume IV of the NTG series⁴ provides an introduction to these topics for readers requiring further information. Furthermore, it is assumed that the reader is familiar with emission rate measurements using conventional approaches. Volume II of the NTG series² provides an introduction to this topic.

SECTION 2

SUMMARY OF RESULTS

The Superfund process consists of three phases: pre-remediation, remediation, and post-remediation. Each of these phases involve several actions or steps that are undertaken to ensure that the site is cleaned up in a controlled manner. Monitoring or other air pathway assessment activities may be needed during the course of these actions. Figure 2-1 shows the various phases of the Superfund process and indicates those steps where the use of OPMs are most likely.

The past several years have seen an increased application of Open Path Monitors (OPMs) to both Superfund and industrial sites. However, this use has been limited and a number of questions remain about the applicability, reliability, and sensitivity of OPM systems. Although OPMs are still undergoing development, there is a current need for guidance to answer these questions and to help users determine when an OPM may be suitable for Superfund applications. This document contains information on the current state of development of various open path monitoring methods, the air monitoring data quality objectives associated with the remediation of Superfund sites, and when an OPM may be a viable option to meet those air monitoring needs.

Since all Superfund sites are unique, this document presents a process for selecting the appropriate AAM tool rather than absolute recommendations. This process considers the following questions:

- 1) What are the goals of the monitoring during this action? For example, is the goal to determine an absolute concentration or is the goal to determine emission rates for use in determining receptor exposure?
- 2) What are the data quality needs? Is screening (qualitative) data adequate or does quantitative information need to be obtained?
- 3) What are the requirements for data turnaround? Is there a concern that short-term action levels may be exceeded?

Phases of the Superfund Process Where Air Monitoring is Conducted

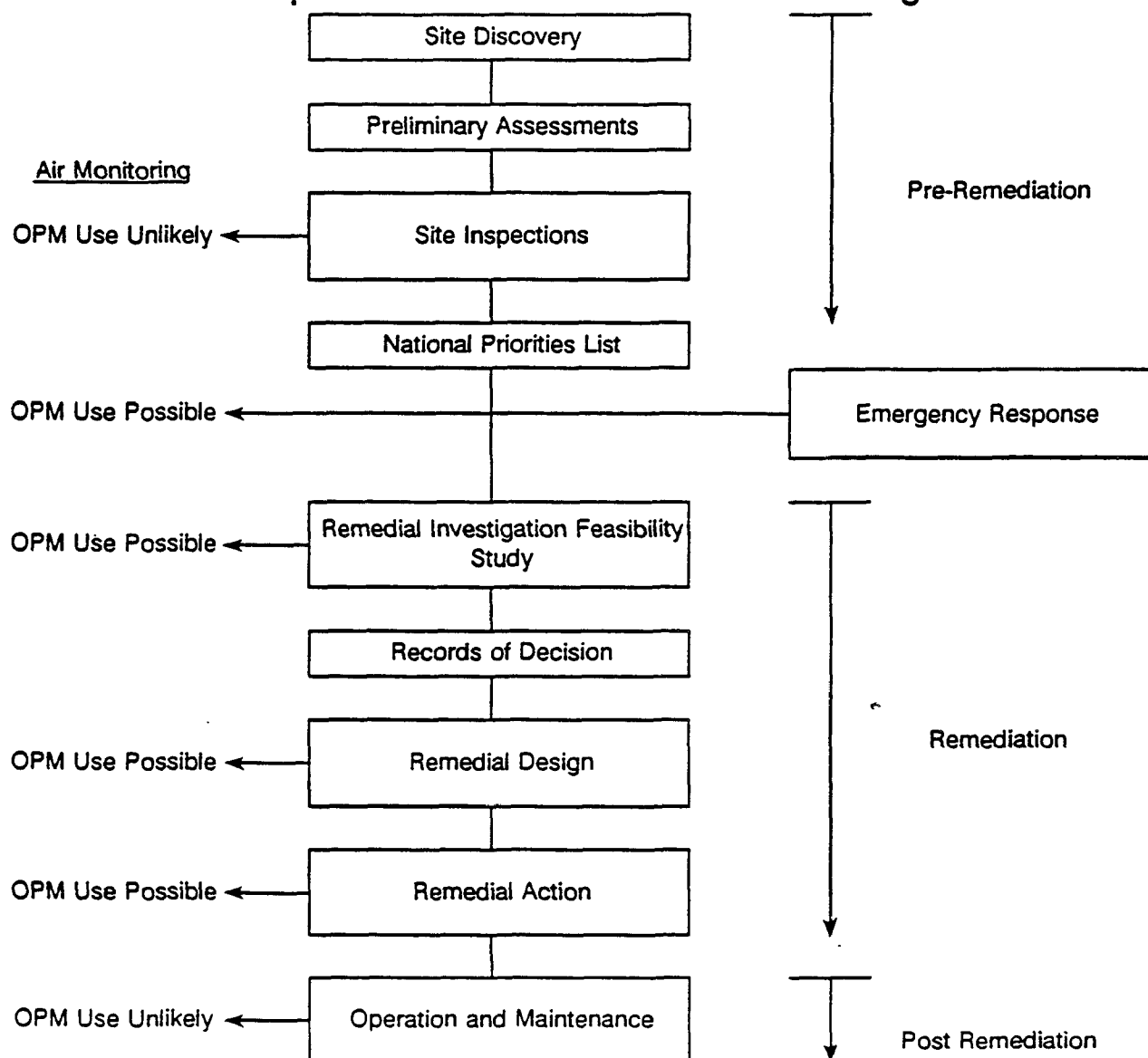


Figure 2-1. Phases of the Superfund Process where Air Monitoring is Conducted.

- 4) What are the time resolution needs? Are the sources highly variable, needing information on the order of minutes to hours, or are they relatively constant?
- 5) What are the ambient concentration levels expected to be during the action?

The answers to these questions define the data quality objectives (DQOs) of a specific application. These DQOs are then compared with the performance capabilities of the various monitoring options (OPMs and conventional approaches). The comparison should help the user decide what type of monitoring would be most appropriate or indicate whether the DQOs should be modified.

Table 2-1 summarizes the information presented for specific steps in the Superfund process. Each action is classified by the type of monitoring needed, the concentration levels likely to be present, the goal of the monitoring, the need for data turnaround, and the need for high-time resolution. The last column contains a decision about what type of monitoring is generally most appropriate. In general, when an absolute ambient concentration level is needed, conventional monitoring is the best option. When emission rate information is needed, OPMs are often the best option. As shown in Table 2-1, OPMs should be considered for application to the FS, ER, and RA since emission rate information is needed, but are not a likely option for the SI, RI, or the Operation and Maintenance (O&M) actions since absolute concentrations at low, ambient levels are needed.

As previously mentioned, OPMs are undergoing rapid development and this may lead to even wider applications of the technology. Some near-term developments and possible field tests that may further the development of OPMs are discussed later in this document. These topics include emission rate measurement tests, monitoring during the RA, quality assurance test, user education, standard operating procedure development, and complex source flux measurements with plume detection. A discussion of improvements that the OPM instrumentation needs, such as lowering of detection limits, expansion of capabilities to the measurement of new compounds, and development of full stand-alone operation, is also included.

**Table 2-1.
Data Quality Needs for Air Monitoring During Various Superfund Actions**

Action	Data Quality Needs	Typical Ambient Concentration Level	Monitoring Goal: Emission rate vs Ambient Air Concentration	Data Turnaround Time	Resolution of Temporal Variability	Monitoring Option
SI	Qualitative (screening)	≤10 ppb	Ambient Air concentration at fence-line	Not Critical	Not Usually Critical	OPM systems are not likely to be used during this action. However, if the concentrations are expected to be near 50 ppb the FTIR is the likely OPM system to choose.
ER	Quantitative	≥200 ppb	Fence-line monitoring or emission rates determination to estimate receptor impact.	Critical to assessment of compliance with short-term action levels	Important to estimate impact at receptors; temporal resolution must be reasonably high	OPM systems may be the monitor of choice. The FTIR is probably the best choice since little is known about the type of emissions.
RI	Semi-quantitative	≤10 ppb	Emission rate determination to assess potential health risk.	Not Critical	Not Usually Critical	OPM systems are not likely to be used during this action. However, if the concentrations are expected to be near 50 ppb the FTIR is the likely OPM system to choose.
FS	Quantitative	100-200 ppb	Emission rate determination to assess receptor exposure.	Not Critical	Key for assessing source variability temporal resolution must be reasonably high.	OPM system may be the monitor of choice. The FTIR is probably the best choice, if little is known about the type of emissions.
RA	Quantitative	≥200 ppb	Fence-line monitoring or emission rates determination to estimate receptor impact.	Critical to assessment of compliance with short-term action levels.	Important to estimate impact at receptors; temporal resolution must be reasonably high.	OPM systems may be the monitor of choice. Species present will dictate choice of system.
O&M	Semi-quantitative (screening)	≤10 ppb	Ambient air concentration at fence-line to determine any site decay.	Not Critical	Not Critical	OPM systems are not likely to be used. However if site decay is possible, stand alone GFC may be an option.

SECTION 3

THE SUPERFUND PROGRAM

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 and uncontrolled waste sites. Under CERCLA and SARA, the U.S. EPA is also responsible for ranking these sites, based on relative risk to the public health, to determine the order of site cleanup. The Superfund process generally consists of three phases: pre-remediation, remediation, and post-remediation. However, if the contamination poses an immediate risk to human health, an emergency removal or stabilization may be undertaken. The following sections describe the actions that make up each of these phases.

Ambient air monitoring and emission measurements may be needed during a number of the steps in the overall Superfund remediation process. Open path monitoring is potentially a cost-effective method for some, but not all, of these steps. Therefore, an understanding of when an OPM may be appropriate requires an understanding of the data needs of each step of the Superfund remediation process. An overview of this process as it relates to Air Pathway Assessments (APA) is given below, followed by a discussion of the four types of air monitoring data that may be needed during the course of the remediation process⁸.

3.1 PRE-REMEDIATION PHASE

The pre-remediation phase is concerned with determining the potential risk to public health and the environment posed by emissions from the site. The pre-remediation phase begins with site discovery. From there, a Preliminary Assessment (PA) is conducted to collect as much information as possible about the pollutants present and their physical state. This is meant to be a low-cost operation and involves collecting

all relevant documentation about the site. EPA uses the information gathered in the PA to determine whether further investigation or action is warranted.

If further investigation is warranted, a site investigation (SI) is conducted. The SI is the first action which employs some form of sample collection and is concerned with determining the immediacy of the health risk that the site poses. Samples are collected from the various media present and analyzed and the results are used to rank the site within the Hazardous Ranking System (HRS) Model. The HRS model ranks the relative contamination the site poses over five pathways. These pathways are: air, direct contact, groundwater, surface water, and fire or explosion. (The direct contact and fire or explosion pathways are evaluated but not currently included in the ranking.) If the site scores higher than some predetermined amount, the site is placed on the National Priorities List (NPL).

3.2 EMERGENCY RESPONSE

Once on the NPL, the necessity of emergency removal is evaluated. If the nature of the site shows a significant health risk, action is taken to remove and stabilize the hazardous waste. The emergency response (ER) action is similar to the Remedial Action (RA) but without the benefit of the information gained during the Feasibility Study (FS). An ER action is usually shorter in duration and more limited in scope than an RA. If no emergency removal action is deemed necessary, the remediation phase begins.

3.3 REMEDIATION PHASE

The remediation phase consists of the Remedial Investigation (RI) and Feasibility Study (FS), producing a Record of Decision (ROD), Remedial Design (RD), and Remedial Action (RA). This phase requires more time than the pre-remediation phase and results in reducing health risks from the site to acceptable levels.

The RI and FS are separate steps but typically they are conducted simultaneously and interactively. During the RI, data are collected to determine the precise nature of the compounds present and the extent of contamination. The data gathered during the RI are used for any risk assessment and to identify cleanup procedures and remedial alternatives. The FS helps to identify the preferred cleanup alternative. Several alternative cleanup methods may be considered and, when warranted, developed. After the FS is completed, a ROD is issued that states EPA's official decision about the preferred approach to cleaning up the site.

Next are the design and implementation of remedial actions. The RD is a detailed plan for remediating a site and the RA can take a variety of forms -- from short-term activities when there is a concern for protecting workers to long-term activities that can take several years.

3.4 POST-REMEDIATION PHASE

Once the remedial activity has ended, a brief monitoring period is initiated to evaluate the effectiveness of the cleanup. This is called the post-remediation or operation and maintenance (O&M) phase. If the ambient air monitoring and other post-remediation testing show that the site meets the site-specific clean-up criteria, the site may then be taken off the NPL.

3.5 GENERAL TYPES OF AIR AND EMISSION MONITORING DATA

Four categories of ambient air measurements may be required at a site:

- 1) Qualitative (screening) assessment of site emissions under baseline or undisturbed conditions;
- 2) Quantitative assessment of site emissions under baseline or undisturbed conditions;
- 3) Quantitative assessment of emissions from pilot-scale remediation activities; and

- 4) Quantitative assessment of the effects on air quality of full-scale remediation activities.

The monitoring goal of these measurements is to determine ambient concentrations at the site fenceline. This is typically done by making measurements both upwind and downwind of the site contamination. The monitoring goal of categories two and three may also be to measure ambient concentrations immediately downwind of the emission source. These data can be combined with tracer gas measurements or atmospheric dispersion model results to back calculate an emission rate from the source. This emission rate can then be used with an atmospheric dispersion model to estimate ambient concentrations at various receptor locations under various meteorological conditions.

Category 1 monitoring is most likely to occur during the SI, early RI, or the O&M steps of the Superfund process. Categories 2, 3, and 4 monitoring are most likely to occur during the RI and O&M, ER, FS, and RA phases.

SECTION 4

DESCRIPTION OF AMBIENT AIR MONITORING AND DATA REDUCTION METHODS

All analytical methods rely on some physical or chemical property of a species for identification and quantitation. Methods such as mass spectroscopy base the identification of species on their mass. Chromatographic methods rely on the efficiency with which a compound binds to a substrate to impede the progress of the species, thus making the transit times through the substrate different for different species. Open path monitoring techniques are structurally specific, i.e., the measurements are based on how the atoms are connected or, for an atomic species, how the electrons are configured. One advantage of OPMs over most conventional methods is their ability to monitor in-situ, i.e., monitoring without the need to collect samples.

This section describes the basics of selected OPMs and of some of the more conventional sampling and analytical methods. There is a brief discussion of the interactions of light and matter, followed by a description of how qualitative and quantitative measurements are made. Section 4.1.3 identifies compounds that are amenable to detection by the three OPMs widely used for environmental applications.

4.1 OPEN PATH TECHNOLOGIES

This section discusses the general principles of optical spectroscopic measurements. The topics covered include general spectroscopic principles^{9,10} and light-matter interactions, which are discussed in terms of their application to ambient air monitoring.

4.1.1 Spectroscopy

Open path monitoring as used in this document refers to the interaction of light with matter (i.e., molecules, atoms, or aerosols and particulate matter) over an open air path (i.e., no sample cell) to yield qualitative and quantitative information about that

matter. This type of measurement falls under the term spectroscopy. A device used to measure the interaction of light and matter is called a spectrometer. A spectrometer consists of four fundamental parts:

- Source: an element that produces light. This will be referred to as either broad band because it produces several colors of light (called frequencies) or laser, which produces a very narrow band of light around a single frequency (referred to as monochromatic or single color);
- Sample: this is the substance being measured. Here, pollutants in the ambient air;
- Dispersive element: an element which separates the light into its component frequencies for analysis. A familiar example of a dispersive element is a prism; and
- Detector: a light sensitive device.

For open air use, no cell is used. Instead, the species of interest are moved through the light beam by the wind. This type of monitor is referred to as an Open Path Monitor (OPM).

The spectrometer described above falls into the class of "active" monitors. Another class, "passive" monitors is also available. The distinction between active and passive is that an active spectrometer has an internal light source.

A conceptualized version of a spectrometer used as an OPM is shown in Figure 4-1. Light emitted from the source travels through the sample, where it strikes the dispersive element and then falls on the detector for analysis. Different spectrometers will accomplish these four steps in different ways, but the necessity of each step is universal. Table 4-1 shows several techniques currently used in the optical remote sensing area¹¹. While several of these methods are appropriate for Superfund sites, others are in the developmental phase but have the potential to ultimately play a significant role in several monitoring scenarios.

Table 4-1.

Optical Remote Sensing

System	Principle of Operation
FTIR	Collects full IR spectrum using broadband source and analyzes spectrum for constituents and concentrations using library spectra.
UV-DOAS	Collects UV spectrum over limited spectral region and measures differential absorption of line centers relative to line wings to deduce gases present and their concentrations.
GFC	Uses a sample of the gas(es) to be detected as a spectral filter and measures the broadband correlation between its spectrum and that of the measurement path to evaluate gas(es) and their concentrations.
Filtered Band-Pass Absorption	Simple band-pass filtered absorption measurement using in- and out-band channels to measure absorption in the band of the gas(es) of interest and their concentrations.
Laser Absorption	Straightforward laser transmissometry using one or more lasers to look in and out of absorption bands to deduce total monochromatic absorption and, consequently, gas concentration.
Photoacoustic Spectroscopy	Measures the pressure rise in a closed chamber arising from collisional deactivation of excited molecules, and is typically carried out in an acoustic chamber to measure response acoustically and after excitation with laser source.
LIDAR	Measures molecular or aerosol backscatter using either differential absorption with two wavelengths or Raman scattering to identify and measure gas concentration; unlike other methods, LIDAR provides ranging information on measurements.
Diode-laser spectroscopy	Developing technology for open-air use. Measures modulation caused by spectrally scanning across a line feature of the gas(es) of interest to identify and deduce concentrations by line-depth absorption.

SOURCE: From Reference 11.

The OPM configuration shown in Figure 4-1 is called a bistatic configuration because the transmitter and receiver are at opposite ends of the monitored path. Another configuration, called the monostatic configuration, is depicted in Figure 4-2. This has both the transmitter and receiver at the same end of the path. The monostatic configuration requires the use of some type of reflecting optic such as a corner cube (often called a retroreflector) at the other end of the beam path. The advantage of a monostatic configuration over a bistatic configuration is that power is needed at only one end of the path. This is an advantage for rural or inaccessible sites.

4.1.2 Light Interactions with Matter¹²

Light comes in a variety of frequencies, all of which, taken as a whole, make up the electromagnetic (EM) spectrum (Figure 4-3). OPM systems typically use either the infrared (IR) or the ultraviolet (UV) region of the EM spectrum. The various types of light differ only in their frequency and therefore in their energy content. The energy of a particular frequency of light is given by the following equation:

$$E = h\nu \quad (\text{Eq. 4-1})$$

where: E = energy (joules);
h = Planck's constant ($h = 6.6262 \times 10^{-34}$ Joule*seconds); and
 ν = frequency in Hertz (sec^{-1}).

Another useful measure of light is its wavelength, which may be derived from the frequency via the following equation:

$$\lambda = \frac{C}{\nu} \quad (\text{Eq. 4-2})$$

where: λ = wavelength (m); and
C = speed of light (m/sec, $C = 2.9979 \times 10^8$ m/sec).

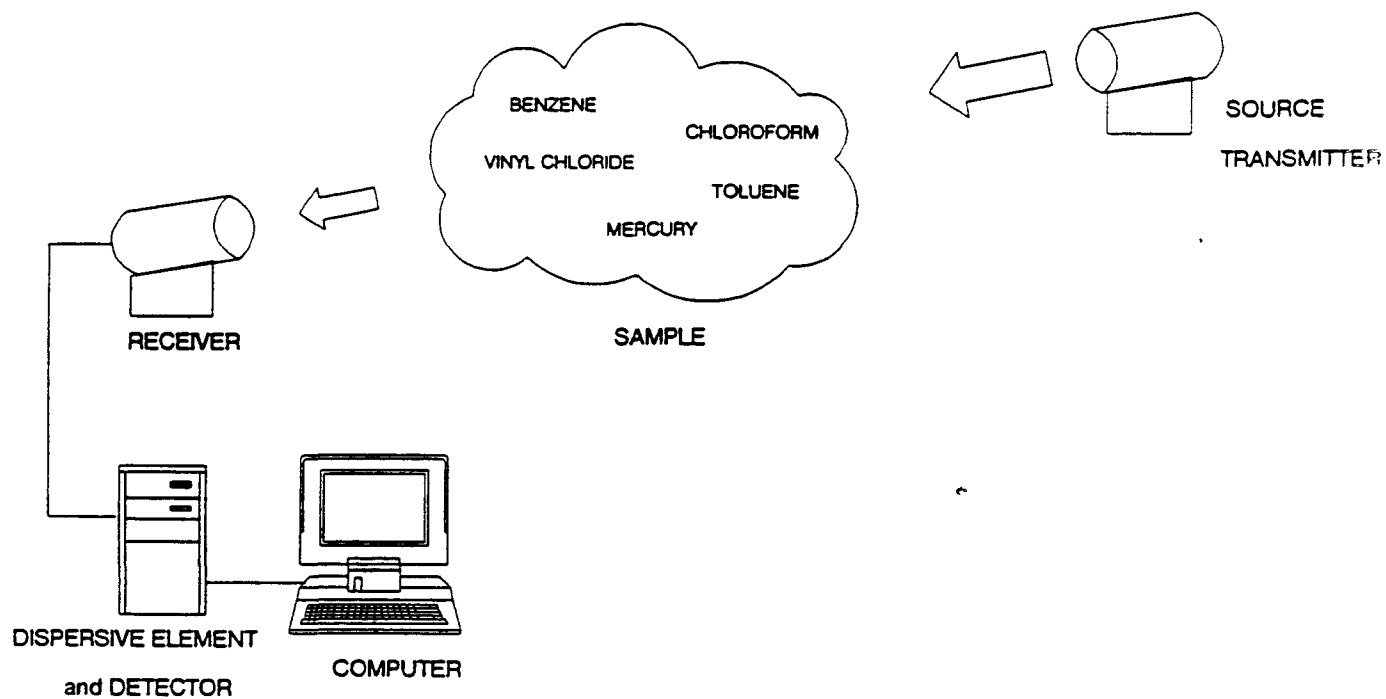


Figure 4-1. Bistatic Configuration of an OPM System.

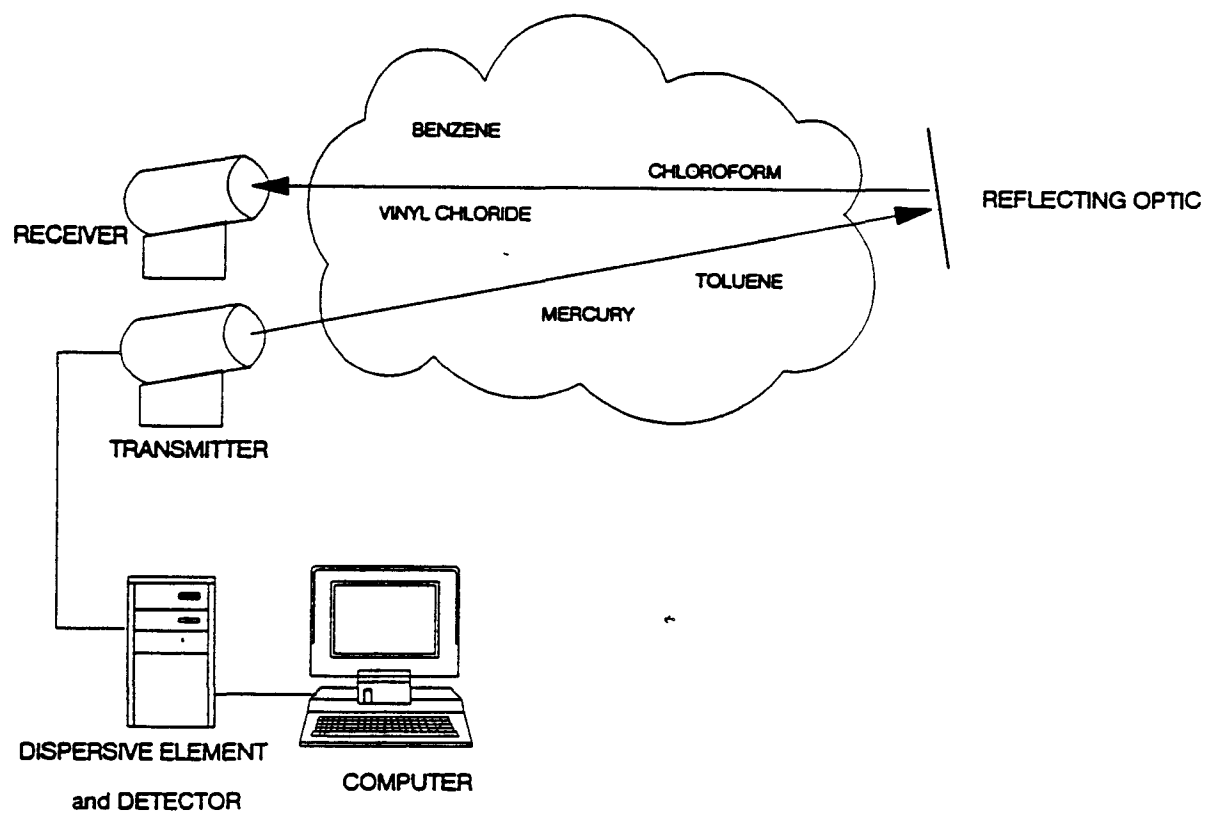


Figure 4-2. Monostatic Configuration of an OPM System.

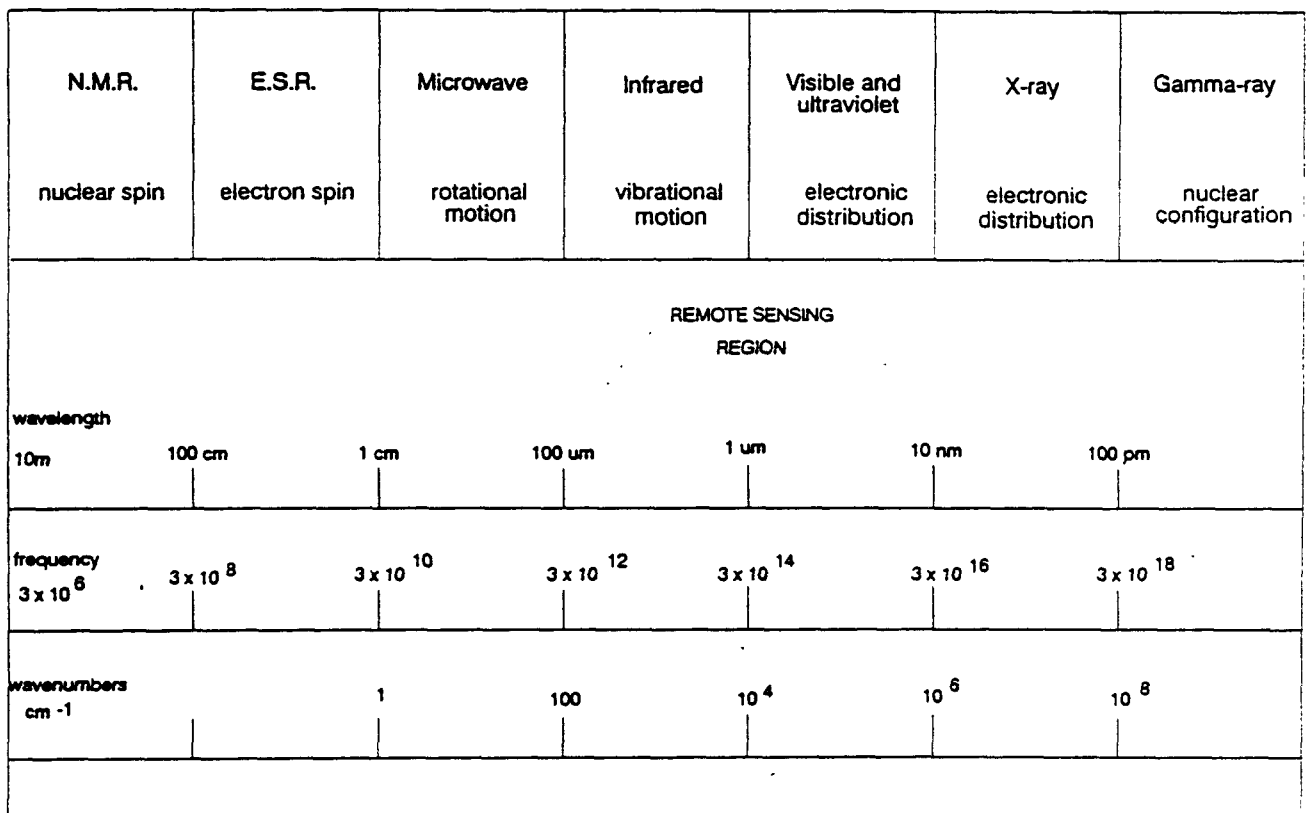


Figure 4-3. Electromagnetic Spectrum.

UV light, because of its higher frequency (higher energy) or shorter wavelength, produces changes in the electron distribution about a molecule. Infrared light produces changes in the motion of the atoms relative to the center of mass of the molecule. UV light is therefore said to produce electronic transitions while infrared light produces vibrational and/or rotational transitions. A transition is a change in the internal energy content of the species.

When the light beam passes through the sample, three processes may occur that change the intensity of the light. All of these processes can provide useful information about the identification, quantitation, or spacial location of the species. They are:

- Absorption, which is the attenuation of the light beam due to the removal of a photon that matches exactly one of the internal motions of the species. The internal energy content of the species is increased.
- Emission, which is the loss of light from the species. The internal energy content of the species is decreased. This light is also at an exact frequency determined by the species. The ability to emit a photon indicates that the species was previously excited by some other type of source.
- Scattering, which is the physical deflection of the photon off of its original course. There are three types of scattering: Mie, Rayleigh, and Raman.

On a molecular level, molecules and atoms can only absorb specific frequencies of light. These frequencies depend on the structure of the molecule or atom. While many molecules may absorb at the same frequency, no two molecules will absorb at all of the same frequencies. Therefore, by using several frequencies, a specific pattern or "finger print" will be obtained that will correspond to a single molecule or atom. Figure 4-4 shows examples of three molecules which absorb in the same frequency region. While the absorptions may be close to one another, the patterns of the molecules are very different which allows separate species to be identified even in the midst of the other species.

Emission spectra, for the most part, contain the same spectral features as absorption spectra. Some excitation process (either light or thermal energy) can be used to produce a species in an excited energy state. The emission of light from this species is then monitored. Figure 4-5 shows the emission process diagrammatically. The excited state E_2 is higher in energy than the other states. The species can lower its energy by emitting light of exactly the energy $E_2 - E_0$, or it can lose the energy in a step-wise fashion. The energy loss may either be as thermal energy (energy of motions imparted through collisions) or as light. If light is emitted it will only occur at the frequency given in the figure. The emission process, however, is not likely to be used in an open path configuration because the sensitivity is generally less than that of absorption.

The scattering process can be divided into two classes, elastic and inelastic. Elastic scattering is a no-energy loss process typical of Mie and Rayleigh scattering. Inelastic scattering causes the photon to change in energy and is typical of Raman scattering. Raman and Rayleigh scattering operate by exciting internal energy states of the molecules. These are species-specific states for the most part and therefore they have the potential to reveal species-specific information. Mie scattering¹³, on the other hand, is the physical deflection of a photon by a particle (see Figure 4-6) that is larger than or roughly equal to the wavelength of the photon.

4.1.3 Techniques for Superfund Applications

Of the eight techniques listed in Table 4-1, three currently can meet certain monitoring needs of the Superfund program. These three are Fourier Transform Infrared (FTIR), Ultraviolet-Differential Optical Absorbance (UV-DOAS), and Gas Filter Correlation (GFC). They offer the highest sensitivity, specificity, and total analysis capability of the techniques listed in Table 4-1. Following is a general description of these systems.

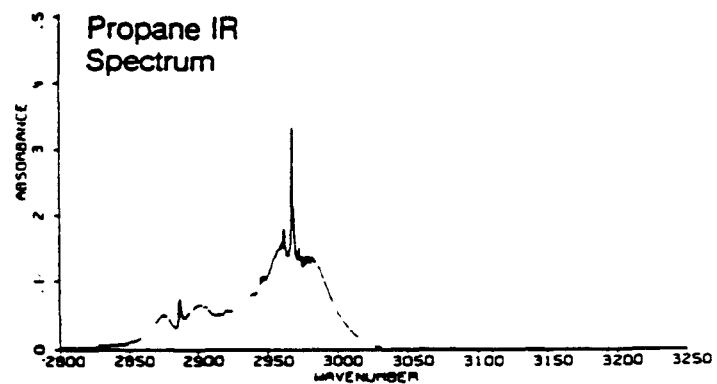
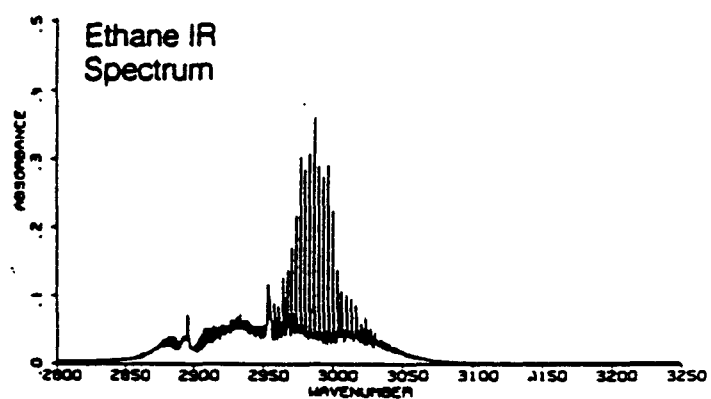
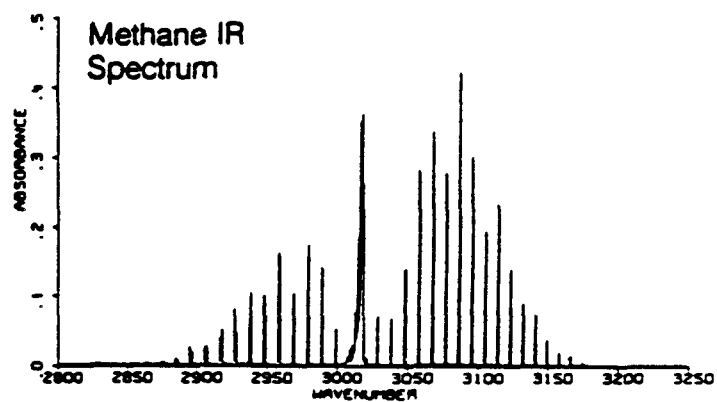


Figure 4-4. Infrared Spectra in the 3,000 cm^{-1} Region.

SOURCE: Supplied by W.F. Herget, Nicolet Instruments.

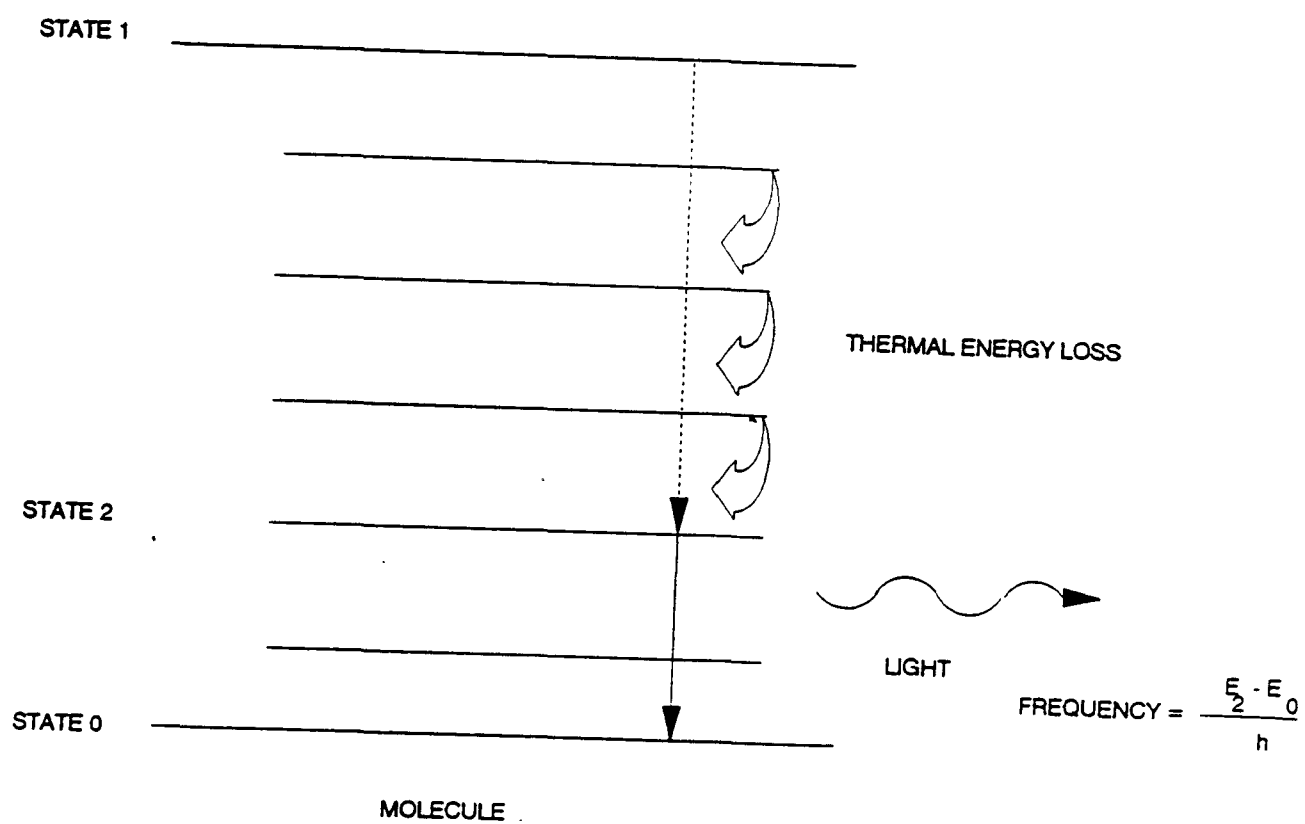


Figure 4-5. Light Emission Process.

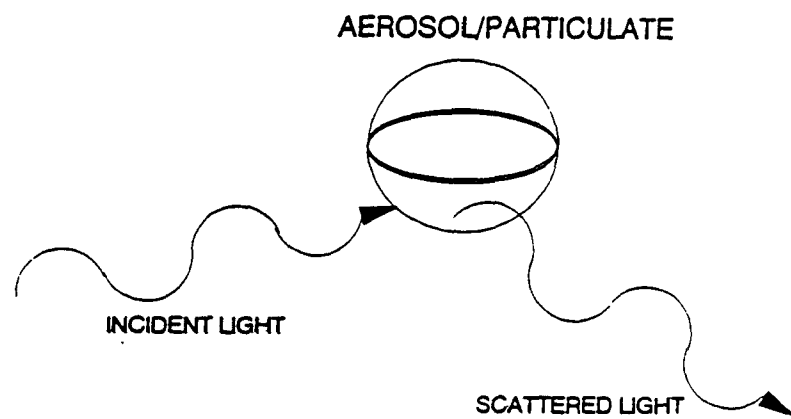


Figure 4-6. Mie Light Scattering.

Gas Filter Correlation (GFC) Spectroscopy

This technique, which is a special case of spectral correlation techniques, is a nondispersive infrared method. It relies on the detection of the correlation between spectral features in the measurement beam and that produced by a reference cell that contains a sample of the species of interest. This technique, since it is non-dispersive, is easily applied, is applicable even in the presence of interferences, and has a very fast (approximately one second) response time. Ten compounds can be monitored with a single system in its current configuration.

Fourier Transform Infrared (FTIR) Spectroscopy

This technique allows collection of the entire infrared spectrum from about 4000 to 200 wave numbers in a few seconds. The advantage of taking the entire spectrum is that if interfering species are present they will not be present at all of the same frequencies throughout the IR. Therefore, careful choice of analysis regions will allow for interference-free detection. FTIR offers the ability to look at numerous species which have infrared active modes. Unfortunately, FTIR is also frequently limited in sensitivity because of the strengths of the IR bands available and the extent of interferences such as water vapor and CO₂. This method would be used in the absorbance mode for Superfund applications.

Ultraviolet-Differential Optical Absorbance (UV-DOAS) Spectroscopy

This is a special case of conventional absorption UV spectroscopy with the appropriate broad-band excitation source such as a Xenon lamp. UV-DOAS looks at the differential absorption of UV lines relative to the baseline, which is usually a relative baseline, not an absolute one. The technique is well developed and requires about 1 minute to identify the concentration of a single species. The UV typically has better sensitivity than the infrared because of the larger UV band strengths, but not all compounds are observable in this region. One advantage, however, is that UV systems can monitor some atomic metal species.

Table 4-2 contains a list of compounds and the current monitoring capability of the three OPMs just discussed. The capability of canisters analyzed by GC/MD-MS is included for comparison. Table 4-2 indicates that infrared methods are incapable of monitoring atomic (e.g., metal) species and that they are also incapable of monitoring a class of compounds called homonuclear diatomics (i.e., Cl_2 , F_2 , O_2 , N_2). Ultraviolet systems are currently incapable of monitoring alkanes, alkenes, and many oxygenated species. While the GFC system can detect most of the same compounds as the FTIR, there is also a question of the stability of the compounds in the sample cell. An "X" in the GFC column refers only to the ability to detect the compound and not its stability. The same information is depicted graphically in Figure 4-7. The solid arrows indicate the classes of compounds that the open path monitoring techniques can detect. Dotted arrows indicate the potential to detect some of the compounds in the class. The dashed arrows indicate that the method may have some problems with these compounds.

This table is not an all-inclusive list of the compounds. Also, it does not attempt to convey how well these systems will detect these compounds. It is simply offered as a guide to users to show the compounds that can potentially be monitored by the systems.

4.2 CONVENTIONAL POINT MONITORING METHODS

Point monitors are, as the name implies, used to monitor ambient pollutant concentrations at a specific point in space for a predetermined time. They are capable of reasonably low detection limits. They generally require the use of some sampling method (i.e., canisters, sorbent tubes, etc.). Unless the analyses are performed at the site, it may take several hours to days before data is available for review.

This section provides a brief description of canister, sorbent tube, and organic vapor analysis (OVA), and the analytical methods used for separation and detection. The important differences between point monitors and path monitors are discussed. However, a more complete discussion is deferred until Section 4.3, where the meaning of a path-weighted concentration and an effective concentration is discussed.

Table 4-2.

Methods for Monitoring Specific Compounds

Compounds	Canister	UV-DOAS	FTIR	GFC
ALKANES				
ethane	X		X	X
propane	X		X	X
n-butane	X		a	a
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
1,1,2-dichloroethane	X		X	X

Table 4-2. (Continued)

Compounds	Canister	UV-DOAS	FTIR	GFC
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
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

Table 4-2. (Continued)

Compounds	Canister	UV-DOAS	FTIR	GFC
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.

Chemical Class	Example Compounds	Capability of OPMs*		
		FTIR	GFC	Canister/GC
Alkanes	Methane, Propane, Hexane, Octane	↓	↓	↓
Alkenes	Ethene, Butene, 1,3-Butadiene	↓	↓	↓
Alkynes	Ethyne	↓	↓	↓
Halogenates	Chloroform, 1,1,1-trichloroethane	↓	↓	↓
Oxygenates	Methanol, Formaldehyde	↓	↓	↓
Sulfur Compounds	Hydrogen Sulfide	↓	↓	↓
Nitrogen Compounds	ammonia, trimethylamine	↓	↓	↓
Aromatics	Benzene, Toluene, Xylenes	↓	↓	↓
Criteria	Ozone, Sulfur Dioxide Nitrogen Dioxide	↓	↓	↓
Methals	Mercury, Lead, Chromium	↓	↓	↓

* Detects all compounds in class ———
 Detects some compounds in class ———
 Method suspect for these compounds - - - -

Figure 4-7. Compounds Measurable by Various Methods.

4.2.1 Canister Sampling and Analysis

A canister is an evacuated stainless steel container with a passivated surface. Sampling with a canister consists of collecting a controlled volume or mass of atmosphere over some time period. The atmosphere collected can then be identified and quantified by gas chromatography (GC), which is a way to separate the compounds by some physical property, such as size, binding strength, or a host of other methods. Once separated, the compounds are then identified and quantified.

Typical detection methods use flame ionization (FID), photoionization (PID), electroconductivity (ECD), and/or mass spectrometry (MS). The former three are collectively known as multiple detection, because they are frequently applied to a single sample analysis. Each detector has its particular strengths and weaknesses for various compounds.

The sampling and analysis methods are therefore referred to as gas chromatography-multiple detection (GC/MD) and gas chromatography-mass spectroscopic (GC/MS). The GC/MD method relies on the chromatographic separation in time to identify the species; the MD detectors are not species-specific. The GC/MS relies to some extent on chromatographic separation in time, but has the advantage of being mass specific and therefore, in many cases offers species-specific detection. Table 4-2 contains a list of compounds that can be monitored by GC/MD and GC/MS. These methods are typically incapable of monitoring criteria pollutants. (The criteria pollutants are ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide, lead, and particulate matter under 10 microns.) Also, the ability of GC/MD or GC/MS to measure most oxygenates and other "polar" compounds is suspect due in part to the sampling methods employed.

4.2.2 Sorbent Tube Sampling and Monitoring

Sorbent tubes contain material that traps contaminants from ambient air via adsorption. Ambient air is drawn through the sorbent tubes at a known rate and, depending on the sorbent material, a specific set of compounds are adsorbed onto the surface of the sorbent. Commonly used sorbents include charcoal, Tenax, XAD-2 resin, and silica gel.

The tubes are desorbed and the pollutants are then analyzed by either GC or liquid chromatography (LC). Again, the chromatography only separates the compounds, detection is accomplished by either: 1) spectroscopic; or 2) a host of other species-specific methods. Sorbent tubes are better suited than canisters for measuring concentrations of polar compounds, but each sorbent material is applicable for fewer compounds than canisters. Background contamination of the sampling media is also a frequent concern.

Sorbent tubes are prone to the same limitations of data turnaround time as canisters are. The type of analysis method needed to detect the compounds listed in Table 4-2 varies from compound to compound. Sorbent tubes are not amenable to sampling for metals or criteria pollutants.

4.2.3 Organic Vapor Analyzers and Field Gas Chromatographs

Organic Vapor Analyzers (OVA) are point monitors that analyze total hydrocarbon emissions using a PID or FID detector. These are portable instruments that can serve as continuous monitors. They only yield total hydrocarbon data and no information on specific compounds. Many similar portable (e.g., HNu 101A) and continuous (e.g., Beckman 400A) analyzers are on the market that, like the OVA, provide only limited information about the specific compounds present in the atmosphere.

Field gas chromatographs (FGC) are identical to the GCs described in Section 4.2.1, but they are more portable. They do not require a sampling method per se, but do require concentration of the atmosphere. They greatly speed data turnaround time (to about one hour) but do not have detection limits as low as laboratory-based GCs.

Both OVAs and FGCs offer an advantage in data turnaround time over their laboratory counterparts. However, they are limited by their speciating capacity and their detection limits. The FGCs also are incapable of monitoring the criteria pollutants and metals.

4.3 IDENTIFICATION AND QUANTITATION OF SPECIES USING OPM SYSTEMS

OPMs are spectroscopic instruments and are therefore able to directly discern information about the structure of species. As stated earlier, each molecule or atom has a "finger print" that can be used to identify the compound. In many OPM systems, the identification is performed by some form of a least squares fit of library spectra to the open air spectra. The least squares method will fit several (sometimes on the order of thousands) spectral points; the goodness of fit indicates how well the species have been identified. Once the species have been identified, the concentration must be determined. This is done by using the Lambert-Beer Law^{10,14} more commonly referred to as Beer's Law. A discussion of the origin of the Lambert-Beer Law appears in Appendix A. The Lambert-Beer Law simply states that the concentration of a particular component in a sample is related to the transmittance of a light beam through that sample and to the length traveled through the sample by that light beam. The transmittance is defined by the equation:

$$T = \frac{I(v)}{I_0(v)} \quad (\text{Eq. 4-3})$$

where: $I_0(v)$ = the intensity in the absence of the sample;
 $I(v)$ = the intensity of the light having passed through the sample.

Taking the negative base ten logarithm of the transmittance defines the absorbance which is given as:

$$A(\nu) = -\log_{10} T = \log_{10} \frac{I_o(\nu)}{I(\nu)} \quad (\text{Eq. 4-4})$$

where: $A(\nu)$ = the absorbance.

The absorbance is a useful quantity because it is directly related to the concentration and path length by:

$$A(\nu) = a(\nu) \cdot b \cdot c \quad (\text{Eq. 4-5})$$

where: b = path length (m);
 c = concentration (ppm); and
 $a(\nu)$ = molecular absorption coefficient ($\text{ppm}^{-1} \cdot \text{m}^{-1}$).

The term $a(\nu)$ is a known function for each molecular species. This equation is correct for a concentration that does not vary with path length. In the ambient atmosphere, the concentration across the path may not be homogeneous. The equation must then be written as (see Appendix A):

$$A(\nu) = a(\nu) \int_0^L c(b) db = a(\nu) \cdot c_{\text{eff}} \cdot L \quad (\text{Eq. 4-6})$$

where: L = length of the path (m); and
 c_{eff} = effective or path-weighted concentration ($\text{ppm} \cdot \text{m}$).

In Equation 4-6, $a(\nu)$ is taken out of the integral under the assumption that temperature and total pressure do not vary significantly over the path.

This equation shows how the concentration depends on the path length. The integral on the left can be rewritten as though an effective concentration across the pathlength is being measured. This effective concentration is the quantity obtained from an OPM and is equivalent to that concentration which, if it is homogeneously distributed

over the path length, gives the same absorbance. This is often referred to as a path-averaged concentration. Dividing each side by $a(v)$ gives:

$$\frac{A(v)}{a(v)} = c_{\text{eff}} \cdot L \quad (\text{Eq. 4-7})$$

For OPMs, the concentration-pathlength product is called the path-weighted concentration. The path-weighted concentration is the invariant parameter associated with these types of measurements. It is a useful quantity because path lengths will vary from site to site. One can estimate what effective concentrations will be necessary on different path lengths to produce the same absorption.

Equation 4-5 shows that the absorbance will increase as the path length increases. Thus, if one is near the detection limit of a particular species, increasing the path length (at least in theory) will decrease the detection limits. This is true only if the lengthening of the path incorporates more and more of the emissions plume. This concept is discussed in greater detail in Section 5.

The response of an OPM can be used to determine a molecular concentration in molecules/cm³. The effective concentration can be converted to ppb or ppm if pressure and temperature are known. The volume monitored by the OPM which is probing a path L is:

$$V = \frac{\pi}{4} d^2 \cdot L \quad (\text{Eq. 4-8})$$

where: d = diameter of the light beam (m).

Using this volume, a total mass in the beam can be determined. Knowledge of the wind speed, or more precisely, the component of wind speed driving the mass through the beam allows calculation of a flux by:

$$\bar{J} = \rho \cdot U \quad (\text{Eq. 4-9})$$

where: J = Emission flux across the beam path in ($\mu\text{g}/\text{m}^2\cdot\text{sec}$);
 ρ = The density of the species in air ($\mu\text{g}/\text{m}^3$); and
 U = The wind speed across the path (m/sec).

An OPM flux measurement is a measure of the amount of mass per second passing through a plane, parallel to the beam path, having a dimension of d x L. Knowing d x L and multiplying the flux by this area gives a measure of the rate of mass crossing the beam.

4.4 APPLICATION OF THE PATH-WEIGHTED CONCENTRATION

A dispersion model can be used to relate path-weighted concentrations to concentrations in ppb or ppm. The units of path-weighted concentration are, for typical air samples, expressed as ppm*m, ppb*m, $\mu\text{g}/\text{m}^2$, molecules/ m^2 , etc. Measurements of quantities with these units can be used to derive input parameters for dispersion modeling. For example, knowledge of a path-weighted concentration and the wind speed allows the determination of a source term that can then be used in a dispersion model to calculate downwind receptor exposure. Two ways of measuring a path-weighted concentration are by OPMs and by point monitors using the transect method⁴. The applications of path-weighted concentrations are described below.

This model, used for illustration, will only consider dispersion of a plume under the Gaussian dispersion assumption¹⁵. The following equation (Turners Equation) governs the gaussian dispersion of a plume traveling in the x direction.

$$\chi(x,y,z) = \frac{Q(t)}{\pi U \sigma_z \sigma_y} \left[\exp \left\{ \frac{-y^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2} \right\} \right] \quad (\text{Eq. 4-10})$$

where: $\chi(x,y,z)$ = the concentration at a point x,y,z;
 Q(t) = the time-dependent source term and has the units of g/sec;
 U = the wind speed; and
 σ_i = the spread of the plume in the i direction (i = y, z).

A one-dimensional view of plume spread is shown in Figure 4-8. If one can obtain path-weighted concentrations in either the y or z direction (or both), calculation of the source term is simplified. For a path-weighted concentration in the y direction, Equation 4-10 becomes:

$$\frac{\int_{-y}^y \chi(x,y,z) dy}{\int_{-y}^y dy} = \frac{Q(t)}{\pi U} \left[\frac{1}{\sigma_z} \exp \left\{ \frac{-z^2}{2\sigma_z^2} \right\} \right] * \frac{\int_{-y}^y \frac{1}{\sigma_y} \exp \left\{ \frac{-y^2}{2\sigma_y^2} \right\} dy}{\int_{-y}^y dy} \quad (\text{Eq. 4-11})$$

and, replacing the integral on the left with the path-weighted concentration and canceling the normalization integrals gives:

$$\hat{\chi}(x,\bar{y},z) = \frac{Q(t)}{\pi U} \left[\frac{1}{\sigma_z} \exp \left\{ \frac{-z^2}{2\sigma_z^2} \right\} \right] * \int_{-y}^y \frac{1}{\sigma_y} \exp \left\{ \frac{-y^2}{2\sigma_y^2} \right\} dy \quad (\text{Eq. 4-12})$$

If the plume is contained fully within the beam path, the integration yields:

$$\int_{-y}^y \frac{1}{\sigma_y} \exp \left\{ \frac{-y^2}{2\sigma_y^2} \right\} dy = \sqrt{2\pi} \quad (\text{Eq. 4-13})$$

leaving:

$$\hat{\chi}(x,\bar{y},z) = \sqrt{\frac{2}{\pi}} \frac{Q(t)}{U} \left[\frac{1}{\sigma_z} \exp \left\{ \frac{-z^2}{2\sigma_z^2} \right\} \right] \quad (\text{Eq. 4-14})$$

If the source is at ground level, $z = 0$ and the equation becomes:

$$\hat{\chi}(x,\bar{y},z) = \sqrt{\frac{2}{\pi}} \frac{Q(t)}{U} \left[\frac{1}{\sigma_z} \exp \left\{ \frac{-0^2}{2\sigma_z^2} \right\} \right] = \sqrt{\frac{2}{\pi}} \frac{Q(t)}{U \sigma_z} \quad (\text{Eq. 4-15})$$

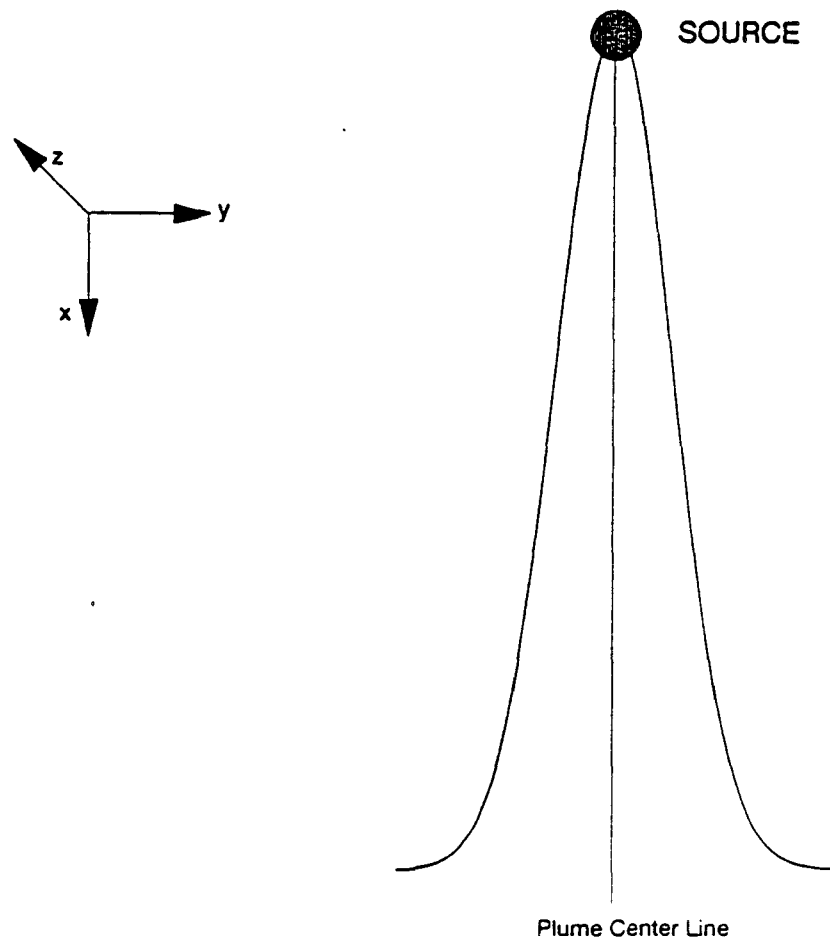


Figure 4-8. Dispersion in the "xy" plane.

The usefulness of the approach is apparent when the equation is used to solve the source term $Q(t)$. This is then:

$$Q(t) = \frac{\hat{\chi}(\bar{x}, \bar{y}, 0) \cdot U \cdot \sigma_z}{\sqrt{\frac{2}{\pi}}} \quad (\text{Eq. 4-16})$$

Now, one only needs to determine σ_z to calculate the source term.

The vertical dispersion, σ_z , can be determined in a variety of ways. Ideally, σ_z could be measured using a lidar system which gives a vertical profile of the plume directly. It may also be evaluated with a vertical array of point samplers, or it may be extrapolated from measurement of the wind direction standard deviation (sigma theta) by using the Pasquill-Gifford stability classes and the associated dispersion curves¹⁶.

Another method is to use a tracer gas method on site. The tracer gas (such as SF_6 if using an FTIR) is released (emitted) at a controlled rate. The path-weighted concentration is measured at a downwind point and this allows calculation of σ_z using the following equation:

$$\sigma_z = \frac{\sqrt{\frac{2}{\pi}} Q(t)_{\text{tracer}}}{\hat{\chi}(\bar{x}, \bar{y}, 0) U} \quad (\text{Eq. 4-17})$$

where: $Q(t)_{\text{tracer}}$ = The emission rate of the tracer gas.

Field measurements of σ_z are preferred to extrapolated or estimated values. Recent studies have shown that even with the measurement of sigma theta, σ_z values determined by stability class estimates can be in error¹⁷.

Another use of the tracer gas method is to directly determine the source term of the emission source. Measuring the path-weighted concentrations of both the tracer and the emissions at some downwind location and taking their ratio will in theory give some knowledge of the ratio of the source term. This is shown in Equation 4-18¹⁸. Since the $Q(t)_{\text{tracer}}$ is known, $Q(t)_{\text{emissions}}$ can be determined. While not all species are likely to behave in the same fashion, the major uncertainty lies in the degree to which the emission source of the tracer gas emulates the characteristics of the true source. This will be especially true of large, heterogeneous area sources.

(Eq. 4-18)

$$\frac{Q(t)_{\text{trace}}}{Q(t)_{\text{emission}}} = \frac{\hat{\chi}_{\text{trace}}}{\chi_{\text{emission}}}$$

where:

- $Q(t)_{\text{trace}}$ = the source term for the tracer gas;
- $Q(t)_{\text{emission}}$ = the source term for the emission source;
- $\hat{\chi}_{\text{trace}}$ = the tracer gas path-weighted concentration; and
- χ_{emission} = the emissions path-weighted concentration.

SECTION 5

SELECTION CRITERIA FOR AMBIENT AIR MONITORING METHODS

During the various activities undertaken over the lifetime of a Superfund site, three types of air monitoring may be necessary. These are:

- Worker or personal monitoring (all activities);
- Emissions monitoring (SI, RI/FS, RA); and
- Fenceline monitoring (RI/FS, RA, O&M).

Personal monitoring is conducted to determine the exposure of workers to hazardous emissions and is therefore only conducted by transportable point monitoring systems. Emission and fenceline monitoring may be conducted by either point or path monitors.

This section discusses topics that directly affect the type of ambient air monitoring (AAM) system used. These are detection limits, time response/data turnaround, and the physical characteristics of the site. The discussion covers some of the misconceptions about detection limits (Section 5.1) and some of the advantages related to fast response times (Section 5.2).

5.1 DETECTION LIMITS

The term "detection limits" can be defined in several ways. EPA has defined some of the commonly used terms, including:

- Method Detection Limit (MDL) -- the concentration level at which a method detects or responds; and
- Limit of Quantitation (LOQ) -- the concentration level at which a method can quantitate a species within some preset precision limits.

Currently there exists no specific protocol for determining of detection limits for OPM systems. Vendors contacted during a telephone survey typically quote the theoretical

detection limits of their instruments, which are analogous to the best-case detection limit for a single analyte. Detection limits under field conditions will be higher (worse). This will be discussed further in Subsection 5.1.2.

5.1.1 Interferants and Misconceptions

The path length parameter associated with the data output of OPMs has created several misconceptions. These misconceptions arise from failure to take into account the limitations of the Lambert-Beer Law given in Equation 4-5. This equation is valid only in certain situations but can be (erroneously) interpreted to imply that lengthening the light path to several kilometers will allow one to attain the desired detection limit. This fails to take into account two very important effects:

- Interferants by other compounds; and
- Signal-to-noise ratios.

When monitoring a multi-component system, it is generally assumed that the absorbance is additive for most concentrations present in the atmosphere. This means that the absorbance at a given frequency is a summation of terms caused by all the molecules and atoms that can absorb at this frequency. Mathematically, this is:

$$A(\nu) = b \cdot \sum_{i=1}^n a_i(\nu) \cdot c_i(b) \quad (\text{Eq. 5-1})$$

where i represents a specific species in the presence of n species.

Equation 5-1 indicates that subtracting the absorbance due to background species and interfering species will leave the spectra of the compound of interest. This assumption is valid when the absorbance of each species can be accurately accounted for; however, problems in cancellation arise when this is not true (i.e., when the absorbance cannot be accurately subtracted). For example, the bands of water and carbon dioxide are numerous and intense in the infrared. In addition, they have a very narrow bandwidth and most FTIRs used as OPMs have insufficient resolution to obtain the exact

absorbance intensities for these narrow bands. Therefore, when detecting VOCs and other species it is important to avoid regions where water and carbon dioxide cannot be entirely accounted for. Unfortunately, this usually eliminates the stronger infrared features of the VOCs of interest and limits the analysis to spectral features that have weak absorption strengths thus increasing the limits of detection. Ultraviolet systems, on the other hand, have less interference from background atmospheric constituents. The absorbencies due to water and carbon dioxide in the UV are weak or nonexistent in the spectral regions of interest.

Some studies have been performed to ascertain detection limits in the presence of interferants under a variety of operating conditions^{11,18,19,20}. However, there is a need to standardize the methods used for ascertaining detection limits. Currently, several methods are used to fit spectra and determine concentrations. Protocols that consider the application of these specific analysis (data reduction) methods must be generally applicable and not limited in scope to a single design or approach.

In addition to interferants, one needs to consider the signal-to-noise ratio that an instrument can obtain. Keeping a signal-noise ratio high enough to detect compounds is not explicitly written into the equations of Section 4. Equation 4-5 can be (erroneously) interpreted as implying that low detection limits are attainable at very long distances; however, the path lengths necessary to achieve these detection limits may be on the order of several kilometers. Such long path lengths are not practical or feasible in many cases. While several kilometer path lengths are theoretically possible even for very confined spaces (via multipassing), the intensity of the light source decreases as the path length increases. This decrease adversely effects the signal-to-noise ratio. In other words, there is point of diminishing returns. Currently, FTIR sources are capable of reasonable source strengths up to approximately 1,000 meters. One should therefore take care in extrapolating detection limits beyond this point and any path length significantly over 1 kilometer for FTIRs is unreasonable. Likewise, UV-DOAS systems are capable of path lengths on the order of 2.5 to 3.0 kilometers, and GFC systems are capable of path lengths up to about 500 meters to 1 km.

The user is cautioned to be skeptical when obtaining detection limit information. While some vendors are aware of the major concerns related to DLs, several vendors were contacted during the survey conducted for this project who were not. The best place to obtain valid detection limit information is generally from previous studies that have used that same instrument. Failing that, check the literature for applications to specific sites of similar devices.

The following subsection gives the, best estimates of a reasonable field-measured detection limit for a given OPM and compounds of interest. In some cases, a range of detection limits is presented because of the variety of vendor responses. When a vendor-quoted detection limit is used, the limit is identified as such. The user should remember that the instrument configuration, (i.e., separate transmitter and receiver pairs versus transceivers), and analysis software may have a significant effect on the field detection limit. Again, the best solution is to know or obtain field-measured detection limits of the specific instrument one is planning to use. Even when using the same instrument, however, changes in the amount of water vapor, as well as the specific mix of compounds from day to day and location-to-location, will also affect the detection limits of infrared systems.

5.1.2 Comparison of Detection Limits

Table 5-1 lists the FTIR, UV-DOAS, and GFC detection limits for 25 compounds²¹ commonly found at Superfund sites. These detection limits, which are reported in ppm*meters (assuming normal temperature and pressure conditions), were obtained from a literature search and a vendor survey. A list of OPM vendors is given in Appendix F. When possible, field detection limits are used; however, owing to the limited information available, many values are taken directly from vendor literature. It should be noted that detection limits are dependent on water vapor, path length, and the spectral analysis region. As Table 5-2 shows, the detection limits quoted by vendors are typically lower than those obtained in the field.

**Table 5-1.
Detection Limits for OPMs¹**

Compound ²	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

¹From References 11, 18, 19, 20, and 30.

²Compounds taken from Reference 21.

ND = Not detectable

NA = Not available

Table 5-2.
Comparison of Detection Limits for Field Measurements
vs. Vendor Specifications

	FTIR (ppm*m)		UV-DOAS	
	Vendor	Field	Vendor	Field
Trichloroethylene	1	2.5	ND	ND
Chloroform	2	3.0	ND	ND
Vinyl chloride	2	13	ND	ND
Chlorobenzene	5	10.6	NA	NA
Benzene	8	26	0.75	0.75
Toluene	8	24	0.75	0.75
m-Xylene	6	10	0.75	0.75

For comparative purposes, the path-weighted concentration in Table 5-1 is divided by 200 meters and tabulated by compound in Table 5-3. However, in many instances, a direct comparison of detection limits for OPMs and action levels is inappropriate (see Section 5.1.3). Table 5-3 also includes the detection limits for the GC/MD method and the long-term (annual) and short-term (1-hour) action levels for these same compounds. All values are given in units of ppb-V. The use of a 200-meter path is arbitrary, and some advantages in detecting compounds may be obtained by going to longer path lengths.

Figure 5-1A shows an emission plume whose width is equal to the path length of the OPM. The path length for this example is 100 meters. The path-weighted concentration of the plume along this path is 80 ppm*m, making the effective concentration 0.80 ppm. If the detection limit is 100 ppm*m (or 1.0 ppm minimum detectable effective concentration) no emissions are detected. However, in theory, increasing the path length by a factor of 2 will decrease the detection limit by a factor of 2. Increasing the path length must be done correctly, however, because this only lowers the detection limit if the path extension includes more of the plume. Figure 5-1B shows the simple extension of the path to twice its original distance (i.e., 200 meters). This has lowered the minimum detectable effective concentration to 0.50 ppm. However, in this example, the path extension does not include more of the plume. This results in decreasing the plume effective concentration by a factor of 2, making the new effective concentration 0.40 ppm, which is still not detectable.

The detection limit can be decreased by multipassing. Figure 5-2 shows the simplest setup for multipassing. Note that the extended light beam transverses a path back through the plume nearly co-linear to that of the first beam. The path-weighted concentration over both paths is nearly the same, e.g. for the example this would be 80 ppm*m, for a total path-weighted concentration of 160 ppm*m (or 1.60 ppm effective concentration). The detection limit is still 100 ppm*m (or 0.50 ppm effective concentration) so the compound is now detectable. Path configurations may be of a variety of geometries but the potential limitations must be considered. For example, the effects of interferants may be more pronounced for longer path lengths whether they are folded or straight.

Table 5-3.

Comparison^{4,5} of Detection Limits and Action Levels

Compound	Canister GC/MD (ppb)	FTIR ppb ³	GFG ppb ³	UV-DOAS ppb ³	Action Levels	
					Short-term ¹ (ppb)	Long-term ¹ (ppb)
Trichloroethylene	0.47	12.5	NA	ND	498	0.109
Chloroform	0.37	15	180	ND	19.6	0.009
Tetrachloroethylene	0.57	3.5	NA	ND	250	0.279
1,1,1-Trichloroethane	0.41*	10-45	NA	ND	1830	183
Methylene chloride	0.38*	150	NA	ND	502	0.606
t-1,2-dichloroethylene	0.52*	10-45	NA	ND	2000	17.72
Vinyl chloride	0.42	10-120	210	ND	10.2	0.005
1,2-dichloroethane	0.39	360	NA	ND	9.90	0.009
Chlorobenzene	0.48	53	NA	NA	100	4.36
1,1-dichloroethane	0.92*	10-45	100	ND	990	124
Carbon Tetrachloride	0.41	10	NA	ND	20.4	0.011
PCB's	NA	a	a	a	b	b
Benzene	0.53	130	300	3.75	0.940	0.038
Toluene	0.17*	120	300	3.75	1000	533
m-Xylene	0.15*	50	300	3.75	998	161
o-Xylene	0.15*	75	300	15	998	161
p-Xylene	0.15*	250	300	3.75	998	69.0
Ethylbenzene	0.67*	80	300	7.5	998	230
Phenol	a	a	a	3.75	49.0	516
Cyanides	ND	d	d	d	b	b
Arsenic Compound	ND	d	d	d	b	b
Cadmium Compound	ND	d	d	d	b	b
Chromium Compound	ND	d	d	d	b	b
Copper Compound	ND	d	d	d	b	b
Lead Compound	ND	d	d	d	b	b
Mercury Compound	ND	d	d	0.025 ^c	b	b
Zinc Compound	ND	d	d	d	b	b

a = potential to detect these compounds

b = compound specific

c = for atomic mercury

d = potential to detect certain compounds

¹ From Reference 22.² Compounds taken from Reference 23.³ Assumes a 200m path length.⁴ Short-term action levels are on an hourly basis and long-term action levels are on an annual basis. The various measurement techniques may yield multiple data points over a one-hour period comparison to the action levels.⁵ A direct comparison of OPM detection limits with action levels may be inappropriate, see Section 5.1.3.

* = Provided by vendor

ND = Not detectable

NA = Not available

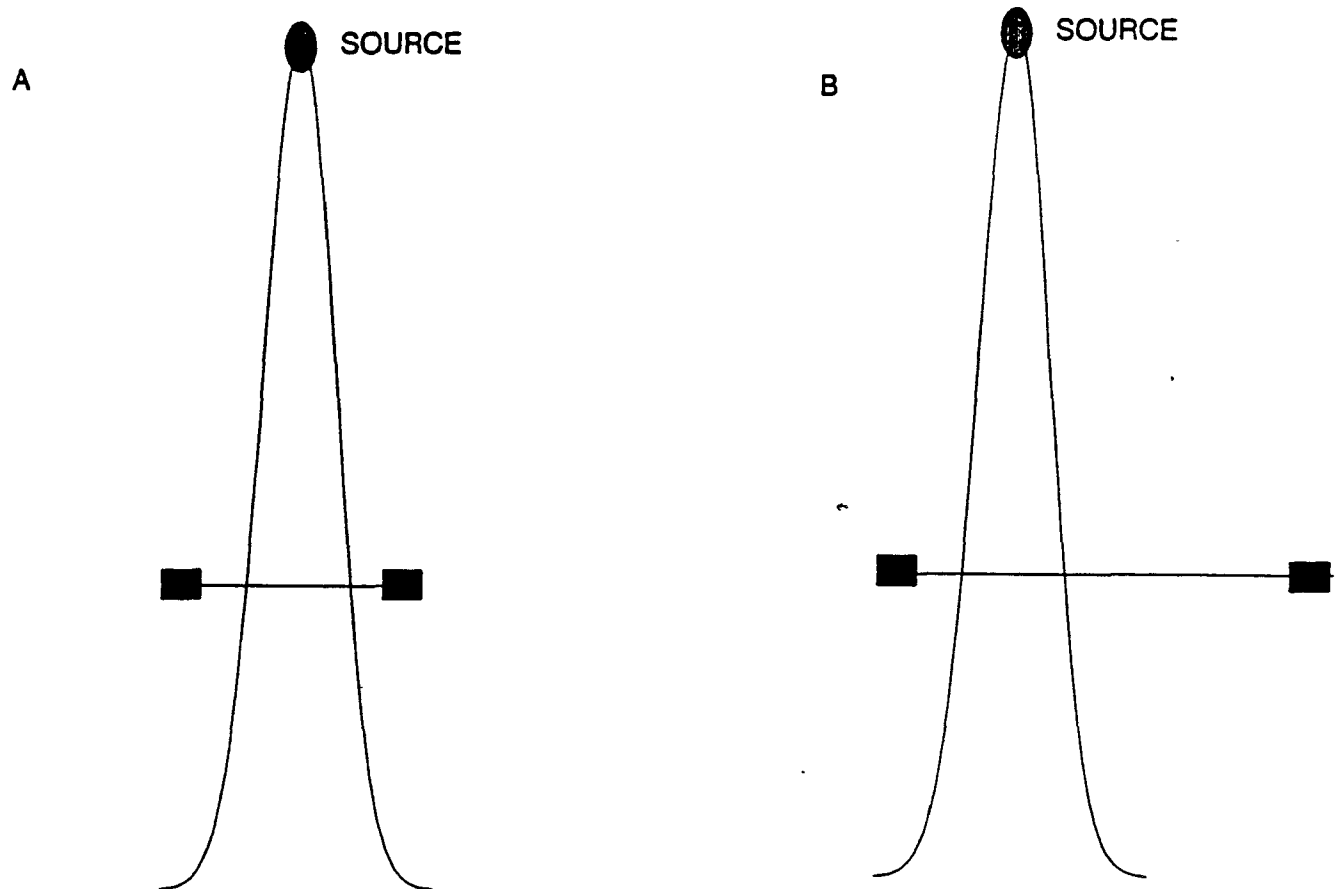


Figure 5-1. Extension of the Light Path.

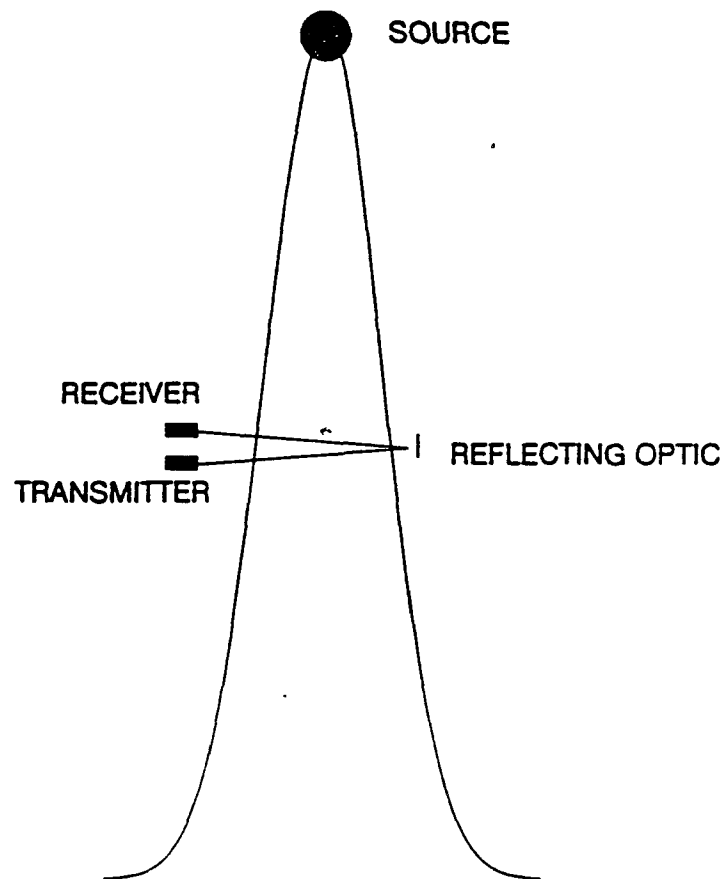


Figure 5-2. Multipassing the Light Beam.

5.1.3 Detection Limit Implications

Examination of the detection limits given in Table 5-2 shows that the OPM limits are orders of magnitude higher than the canister-GC systems for 200-m path lengths and a factor of two or three increase in the path length by proper multi-passing will not greatly alter the comparison. The key question, however, is whether a measured concentration level equal to the detection limit for a particular compound is sufficient to meet the program objectives. Even though the concentration at the fenceline may be below the detection limit, the more relevant question, in many instances, is what is the concentration at receptor(s) further downwind. As shown in Section 3.4, the source term may be calculated using the path-weighted concentration. The source term can then be used with the aid of a dispersion model to predict the concentration at the receptor. In this way, sampling methods can be used to evaluate adherence to action levels below the detection limit of the sampling method.

This concept is the basis for the transect method with point samplers. By placing a row of canisters or other samplers downwind of the site and normal to the wind direction, a path-weighted concentration can be obtained. A two-dimensional array of samplers can be used to define the cross-sectioned plume area.

The advantages of using an OPM with dispersion models instead of point samplers with dispersion models are:

- The likelihood of 100% plume capture is increased; i.e., there is less a chance that the plume will escape detection by either going over, under, or through the sampling system;
- A truer average plume inclusion is obtained;
- There is less of a problem of placing the samplers, where physical constraints (such as lagoons or pits) are present, however, a clear line-of-sight is necessary; and

- There is a time response factor that allows for near real-time updating of the source term and therefore of the receptor concentration that can aid in the assessment of short-term action levels (see the next subsection).

The disadvantage of OPMs relative to point monitor is the obtainable detection limits. However, as stated above the question is whether a compound present at the detection limit at the fenceline represents an unacceptable risk to downwind receptors.

5.2 RESPONSE TIME OF CONVENTIONAL AND OPEN-PATH MONITOR

One advantage of OPMs is the potential ability to report essentially realtime compound data. This contrasts with most conventional sampling and analysis methods that require the collected sample to be analyzed at a laboratory. These methods will usually have a turnaround time of at least 24-48 hours. While field GCs may be used, these will have run times of approximately 30 minutes to one hour, with some finite recycling time, giving an overall data turnaround time of approximately 1 to 1.5 hours. Clearly, the OPMs are superior in this respect, reporting preliminary concentration data on the order of minutes. As such, they are comparable to continuous analyzers. Some OPMs, however, require manual data verification and partial reduction, which increases the turnaround time for validated data.

Having near real-time data allows the user to correlate site operations with emissions. For example, during many types of site activity, the emission rate is likely to vary with amount of activity, the location of the activity, and the depth of disruption (i.e., excavation, drilling, etc.) required. A canister system "senses" all of this activity but time-averages it over the course of sample collection. An OPM, on the other hand, reports frequent concentration updates and allows better short-term resolution of emissions and any fluctuations in emissions. This is shown graphically in Figure 5-3 .

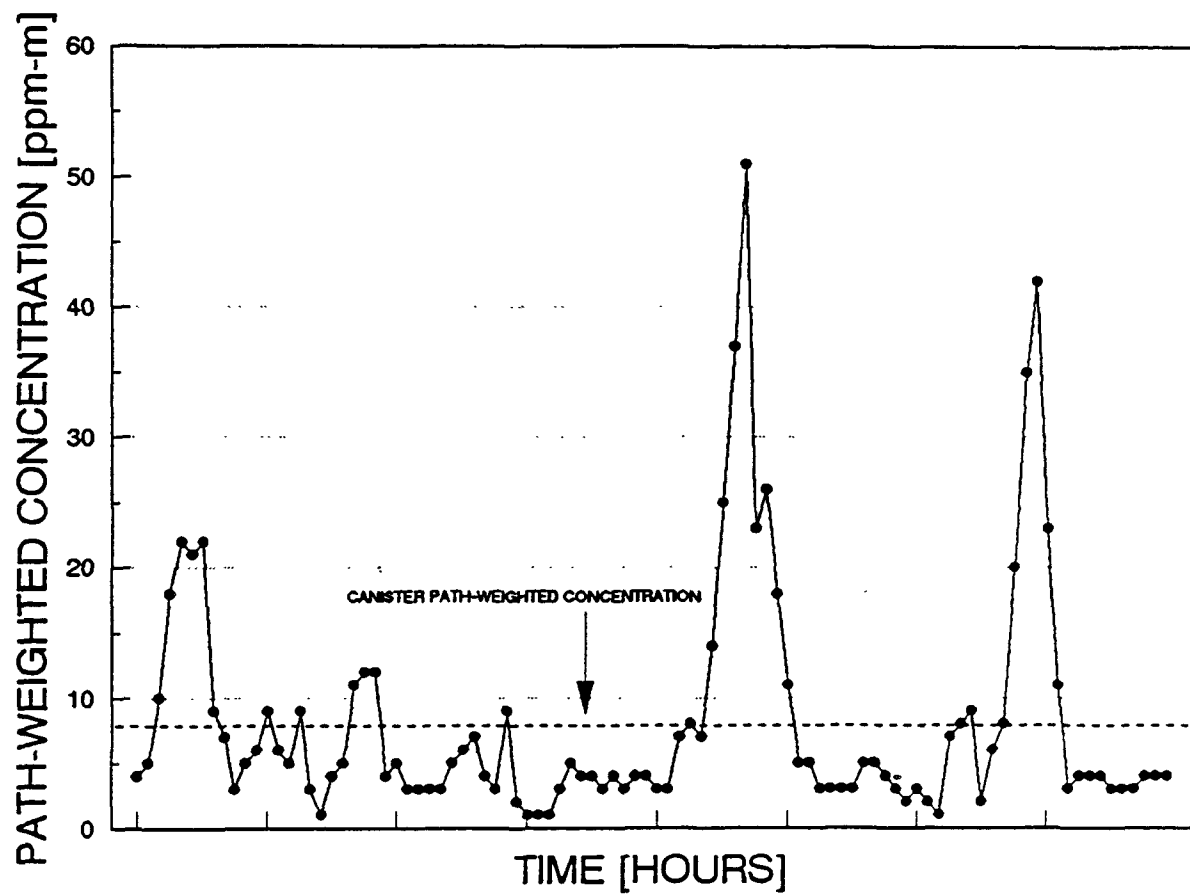


Figure 5-3. Emission Time Variability

The curve in Figure 5-3 represents the individual path-weighted concentration values of compound x as a function of time. Note that some high emissions values are measured for a very short duration. The dotted line represents the time-averaged value collected by the canister. Clearly, the canister data provides no information about the emission spikes that occurred. Time-averaging the OPM data would give nearly the same value as the canister. This shows how real-time data can be used to assess the risk of short-term exposures. While the duration of canister sampling could be shortened, a practical limit in the number of samples that can be taken is soon reached. In addition, if a concentration reaches the point where there is a significant risk to downwind receptors, the data turn-around time the OPM will allow for a quicker shutdown of site activity. Sampling and analysis methods with longer turnaround times only allow for hind-sight judgements about such matters; therefore, short duration sampling with portable analyzers is typically used. However, the lack of specificity of such analyzers can result in overly conservative decisions about shutdown.

5.3 PHYSICAL SITE LIMITATIONS

The final consideration is the physical limitations of the site to be monitored. These limitations include size, proximity to receptors, and obstructions such as trees, geography, debris, lagoons, etc. All of these physical limitations will affect the type and cost of the monitoring system chosen. For example, a site several acres in size will have relatively long fencelines to monitor and require the placement of several point samplers. Alternatively, the OPM, while having a finite range, can cover hundreds of meters of fenceline. A site with a number of obstructions or complex terrain, however, may not yield a clear line of site. This is not a problem for point monitors. It often requires ingenuity (and risk to workers) to place point samplers near lagoons or pits, while OPMs may be able to "shoot" across the site. Other potential physical problems associated with OPMs and point-sampler system configurations can be easily envisioned.

5.4 SUMMARY OF ADVANTAGES AND DISADVANTAGES

Table 5-4 lists the advantages and disadvantages of point and open path monitoring systems. Continuous point monitors are not considered because of their general inability to provide data for specific VOCs. There are six categories: detection limits, data turnaround time, amenability to dispersion model input, dealing with unknowns, availability of guidance and standard operating procedures, and physical site layout.

5.5 MONITORING DURING SITE ACTIVITIES

The individual characteristics of each Superfund site will affect the choice of the monitoring system for each of the actions undertaken. However, there is a fundamental set of questions and goals to address. These are:

- Goal of the Monitoring -- Define the overall goal of both the remediation activity and the air monitoring;
- Types and Amounts of Emissions Present -- Estimate the types of emissions expected and how well each monitoring system will detect these emissions;
- Physical Geography of the Site -- Consider the size, topography and any obstructions present;
- Proximity to receptors -- Estimate the dispersion of emissions to assess the effect that the emissions have on downwind receptors. The short-term exposure monitoring may also be necessary if the receptors are close to the site. This may affect the need for rapid data turnaround; and
- Actions Taken -- Consider how much of the site will be disturbed by sampling or pilot scale activities and how this will affect the level of emissions and possible placement of the instrumentation.

For some activities, choice of an appropriate monitoring system will be clear, while for others specific details of the sites will govern the choice of the system. In some scenarios, it will probably be advantageous to use both an OPM system and a point sampling system.

Table 5-4.

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.	Not 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

SECTION 6

OPEN PATH MONITORING DURING PRE-REMEDICATION

As discussed in Section 3.0 the activities during pre-remediation carry the site from site discovery through the SI. The only actions that require the use of a monitoring system, however, are those undertaken during the SI. The primary goal of the SI is to conclusively demonstrate what types and general levels of emissions are emanating from the site, as opposed to some upwind source. This monitoring is conducted at both the upwind and downwind fencelines. The subsections that follow discuss the monitoring needs of the SI.

6.1 MONITORING NEEDS DURING THE SI

As discussed in Section 3.1, the site is in an undisturbed or baseline state during the SI. The undisturbed site will typically have only low levels of emissions, especially if the waste is below surface or if the site is an older one where the volatile compounds have already dissipated from the surface layer. These concentration levels at the fenceline are typically in the 1- 10 ppb range. In addition, little is usually known at this point about the type of emissions, the magnitude of potential emissions present, or the location of the emitting sources. Therefore:

- The monitoring system must be able to detect a broad range of compounds, since it is unlikely that the contaminants present will be well known at this stage; and
- The monitoring system must not only have the sensitivity to detect the level of compounds present but also the sensitivity to distinguish between emissions due to upwind sources and those due to on-site sources.

With regard to physical layout, the monitoring system must be sure to intersect the plume of emissions emanating from both upwind and site sources. The plume must not evade the system by going around, under, or over the monitoring path. Thus, a physical inspection of the site and site-specific meteorology and dispersion modeling

must be used to ascertain the best placement of the system or systems. Some of the important meteorological considerations are discussed in Section 4.4.

Again, the goal of the SI is to conclusively demonstrate what emissions, if any, are coming from the site in question. This typically entails two monitoring sessions (though the downwind-only monitoring may be omitted in many cases). The first is monitoring downwind of the site to determine the presence of emissions. If emissions are found, the site is monitored both upwind and downwind of the site simultaneously. The difference in the emissions detected by upwind and downwind monitoring will determine the existence of site emissions. As shown in Figure 6-1, the monitoring system is configured normal to the wind direction, so that the emissions are carried through the monitored path. The monitored path must be long enough so that any plumes are located completely within the monitoring path. Also, the sensitivity of the monitoring system to wind direction and stability class must be evaluated for each site.

6.2 COMPARISON OF OPM AND POINT MONITORING SYSTEMS

The first consideration in developing any monitoring approach is the type of species likely to be present at the site. This is important, because a given system may simply not be able to detect the compounds present. The user is therefore referred to Table 4-2 for a list of compounds and applicable monitoring systems. Again, this is not an exhaustive list but should be a useful first approximation.

During the SI, the lack of historical information on the compounds present makes the task of identifying the appropriate monitoring system difficult without resorting to a trial-and-error approach. It is advisable, therefore, to employ a technique that can detect a wide range of compounds. If reliable information is available from any site records, then a more informed choice of system can be made. In general, however, the more classes of contaminants a monitoring system can detect, the better. Once the choice of systems has been somewhat narrowed, the important selection criteria are identification and quantitation of the specific compounds present.

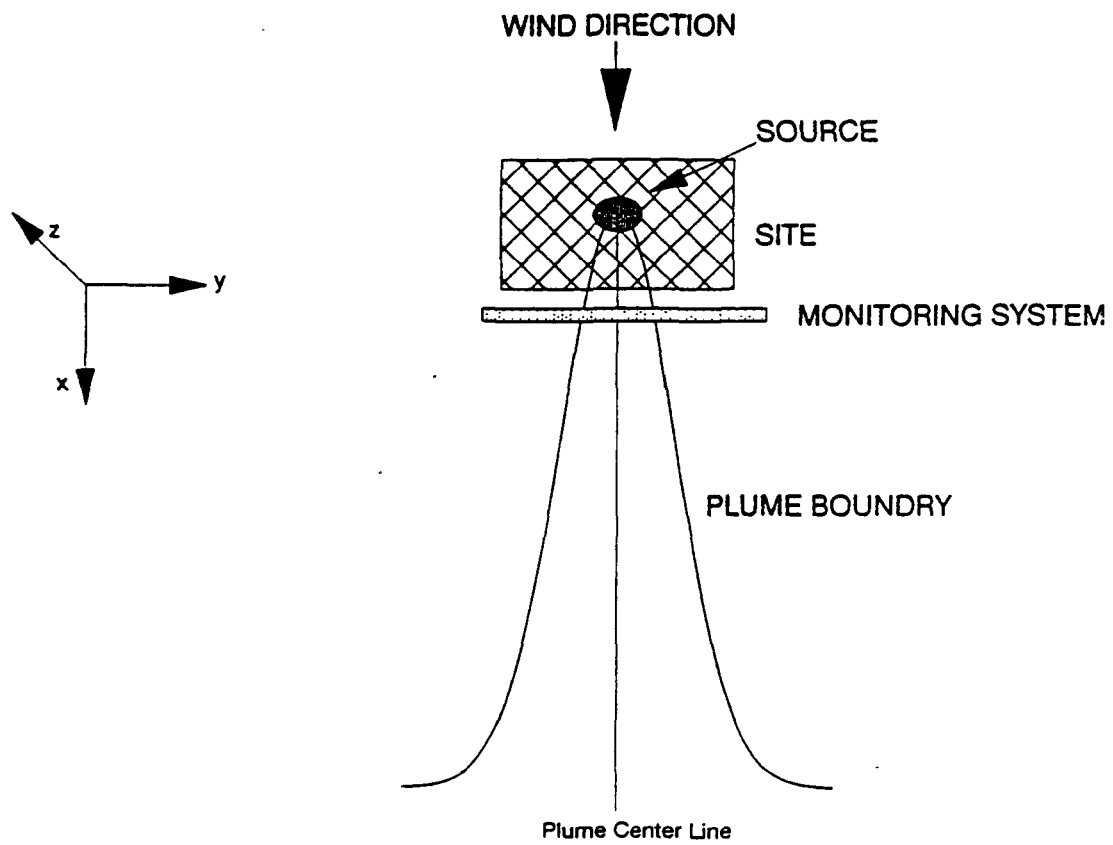


Figure 6-1. Monitoring System Setup.

While it is an easy matter to monitor both upwind and downwind of a site, it is more difficult to demonstrate that an emissions plume has not evaded the system, i.e., to prove that a false negative does not exist. The ability of the plume to pass around, under, or over a point monitor can be ascertained by using site-specific meteorological data and information on the local terrain. However, it is also possible for the plume to pass through the monitoring system without detection. For example, point samplers will generally be set up equidistant along a path. Thus, there are some areas, (i.e., between the samplers) that are not monitored, and very narrow plumes may escape detection by going between the point monitoring stations. OPMs may suffer from the same problem. While the light beam will interact with any plume coming across the beam path, the concentration of the constituents may be below the detection limits of the device or situated above or below the path. In the case of a narrow plume, dispersion modeling may be necessary to determine the probability of such events. For concentrations below the detection limit of the method, it will be impossible to determine if an emission plume is present.

Another consideration when selecting a monitoring approach is the size of the emitting area. In general, the larger the area, the greater the potential of multiple sources and the longer the fence line to monitor. These considerations magnify the concern about plume capture. There is also a concern about the topography of the site (see Section 5.3) and the number of point monitors needed, as well as the path length and detection limits of the OPMs.

Temporal variability in the emission rate is also a concern when choosing a monitoring system. The emission rate, $Q(t)$, of both the on-site source and any upwind sources (Section 4.4) may vary, depending on the soil type and moisture content, temperature, wind speed, etc. This could greatly affect the use of time-averaged approaches of long duration or poorly timed sampling events. Figure 5-3 shows that a time-dependent emissions source can go through periods of very high emissions that, because of the time averaging nature of most point samplers, will not be detected using

conventional sampling approaches. Secondly, periodic or one-time sampling events may miss portions or the entirety of the emissions from intermittent sources.

The primary goals of the SI, however, are to demonstrate the presence of any emissions from the site, and to make a preliminary identification of the emissions source. For this, the system must be able to detect the presence of the plume distinct from any background or upwind sources. Canister type monitoring (e.g., EPA Method TO-14) has detection limits below or near VOC concentration at typical background levels. Conversely, OPMs do not generally have the ability to detect species at this level. Several recent studies^{25,26} using OPMs during the SI reported non-detects for their target analytes. Therefore, the detection limits of the OPMs make them an unlikely candidate for use during the SI, despite their advantages for detecting temporal variations in the sources spatially variable emissions.

6.3 SELECTION OF A SPECIFIC OPEN PATH MONITORING

If the situation is suited to open path monitoring, one has at least three options of OPMs to choose from (other options are presented in Appendix B). The compound list should be compared with the list of compounds in Table 4-2. Next, the required detection limits should be compared with those presented in Table 5-1, keeping in mind the physical limitations imposed by the site. As previously discussed, longer path lengths may decrease the detection limits if the gases are distributed over this path.

The use of OPMs for SI applications is generally not advisable. If the use of an OPM system is warranted, an FTIR system will probably be the best choice. The FTIR is capable of monitoring the greatest range of compounds, among open path monitoring systems, an asset when little information is available concerning the types of emissions present. However, the detection limits of FTIR systems may not be low enough to detect levels of emissions that may be significant from a health risk standpoint. This will be particularly true of compounds such as benzene. For BTEX compounds, the UV-DOAS may be more applicable, since it is vastly more sensitive than FTIR systems.

Longer path lengths, however, may improve the FTIR's detection limits to acceptable levels for some of these compounds. All of the open path monitoring techniques are capable of monitoring over very short time cycles, which allows the temporal variations in the source to be characterized.

6.4 COMBINATION OF MONITORING SYSTEMS

In some scenarios, for both the SI and for subsequent activities, a combination approach using both a point sampler and an OPMs may be desirable. If the detection limits of the point monitoring systems can be used to complement the range and temporal advantages of the OPMs, a powerful monitoring tool will be available. The following example shows how these systems might be combined for use in the SI.

As mentioned earlier, the OPMs need not detect all of the compounds present to identify the origin of a plume. If some compounds that the OPM can detect well are present, those compounds may be used as surrogate or indicator compounds¹⁸. That is, a compound that will mimic the physical or meteorological behavior of all the compounds present. The surrogates may then be monitored to obtain information about the temporal variation of the source and could be used to demonstrate the origin of this compound. This would allow constant updating of the source term. The addition of point samplers would allow many compounds below the detection limits of the OPM to be detected. Fewer point samples would have to be taken since they can now be timed to coincide with high levels of emissions, as determined by the OPM.

The point samplers may also be used upwind or downwind to determine the origin of other compounds. Synchronizing the point samplers with the OPM will allow the origin of the on-site plume to be determined. Calculation of the source term from dispersion modeling will allow the user information about the plume spread. This, in turn, allows placement of the point samplers so that the likelihood of plume detection is improved.

SECTION 7

OPEN PATH MONITORING DURING REMEDIATION

As discussed in Section 3.0, activities during the remediation phase that may require monitoring are the Remedial Investigation (RI), Feasibility Study (FS), and Remedial Action (RA). Two types of air monitoring are of interest: 1) fenceline ambient air monitoring, and 2) ambient air monitoring just downwind of the emission source under prescribed conditions to develop emission rate or flux estimates. Air monitoring will also generally be conducted during the RI/FS and RA to determine exposure of on-site workers. Since workers tend to move around during the course of a day, the exposure monitors must also be portable. This type of industrial hygiene monitoring is typically performed using low-volume sampling pumps and sorbent tubes or passive dosimeters attached to the worker. Open path monitoring is not a valid alternative for this type of air monitoring.

The rest of this section addresses the potential uses of OPMs during the RI, FS, and RA steps of the Superfund process. The RI, FS, and RA may each require different approaches to monitoring. For the FS and RA, the site tends to be in a disturbed state during these steps and the resulting exposed, disturbed contaminated material will have much higher emission fluxes than for the baseline, undisturbed case.

The emergency response (ER) action will consist of steps similar to those of the RA; therefore, the remainder of this document will treat the ER as part of the RA, pointing out where they differ and where other actions may be appropriate.

The RI is generally an undisturbed site investigation where the goal is to obtain a more detailed knowledge of the potential air contaminants present. Certain activities during the RI, however, such as drilling or trenching, may increase the emissions from the site over baseline levels. The monitoring needs are similar to those of the SI but the speciation of compounds and the location of emission sources are studied in greater detail. Since the monitoring needs of the RI are basically similar to those of the SI, the

information presented in Section 6 for SI activities generally applies except when the site is disturbed. Then the subsequent comments apply.

Monitoring may also be performed during the RI to determine the risk potential of the site. This monitoring may be performed directly at specific downwind receptor locations or indirectly by making emission rate estimations for subsequent use with a dispersion model to estimate concentrations at downwind receptor locations. Monitoring at specific receptor locations is likely to be conducted with point samplers (e.g., canisters, Tenax sorbent tubes), though open path monitoring could also be employed if concentrations are sufficiently high. Monitoring to develop emission rates could be performed using either conventional sampling methods or OPM.

The FS develops and evaluates the possible remediation alternatives. The FS may involve testing some options on a pilot-scale basis, as well as evaluating possible control technologies. Air monitoring during the FS may be performed to investigate the emission rates as a function of site, waste, and operational variables. The monitoring goal during the FS is to determine the emissions rates that will probably be encountered during the RA. The RA is the full implementation of the chosen remedial alternative and can proceed over several years. Monitoring during the RA step usually addresses the risk the site emissions pose to downwind receptors. These emissions are likely to be significantly higher than those during any other step in the Superfund process, since, at least for ex-situ remediation processes, greater volumes of contaminated material are exposed and handled. The monitoring will generally take place at the fenceline to predict worst-case downwind receptor risk. Monitoring at specific receptor locations (e.g., the nearest downwind residence) may also be conducted. This monitoring will be analogous to fenceline monitoring and the type of system used will depend on the proximity of the receptors to the site.

The following subsections discuss the specific monitoring needs of each of these activities (RI, FS, and RA). Information is presented about the necessary monitoring specifications in light of the goals of the activity. General guidance is offered for selecting a monitoring system.

7.1 MONITORING NEEDS DURING THE REMEDIAL INVESTIGATION

Determination of emission fluxes during the RI will require identification of the compounds present in the contaminant plume and determination of the average concentration of each contaminant of interest in the plume. The temporal variability in the emission flux will also generally be of interest. This information can then be used to determine the emission potential of the site; therefore, the monitor must be capable of:

- Providing data of a sufficient temporal resolution to assess the emissions rate; and
- Providing a sensitivity and selectivity equivalent to that required during the SI.

7.1.1 Comparison of OPMs and Point Monitors

The first consideration is the list of compounds to be monitored. There should be some measurement data available from the SI or site records to support development of a target list. This list should be compared to the list of compounds in Table 4-2. It is also necessary to compare the detection limits and the risk levels associated with the compounds. As previously discussed, it may be possible to meet the monitoring objectives, even if the chosen monitoring method has a detection limit for a given compound higher than the health-based action level for that same compound.

The emission rates from the site and the resulting ambient concentrations are typically low for undisturbed sites. Therefore, the monitoring system used during the RI must be able to detect the compounds of interest at low levels (e.g., 1-10 ppbv). This requirement for high sensitivity will severely limit the choice of OPMs. Since some

knowledge of the compounds present at the site should have been developed during the SI step, identification of detectable compounds by OPMs should be readily achievable. This will then help identify surrogates (see Section 7.1.3). In any event, the OPM must be able to detect at least some of the compounds present in the plume from the site at the levels expected. If the sensitivity of the OPM is not adequate to meet this need, conventional sampling methods will definitely be a better choice. Conventional air monitoring methods will probably be the preferred choice for most RI applications.

7.1.2 Selection of a Specific OPM

The OPM needs to have a wide selectivity to be appropriate for monitoring during the RI; therefore, the FTIR is the likely OPM of choice. Unless a surrogate compound can be identified (see below), however, an OPM may not be appropriate because of the detection limits observable with OPMs.

7.1.3 Combinations of OPMs and Point Monitors

The monitoring needed for an RI might be accomplished with a combination of conventional point samplers and OPMs. This combination would be similar to that previously described for the SI, with the addition of taking the ratio of the other compounds detected by the conventional monitoring method to that of the surrogate detected with the OPM. As before, the surrogate is a compound emitted from the site that can be detected with the OPM and that can therefore be used to estimate the behavior of other compounds emitted from the site at levels too low to be detected using the OPM. The ratios would be used to estimate the concentration of the nonsurrogate compounds at the receptors.

7.2 MONITORING NEEDS DURING PILOT-SCALE ACTIVITIES

Pilot-scale activities during the FS may result in substantially more emissions from the site than was the case during earlier steps. The primary use of an OPM would be to make measurements close to the pilot-scale unit to measure emission rates. The measurements are generally performed as close to the emission source as feasible so that the measured ambient concentrations will be as high as possible. These concentrations may be in the range of 100 to 200 ppb per compound. Farther downwind, of course, the concentrations will decrease because of dispersion, and detection is still possible to the extent that the OPM can encompass most of the plume volume. The total mass of contaminants released from pilot-scale activities is likely to be small, so impacts at the fenceline can be expected to be minimal. Therefore, OPMs are generally no more appropriate as a fenceline monitor during the FS than they were during the SI or RI steps.

Compared to the baseline emissions seen during the SI or RI, activities undertaken during the FS will cause significant changes in both the amount and type of emissions present. The monitoring system, therefore, must have:

- Detection limits at or below the concentration levels of the compounds of interest;
- Sufficient temporal resolution to determine the time variability of emissions; and
- Ample flexibility in the range of compounds that can be detected.

Earlier investigatory activities should have determined most of the compounds present in the waste at the site, so the monitoring system will not need the broad species identification capability of the systems used in the SI and RI steps.

7.2.1 Comparison of OPMs and Point Monitors

The goal of monitoring during any FS pilot-scale operations will generally be to determine emission fluxes or rates that can be ratioed to estimate potential emission rates during full-scale remediation. This monitoring must therefore have a reasonably high degree of temporal resolution so that variations in emissions rates can be determined. The detection limits are a secondary concern for the following reasons:

- The levels of the compounds emitted will be greatly elevated above baseline levels, so the measured levels are more likely to exceed the detection limits of the OPMs;
- The monitoring systems can be placed close to the site of the remedial activity, which allows the plume to be monitored at points where the diffusion in the xz plane may not be as severe as it will be further away in the x direction.

However, if no compound is present above the detection limit of the monitoring system, a more sensitive method must be applied.

Several recent studies^{17,18,25} have used OPMs in conjunction with dispersion models to predict downwind impacts¹⁷ or measure on-site meteorological parameters.²⁵ One study¹⁸ used an FTIR to monitor compounds from a pilot scale dewatering action and used the path-weighted concentrations to calculate the source term. No monitoring was conducted at downwind receptors for comparison however, so the accuracy of the method could not be determined.

7.2.2 Selection of a Specific OPM

Since the compounds present at the site should be reasonably well known at this step of the process, it is straightforward to determine the overlap of the compound list with that in Table 4-2. The primary consideration will be the applicability of a given OPM to the compounds of interest. The detection limits of the OPM will be a secondary consideration.

7.2.3 Combination of OPMs and CPMs

The combination approach described in Section 6.1.3 could also be applied during this activity.

7.3 MONITORING NEEDS DURING THE REMEDIAL ACTION

The primary goal of monitoring during the RA is to protect human health and the environment. This monitoring is therefore employed at the downwind fenceline or point of plume impact (see below). One key requirement of any monitoring system for use during the RA is that it provide rapid feedback to site personnel so that they can halt or modify the remediation activities if fenceline action levels are exceeded.

Since the primary objective is to protect human health and the environment, dispersion models play an important role in extrapolating fenceline concentrations to receptor concentrations. Note that the concentration at the actual site fenceline may not be a critical piece of information. Rather, only a knowledge of the upper limit (i.e., effective action level) fenceline concentration may be important. If this upper limit is known, it can be used to ascertain a source term for use as input to a dispersion model in cases where the compound is not detected at the fenceline. The dispersion model can then be used to calculate the maximum impact at the receptor.

The chosen monitoring system must be capable of the following, regardless of the type of remedial or sampling action :

- The system must be able to measure the compounds identified in the site emissions during previous actions (RI, FS, etc.) or, for the ER, the system must be able to identify a wide range of compounds, since little information may be available; and
- The system must have detection limits sufficiently low that (estimated or measured) ambient concentrations at receptors of interest can be compared with action levels, regardless of the placement of the monitoring system.

It is also useful if the system can determine both short-term and long-term exceedances of the health based action levels.

There must be a reasonable surety that the monitoring system will intercept the emission plume downwind of the site. One important consideration is meteorological conditions, such as stability, that affect dispersion of the plume. Thus, the sensitivity of the system to deviations in the wind direction must be considered.

7.3.1 Applications to Specific Remediation Approaches

This section considers some of the more commonly used remediation technologies as examples for monitoring assessment. These technologies are divided into two classes: point sources and area sources. The example technologies are:

- Air Stripping;
- Incineration; and
- Excavation.

While many other remediation technologies exist, these three are adequate to illustrate the general issues related to ambient air monitoring for any remediation alternative.

7.3.2 Point Source

In atmospheric dispersion modeling, emissions from point sources are generally easier to characterize than those from areas sources. Emissions from point sources are adequately described by the typical Gaussian dispersion and model input parameters are readily obtained. In addition, tracer gas releases can be used to effectively mimic the behavior of the point sources and allow for a simple estimation of emission rates using Equation 4-18.

Two remediation options that involve point sources of emissions are air stripping and incineration. In both of these, the emissions emanate from an elevated release point and the emitted gas will have some velocity in the vertical (z) direction because of the elevated temperature of the exhaust gas or the effect of a mechanical blower or fan. The height of the emissions stack, the velocity of the exit gas, and the thermal buoyancy of the plume will affect how far downwind of the source that plume encounters the ground. This can be as far as several kilometers downwind of the site. Thus, placement of the monitoring system is no longer a trivial task.

The behavior of the plume under various conditions can be estimated using an atmospheric dispersion model and this information can be used to select the monitoring locations or path. The dispersion model must also be used to calculate the plume spread at the point of impact so that some estimation of the needed path length for plume inclusion can be made.

In addition to stack emissions, other sources may exist at the site, such as material storage and handling facilities. Uncontrolled emissions from storage piles or lagoons and waste processing and feed units are likely to be much higher than stack emissions; therefore, some type of fenceline monitoring may be warranted, even if the plume from the stack(s) passes over the fenceline at some considerable height.

Emissions may also be monitored directly in any process stack, vent, or flue. These emission rate values can then be used with an atmospheric dispersion model to estimate downwind ambient concentrations. Cross stack monitoring²³ would allow the ambient concentrations at the receptors to be estimated without the need for monitoring downwind plumes.

Air Stripping

An air stripper is used to remove volatile compounds from water by introducing contaminated water at the top of a packed tower and having air flow countercurrent to the water flow to effect mass transfer of the VOCs to the air phase. Control devices

such as carbon adsorption systems or thermal oxidation units may be used to reduce the emissions from the air stripper. The control devices may change the temperature of the emission plume, as well as its composition.

The plume emitted from an air stripper will have a high water content. The elevated concentrations of water in the plume may affect the use of infrared measurement techniques. As discussed in Sections 4 and 5, the interference caused by water can adversely affect the detection limits. In addition, control devices obviously eliminate a significant portion of the emissions (e.g., 90-99%). The control devices will result in lower concentrations downwind of the air stripper and this must be considered when selecting a monitoring system; i.e., the necessary detection limits at the point of plume impact may need to be revised.

Incineration

An incinerator is a thermal treatment device that reduces the volume and toxicity of the contaminated material by combustion. Ideally, organic compounds are oxidized to carbon dioxide and water vapor, and the halogenated material is converted to these same compounds plus acid gases. No combustion process is 100% efficient, so some material is not combusted and passes through the system unchanged. Also, products of incomplete combustion (PICs) may be formed and emitted. No control devices for VOCs are used with incineration. Control devices for particulate matter and acid gases, however, will remove some organic compounds in addition to altering the characteristics of the emissions plume.

Since incineration is designed to change the character of the waste stream being treated, the type of emissions that need to be monitored may be changed from what is originally present in the waste because of changes in the relative composition of the material and the presence of PICs. PICs are waste stream dependent but can include polycyclic aromatic hydrocarbons (PAH's), polychlorinated biphenyls (PCBs), chlorinated benzenes, chlorinated dioxins, and chlorinated furans. These compounds are difficult to monitor with many of the current open path monitoring methods²³. The user should

obtain some information about the possible combustion by-products before selecting a monitoring system.

7.3.3 Area Sources

Area sources are generally large, heterogeneous, ground-level emission sources. They may contain multiple areas with vastly differing emission rates. Modeling the emissions from an area source is more difficult than modeling emissions from a point source, since the necessary input parameters to the model are usually known with much less certainty. The output of emission models for area sources tends to have a large uncertainty associated with it. Tracer gas methods may also be somewhat difficult to employ since the degree to which a single point emission or an array of point emissions mimics the true source is uncertain.

Monitoring methods to determine emission rates from area sources have typically used flux chambers, the transect method (an array of samplers in both the y and z directions), or OPMs. While the flux chamber isolates and measures an emissions rate from a local area source, they are limited in size to only a few square meters. The degree to which the sampled area represents the entire source affects the number of points that need to be sampled and the representativeness of the overall data set. Flux chambers are best suited for relatively small, homogeneous area sources. The other two measurement options have been compared throughout this document. These methods yield an emission rate that can be thought of as emanating from a theoretical point source located some distance upwind of the site, called a virtual point source²⁴. One common example of an area source during remediation is material handling operations such as excavation. The monitoring issues related to excavation are significantly different from those encountered during air stripping and incineration.

Excavation

Excavation is the physical removal of the contaminated soil or waste from its subsurface location at the site. The excavated material may be returned to the excavation pit, transferred to an on-site remediation process or storage area, or transported to an off-site remediation or disposal process. The excavation process requires the use of heavy equipment such as backhoes that emit compounds associated with the combustion of diesel fuel. In addition, large amounts of dust may become airborne during material handling activities.

As is true for any RA, monitoring will primarily be performed to evaluate the exposure of downwind receptors to site emissions. For excavation, this monitoring can take place at the fenceline of the site. The highest release point of the emissions will be from the elevated backhoe or scoop of the heavy equipment. There will be little or no velocity component in the z direction; therefore, the plume should quickly reach ground level.

The dust stirred up during site activities is a potential problem for OPMs. The dust may coat the optics and, to a lesser extent, it may cause Mie scattering if the dust is of a certain size. From a health stand point, particulate matter (PM) and associated contaminants such as heavy metals can contribute to the total risk from the air pathway. Thus the PM is itself a candidate for monitoring. This topic is discussed further in Section 9.0.

The air monitoring during the RA is concerned with evaluating the concentration levels and any risk these levels pose at the downwind receptors. For the calculation of long-term risk, action levels may be set for the acceptable fenceline concentrations. Exceedances of these action levels are only a concern if the exceedances are large or persistent. Another approach that may be employed is to generate a running cumulative emissions estimate made over the lifetime of the site. This total can be used to set the operating rate of the RA or the efficiency required for any control devices. In either case, the data turnaround time is not as critical for this assessment as it is for assessing

the risk for short-term exposure. The monitoring can be accomplished by either OPMs or CPMs.

As previously discussed, short-term risk addresses compounds that may pose a health risk even for very brief exposures because of their action as an asphyxiant, poison, etc. Evaluation of short-term risk requires a timely update of the ambient air concentrations. Activities such as excavation may result in large spikes of emissions for short durations of time. While points samplers are capable of detecting such spikes, the sample collection period must closely coincide with the lifetime of the emission spike or it will be missed entirely or the time averaging nature of the sampling will obscure the severity of the spike. Exact timing of sample start and sample finish to coincide with emission spikes is not practical for the vast majority of situations.

The suitability of an OPM for determining both short-term and long-term adverse effects on air quality should be considered. For long-term effects, a preliminary check is to compare the detection limits with long-term health-based action levels. Another possible check is to use the detection limits of the OPM as input to a dispersion model and determine the average concentrations at receptor locations over an appropriate time interval. This will give some idea about whether the monitoring systems will have adequate sensitivity. For short-term effects, the emission rate data acquired during any FS pilot scale operations should be reviewed to see what maximum emission levels can be expected. The OPMs detection limits should also be checked against short-term health-based action levels.

Applications of OPMs to the RA have been limited primarily because few Superfund sites have reached the RA. OPMs have however been applied in heavily industrial areas^{11,19} where numerous types of emissions are present. The industrial applications have shown the utility of OPMs when concentrations reach 25 to 50 ppb or above. Since these emission levels are likely to be reached during the RA. It is expected that OPMs will be a monitoring option.

7.3.4 Selecting an OPM

The type of OPM to be used during an RA will depend on the compounds present and the type of activity. Since FTIRs and GFCs will be affected by high levels of CO₂ and water vapor, the expected concentrations of these interferents should be considered when estimating field detection limits. The use of UV-DOAS avoids most problems with these interferents, but the systems may not have the desired selectivity range needed to detect all of the compounds present. The likely monitoring option for the ER is the FTIR.

7.3.5 Receptor Confirmatory Monitoring

As previously discussed, monitoring at receptor locations of greatest concern may be conducted in addition to any fenceline monitoring. This confirmatory monitor is generally best conducted with point samplers. This recommendation, however, depends on the proximity to the source and the possibility of short-term exposure exceedances.

SECTION 8

OPEN PATH MONITORING DURING POST-REMEDIATION

Monitoring, after the completion of the remedial phase, is conducted to ensure the site is clean and that it does not emit compounds at a hazardous level. This monitoring is conducted under undisturbed conditions and close to the area of the remedial activity. If the remedial option did in fact clean up the vast majority of the contaminants, then the emissions will be low. Therefore, the monitoring system must be able to detect the emitted compounds at very low concentrations.

The previous monitoring activities at the site should have revealed a wealth of knowledge about the amounts, location, and types of compounds present. This knowledge should make identification of the type of system capable of monitoring these compounds straightforward. Time response is not as critical an issue as during earlier phases nor is determining variability in the emissions. The question therefore is primarily one of sensitivity for assessment of risk.

Since the levels of compounds emitted are likely to be no higher than those encountered in the SI, the user should review any air concentration data from the SI (or RI) steps at the site. After review, the decision can be made as to whether the sensitivity of the OPMs is sufficient. If not, as is likely be the case, the appropriate point monitor may be determined.

Since the rate of decrease of residual emissions from the site may also be an issue, one useful application of the OPM is as a continuous or semi-continuous monitor. OPM's can be left to operate in an unattended fashion¹¹. They can be controlled remotely via phone modems and the data monitored from a remote location. This has the advantage of keeping the monitoring cost reasonably low and also diminishing the number of site visits. For this type of monitoring, GFC is an option along with FTIR and UV-DOAS.

SECTION 9

FUTURE DIRECTION OF OPM RESEARCH AND USE OF OPMs FOR SUPERFUND APPLICATIONS

The previous sections discussed OPMs and point monitoring systems and their application to Superfund monitoring activities. The field of open path monitoring is still "coming of age" and many of the concepts and practices associated with these technologies are new. OPMs offer many potential opportunities for monitoring sites in a more cost-effective but data-intensive manner than conventional AAM methods.

This section discusses what steps need to be taken and what studies need to be performed to get the maximum benefit from OPM technology for the Superfund program. An overview is first presented, then this section discusses some of the areas where further efforts are needed to expand and refine the capabilities of OPMs. These areas are:

- Quality assurance and quality control tests;
- Emission rate measurements; and
- Complex source flux measurements.

Improvements in these areas will help facilitate and encourage the use of OPMs. These areas are discussed in Section 9.2, Field Measurements and Operation Protocol Developments.

A second developmental area for OPMs is improvement of both hardware and software. These improvements will probably include:

- Reduction of detection limits;
- Expansion of the capabilities of OPMs to allow measurement of other classes of compounds;
- Development of stand alone operation; and
- Measurement of I_o .

These topics are discussed in Section 9.3, OPM Hardware and Software Development. The need for information transfer and user education is discussed in Section 9.4.

9.1 OVERVIEW

Open path monitoring has the potential to eventually be able to provide accurate, cost-effective data for many Superfund applications. These systems would provide site managers with timely, pertinent information about exposure via the air pathway and would ultimately result in faster and safer remediations. Much work, however, remains to be done before OPMs realize their full potential for AAM at Superfund sites.

The biggest need is for EPA to develop a long-term developmental plan for the use of optical remote sensing methods, including OPMs, for environmental applications. This scope obviously exceeds just Superfund sites. The basic questions that need to be addressed are:

- 1) Current and future capabilities of optical remote sensor (ORS) technologies;
- 2) Current and future monitoring needs;
- 3) Current applicability of ORS systems;
- 4) Recommended developmental and evaluative studies; and
- 5) Development of standard procedures and practices.

This information is necessary before a long-term plan can be developed to guide the development of ORS and OPM as standard compliance-type methods. The U.S. EPA's Office of Air Quality Planning and Standards and the Office of Research and Development have begun the process of developing such a long-term plan with input from academia, industry, other users, and equipment vendors.

It is hoped that ultimately the capabilities of various OPM technologies will be well-demonstrated for environmental applications, that standard operating protocols will be available, and that minimum performance specifications or requirements will be established.

The recommendations given in this document are necessarily based on the current knowledge of the capabilities of OPMs. As mentioned previously, only a limited number of applications have been attempted to date at Superfund and other hazardous waste sites. The number of field applications to date is small and these efforts have been limited in scope. Furthermore, the use of OPMs requires a high degree of technical expertise in both spectroscopy and ambient air monitoring. These factors have lead to many questions and some apprehension about the use of these methods. This section discusses some of the important issues and tests that are needed to address these concerns and to help ensure the proper use of OPMs.

9.2.1 Quality Assurance and Quality Control

Quality Assurance (QA) and Quality Control (QC) tests are necessary in ambient air monitoring to provide a mechanism for the ongoing control and evaluation of data quality throughout a measurement program. They also ensure that the data collected are of known accuracy and precision. For conventional AAM, these QA/QC tests generally take the form of performance and systems audits, the collection of replicate samples, the analysis of spiked samples, the analysis of system and analytical blanks, etc. Analogous QA/QC tests for OPMs have yet to be developed and accepted as part of standard operating procedures (SOPs).

The QA/QC tests appropriate for conventional AAM methods are not generally applicable to OPM methods because of inherent differences in the methods. Conventional approaches generally involve the physical collection of an air sample at a discrete point using a pump or vacuum to draw the air into a collection device or through a filter or sorbent, while OPMs do not involve any physical collection or compositing of the sample. The QA/QC tests used to date for OPMs involve checks of the instrumentation itself and checks of the sampling strategy (i.e., light path location, frequency of sampling, when to sample, etc.). Checks of the instrumentation generally

involve collecting data from a standard gas in a closed cell and using these data to demonstrate whether the OPM system is operating in accordance with some set of established guidelines. These cell tests, however, are not directly comparable to data from open paths since there is no accounting for light losses due to divergence, rapidly varying path concentrations in the atmosphere, interferences, etc.

Similar limitations exist for QA/QC tests to evaluate the sampling strategy selected for a given application. While no standard procedures have emerged, some potential methods have been suggested and attempted in the field. Data accuracy can be determined by collecting background spectra and through the use of tracer gases and confirmatory sampling.

The background tests involve collecting data under field conditions without an active emission source. For example, to determine excavation emissions data could be collected before the excavation equipment is turned on to get background or baseline data. A second set of data could be collected with the excavation equipment running but before excavation of any material to determine emissions from the excavation equipment itself. For measurements during the RI, blank tests could be performed by setting up the OPM upwind of the emission source under conditions (e.g., path length, number of beam reflections) that match as closely as possible the conditions encountered downwind of the emission source.

The accuracy of OPM data can be evaluated using a tracer gas release that closely mimics the emission source. The validity of this approach depends on how closely the tracer gas mimics the release, transport, and analysis of the target analytes. For Superfund applications, the limiting factors will generally be the ability to create an area emission source of the tracer gas and getting the release point(s) to coincide with the actual emission source. The validity of the Gaussian dispersion model inherent to this approach will also depend on a number of factors. In general, it will not be valid over short distances (e.g., <50-100m). Another approach for determining the accuracy of OPM data is to set up a series of point samplers along the line of the light beam. While

an excellent check of OPM performance for evaluative studies, this approach has several drawbacks as a routine QC test such as cost and data turnaround time.

The assessment of the precision of OPMs is not as critical an issue as it is with conventional monitoring systems. OPMs collect large numbers of spectra and average these spectra. Least squares fitting of reference spectra to these averaged spectra is then done using thousands of points, each a measure of the concentration. This large number of measurements of the concentration allows rapid assessment of the instrument precision.

9.2.2 Measurement of Emissions Rates

One of the advantages of OPMs over most conventional AAM methods is the ability to use the path-weighted concentration to calculate a source term or emission rate. While theoretically this is readily achievable, the accuracy and precision of this method have not been adequately tested. Since emission rate determination is a key area for application of OPMs for Superfund, test should be performed to validate this application. This would involve evaluation of the atmospheric dispersion model used to back calculate an emission rate as well as an evaluation of the approach for collecting the OPM data.

For example, tests similar to those conducted by EPA region VII²⁹ where mixtures of gases were released at a known rate and detected downwind could be used as a starting point for these evaluations. The OPM could be placed close to the source along with a row of canisters (transect method) for purposes of comparison and normalization. A dispersion model would then be used to predict the concentration at a receptor some distance downwind with OPM data as input. The receptor could be a single canister or another row of canisters.

This test would allow prediction of the emissions rate that could then be compared to the known emission rate. The predicted receptor concentration could then

be compared to the measured concentration at the receptor. The row of canisters would be used to normalize the path-weighted concentration and to act as a reference method. A series of such tests are needed to assess the validity of this approach for varying source strengths, release points, meteorological conditions, terrain and so forth.

9.2.3 Complex Source Flux Measurement

Many Superfund sites and industrial complexes have multiple sources of varying emissions. The plumes from these sources are often mixed by the time they reach the site fenceline. In addition, the extent of the plume is generally not well known making the certainty of plume capture difficult. It would therefore be advantageous to develop integrated electro/electro-optical monitoring systems that would sense the extent of a plume (with LIDAR) and measure the concentration of the species present in the plume in both the horizontal and vertical directions (with OPMs). This would in effect, involve monitoring everything that passes through a plane parallel to the site. Coupling these systems with radars, sodars or meteorological towers (depending on source height and complexity) could then allow the determination of wind fields that could in turn be used to determine the total flux of emissions from the site.

There have been some conceptual designs for such monitoring systems but a great deal of work would have to be done before they could be ready for testing. However, this type of emissions measurement would be very comprehensive and could potentially be used as the standard for assessing total emission from a site or complex. It therefore has great promise for emission inventory type work.

9.3 OPM HARDWARE AND SOFTWARE DEVELOPMENT

Currently, one of the major drawbacks to the use of OPMs is their inability to measure very low concentrations (1-5 ppb). Sensitivity to low concentrations is a key issue when conducting monitoring in the SI, RI and O&M. There are certain fundamental hardware and software problems that must be overcome which will allow

the detection limits to be lowered. In addition to detection limits, two other problems: stand alone operation and expansion of OPMs to new chemical classes are discussed below.

9.3.1 Reduction of Detection Limits

The disadvantage of OPMs, compared to point monitors is their detection limits. Several hundred meter pathlengths are often necessary to produce detection limits in the single digit ppb range for most compounds. However, when using infrared methods single digit ppb detection limits are not reached even at 500 meters for compounds such as benzene and toluene (see Table 5-3).

Improvements in detection limits will likely be based on an increase in the signal-to-noise ratio and accurate removal of any interferants. The signal-to-noise ratio increase may be accomplished by making the detection system more sensitive, improving the properties of the light source, or having more efficient light collection to improve the signal intensity²⁷. The interferant issue must be addressed by accurate assessment of the interfering compounds present and their spectra. In particular, the effects of water and carbon dioxide in the infrared must be fully accounted for in all aspects including their non-linear behavior. Accurate removal of the water and carbon dioxide from the spectra using mathematical methods will in principle give access to new regions of the spectra, i.e., regions where other molecules have stronger absorptions. One attempt to remove the water problem has been to collect reference spectra at several concentrations and remove the water using the spectra that is in closest agreement. This has not been completely proven and requires the fitting of several different spectra in a trial-and-error manner. Even in this case however, the large span of absorbance frequently makes complete cancellation of water vapor and carbon dioxide impossible.

Another issue where detection limits are important is the ability to detect "other classes of compounds." These compounds include metals in both atomic and complexed forms, polycyclic aromatic hydrocarbons (PAH's), and the chlorinated varieties of dioxins/furans, and compounds bound to particulate matter (PM). In addition, the increasing interest in dust emissions makes PM monitoring a likely requirement. These classes of compounds are found at Superfund sites but can rarely be detected using OPMs because they are below the detection limits and OPM methods are unable to sense their presence.

Metals in their atomic state are not capable of being monitored with infrared technologies. They can however, be monitored by ultraviolet methods. Both path and point variety methods need to be developed that will accurately characterize these emissions. Metal atoms in a chemical complex are much harder to account for since different complexes will have different structures. However, metals in different oxidation states have very different risk potentials and spectroscopic techniques have been shown to be sensitive to these different states²⁸. Therefore, some investigation of these techniques is warranted to application to just such monitoring.

Other compounds such as PAH's, dioxins, and furans have extremely low action levels. Sensitive instruments must be used to detect these species at these levels. ORS methods have been reviewed for application as CEMs for these compounds at municipal solid waste incinerators²³ and laser induced fluorescence (LIF) methods were recommended for their detection. Various methods for application to these compounds were discussed in this report. A description of these methods are included in Appendix B.

Finally, not all emissions are expelled in the molecular or atomic form but may undergo some form of association with other compounds such as molecules or particulate matter. These complexes are not well detected by any of the conventional

methods. OPMs may have the ability to detect these species when associated or bound to particulate matter.

9.3.3 Stand Alone Operation

All OPMs are equipped with computers that at the very minimum, collect, process, and store data. In fact, much credit for allowing some of the ORS systems to be used as AAM goes to improvements in computing capability. The uses of the computer control has, however, not been fully exploited.

The use of the computer could be expanded to include stand alone operation in which the computer collected data in an unattended fashion. This lowers labor costs and frees the operators for other duties. This type of data collection has been tried recently with good success¹¹. It is not without problems, however; and efforts need to be made to introduce artificial intelligence systems and expert systems that can investigate and correct problems that may arise.

Another use of the artificial intelligence would be to have a system capable of detecting the presence and location of an emissions plume. The extent of the plume could be mapped out by the LIDAR methods and the system could be updated to follow the evolution of the plume. This would require the introduction of meteorological data to assess the plume direction.

A complete package for monitoring the flux of emissions from complex sources may be assembled by adding a wind field profiler. This profiler could come in the form of a simple met tower if vertical plume dispersion is low or depending on complexity, a sodar or radar system. The profiler would measure the local wind fields throughout the distributed source area.

Advances in this area would eliminate much of the worry over plume capture and dispersion assumptions. The operation could be performed remotely by using phone modems and in a very cost effective manner. In addition, the concern over tracer gases mimicking the source would no longer be a concern.

9.3.4 Measurement of I_0

Appendix A contains a derivation of the fundamental equation used in open path monitoring to relate a measured parameter, light intensity, to concentration. Equation A-12 shows that the absorbance, which is directly related to concentration, is equal to the logarithm of the ratio of two intensities. The first intensity, $I(v)$, is the intensity measured after the light beam passes through a sample. The second intensity, $I_0(v)$, is defined as the light intensity which is incident on the sample. In practice, $I_0(v)$ is modified by the detector response, divergence losses, and reflective losses from the optics and the combined effect of these is called the instrument response function, $R(v,l)$. A measurement which includes these effects may be written as:

$$I_0'(v) = I_0(v) \cdot R(v,l) \quad (\text{Eq. 9-1})$$

where: $I_0'(v)$ = the modified $I_0(v)$;
 $R(v,l)$ = the instrument response function; and
 l = the path length.

$R(v,l)$ includes the contributions of the detector, the optics and any loss due to beam divergence over an open-path. Since only the beam divergence is dependent on path length, $R(v,l)$ may be written as:

$$R(v,l) = R(v) \cdot r(l) \quad (\text{Eq. 9-2})$$

where: $R(v)$ = contains the frequency dependent responses; and
 $r(l)$ = the path length dependent divergence loss.

In similar fashion, the intensity measured when the sample is present, $I(v)$, may be written as:

$$I(\nu) = I_0(\nu) \cdot R(\nu) \cdot r(l) \cdot \tau(\nu) \quad (\text{Eq. 9-3})$$

where: $\tau(\nu)$ = the frequency dependent term due to attenuation of the light beam by ambient species.

The transmittance may be calculated taking the ratio of $I(\nu)$ to $I_0'(\nu)$.

This yields:

$$T = \frac{I(\nu)}{I_0'(\nu)} = \frac{I_0(\nu) \cdot R(\nu) \cdot r(l) \cdot \tau(\nu)}{I_0(\nu) \cdot R(\nu) \cdot r(l)} = \tau(\nu) \quad (\text{Eq. 9-4})$$

and cancelling like terms leaves only the term due to ambient species, $\tau(\nu)$.

$I_0'(\nu)$ may be measured by conducting a short path measurement (i.e. a path length of approximately 1 meter)³¹. This measurement contains the appropriate instrument response function plus some contribution due to ambient species. A baseline fit may then be made to the spectra which eliminates the contribution of the ambient species. This baseline fit is then $I_0'(\nu)$ for $r(l) = 1$. To correct for $r(l)$, a second measurement must be made and baseline fit to a spectrum collected over the path length to be measured. The ratio of the short path baseline to the long path baseline is then $r(l)$.

Sometimes, measurements of $I_0'(\nu)$ are conducted over the full measurement path and they include absorptions of ambient species. This measurement is more correctly termed a background measurement, $I_b(\nu)$. For $I_b(\nu)$, equation 9-1 can be written as:

$$I_b(\nu) = I_0'(\nu) \cdot \tau_{CA}(\nu) = I_0(\nu) \cdot R(\nu) \cdot r(l) \cdot \tau_{CA}(\nu) \quad (\text{Eq. 9-5})$$

where $\tau_{CA}(\nu)$ is the frequency dependent term due to the attenuation of the light beam by ambient species in "clean air". This measurement is generally conducted upwind of the monitored site (or on some sample which is assumed to contain none of the species of interest) on a path which is of the same length as that to be monitored. Here, the measurement contains the ambient species (which are primarily water vapor, carbon

monoxide, dinitrogen oxide, carbon dioxide, etc). This spectrum is then used to ratio against the measured $I(\nu)$ spectra taken downwind of the site.

Measurement of $I_b(\nu)$ and its use as $I_0'(\nu)$ has the advantage that a long path water vapor reference spectra is not needed since the water vapor component will be cancelled if the spectra are taken near enough in time to one another. The disadvantage to this method is that the spectra often do not completely cancel. This incomplete cancellation is due to frequency shifts of the spectra arising from changes in alignment or instabilities in the interferometer as well as changes in the ambient gas concentrations.

The nature of the incomplete cancellation can be seen if the frequency and concentration sensitivities of each of the terms in equation 9-3 is examined. First, $I_0'(\nu)$ and $R(\nu)$ are independent of ambient gas concentration while $\tau(\nu)$ is not. Secondly, each term may be classified as either a slowly or rapidly varying function of ν . $I_0'(\nu)$, and $R(\nu)$ are slowly varying functions of ν while $\tau(\nu)$ is a rapidly varying function of ν . Thus, $\tau(\nu)$ will be effected to a much greater extend by frequency shifts than will $I_0'(\nu)$ or $R(\nu)$. Measurement of $I_0'(\nu)$ on the other hand is not sensitive to the spectral shifts since it does not contain any rapidly varying functions of frequency. Use of $I_0'(\nu)$ however, does require that a water vapor spectrum be used for quantitation.

The measurement of $I_0'(\nu)$ should be undertaken when a good long path water vapor spectrum can be obtained. This method removes the severe problems associated with spectral shifts or gas concentration variation and also limits the number of upwind measurements that need to be made. This method also relies on the ability of the quantitation method to remove water vapor from the spectrum.

If a quality, long path water vapor spectrum is not available, $I_b(\nu)$ can be measured. However, the spectral shifts and gas concentration must be fully accounted for. In addition, any other species that are present in the $I_b(\nu)$ spectrum must be removed to ensure that they will not affect the downwind measurements.

Perhaps the largest stumbling block limiting the use of OPMs by the general AAM community is a lack of knowledge of the system's capabilities. These systems are not the final solution to all monitoring problems and needs, but should be viewed as another tool in the array of monitoring options. While these systems have some significant advantages over the conventional AAM systems, they also have their disadvantages. The capabilities and limitations of these systems need to be clearly understood so that they may be applied to appropriate monitoring scenarios.

Guidance documents such as the Open Path-FTIR⁷ manual under preparation need to be completed along with manuals for other appropriate OPMs. Standard operating procedures and specific performance criteria need to be developed that will allow consistent measurement of detection limits and consistent checks of the operational status of the systems. Finally, there is an urgent need for standardized quality assurance and quality control methods. Some attempts have been made in this direction and the OP-FTIR document is expected to address this topic in some detail.

Technology and information transfer will play an important part if open path monitoring approaches are to enjoy widespread, successful application at Superfund sites. The greatest challenge will be to get the available technical information and guidance to the decision makers and workers at each Superfund site. This effort will require developmental experiments/studies and the preparation of guidance documents based on the results of these studies. Furthermore, this information will need to be packaged and distributed via workshops, announcements, project summaries, conference presentations, and journal publications.

SECTION 10

TECHNOLOGY UPDATES

Optical remote sensing is a rapidly developing field and the monitoring systems considered here are only a small portion of the monitors available or becoming available. Appendix B contains a descriptions of several ORS methods that are either available or in the developmental phase for application to environmental monitoring. Some of these methods are modifications of the methods described in Section 4.4. Also, some of these methods will be used strictly as point monitors, while others can be used as either OPMs or point monitors.

Application of new ORS technologies creates a need to keep users of monitoring technologies up to date. To accomplish this, EPA is considering regularly updating this document via the distribution of brief inserts. The inserts would describe the new technology, the compounds it can detect, its detection limits, and it applicability to Superfund work. These updates could take the form of an insert that will be sent to registered recipients of this document.

These updates would have the following suggested format:

- An introductory section describing the principles of operation of the system, the compounds it could detect, whether it would function as a point monitor or a path monitor, and its detection limits;
- A section on what advantages and capabilities this technology would bring to Superfund monitoring. This would include information on time response, the ability to detect metal or other compounds, areas where it may be more sensitive than other monitors, etc.;
- A section describing which activities this system would be most useful for and a description of its implementation.; and
- A section on the application of this technology and what needs to done to evaluate its capabilities as a monitor for the Superfund program.

The information for these updates would come predominantly from the literature or instrument manufacturers, but some hands-on investigation may be warranted. The next 18 to 24 months is likely to see an exponential increase of new applications of available and developmental technologies and officials in charge of implementing these methods need accurate and up-to-date information on these technologies.

Within this same 18- to 24-month period, the abilities of the available ORS systems are likely to increase. There is considerable interest in increasing the sensitivity of the available OPMs, particularly the FTIR. This must be watched closely since there are certainly gains to be made that may eliminate many of the detection limit concerns.

SECTION 11

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APPENDIX A
THE LAMBERT-BEER LAW

APPENDIX A

What follows is a brief description of the Lambert-Beer Law^{10,14} commonly referred to as Beers Law. The Lambert-Beer Law is used to relate the concentration of absorbers in media to the light attenuation caused by those absorbers. This discussion will walk through a derivation of the form of the law (Equation 3-5) most commonly used.

Consider a collimated beam of light incident on an absorbing medium as shown in Figure A-1. The power absorbed by a slab of the medium between x and $x + dx$ is dP . The amount of power decreased per unit length is $-dP/dx$. In general, light detection equipment is not suited for power determination, but for power per unit area measurements. Power per unit area is defined as intensity or

$$I = \frac{P}{A} \quad (A-1)$$

Therefore the intensity decreased per unit length is $-dI/dx$. The amount of intensity decreased is proportional to the incident intensity and this may be written as:

$$\frac{-dI(v)}{dx} = kI(v) \quad (A-2)$$

where k is the proportionality constant. Collecting like terms gives:

$$\frac{-dI(v)}{I(v)} = k dx \quad (A-3)$$

and integrating both sides yields:

$$-\int \frac{dI(v)}{I(v)} = \int_0^L k dx \quad (A-4)$$

$$-[\ln I_x(v) - \ln I_o(v)] = \int_0^L k dx \quad (A-5)$$

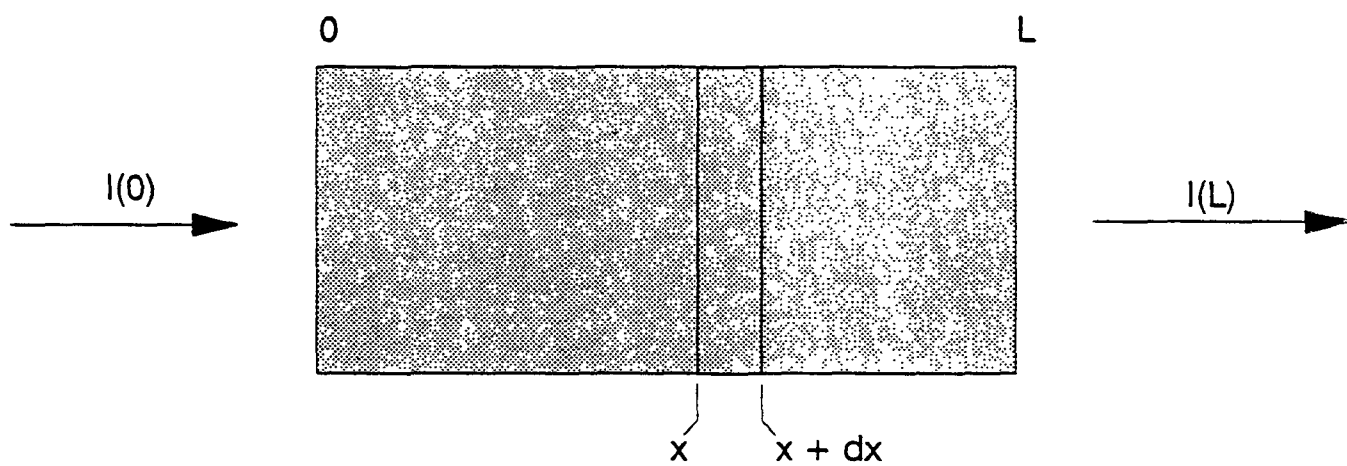


Figure A-1. Light Incident on an Absorbing Medium.

$$\ln \frac{I_x(\nu)}{I_o(\nu)} = -\int_0^L k dx \quad (A-6)$$

Removing the logarithm gives the general distance dependent Lambert Law (A-7). Lambert found that for a given concentration of absorbers the light intensity decreased logarithmically with distance:

$$I_x(\nu) = I_o(\nu) e^{-\int_0^L k dx} \quad (A-7)$$

The integral:

$$\int_0^L k dx \quad (A-8)$$

is called the optical depth.

Beer is generally given credit for finding that increasing the number of absorbers had the same effect as Lambert had observed, namely a logarithmic decrease in the light intensity. Therefore, the proportionality constant is related to the concentration by:

$$k = \alpha C \quad (A-9)$$

where C is the concentration; α the new proportionality constant which is the molecular absorption coefficient.

Combining this with Equation A-7 gives:

$$I_x(\nu) = I_o(\nu) e^{-\int_0^L \alpha(\nu, x) \cdot C(x) \cdot dx} \quad (A-10)$$

Dividing both sides by $I_o(\nu)$, gives the transmittance, T.

$$T = \frac{I_x(\nu)}{I_o(\nu)} = e^{-\int_0^L \alpha(\nu, x) \cdot C(x) \cdot dx} \quad (A-11)$$

Taking the negative base ten logarithm of the transmittance gives the absorbance $A(\nu)$, or:

$$A(\nu) = -\log_{10} T = \log_{10} \frac{I_o(\nu)}{I_x(\nu)} = 0.4343 \int_0^L \alpha(\nu, x) \cdot C(x) \cdot dx \quad (A-12)$$

To this point all of the parameters are distance dependent and we have had no need to consider the homogeneity of the concentration. If we first remove the distance dependence on $\alpha(\nu, x) = \alpha(\nu)$ which is a reasonable assumption if the total pressure and temperature along the path do not vary significantly, we can rewrite Equation A-12 as:

$$A(\nu) = a(\nu) \cdot \int_0^L C(x) dx \quad (A-13)$$

where the 0.4343 has been incorporated into the absorption coefficient. This equation is identical to Equation 3-6. The derivation then continues by assigning an effective concentration as:

$$A(\nu) = a(\nu) \cdot C_{\text{eff}} \cdot L \quad (A-14)$$

The effective concentration is the homogeneous concentration which would yield that same integrated value.

APPENDIX B
POTENTIAL OPTICAL REMOTE SENSING METHODS

SOURCE: Reference 23

APPENDIX B

POTENTIAL OPTICAL REMOTE SENSING METHODS

Twelve technologies which are either available or under development for application to environmental monitoring are:

- Gas Filter Correlation (GFC) Spectroscopy
- Fourier Transform Infrared (FTIR) Spectroscopy
- Ultraviolet (UV-DOAS) Absorbance Spectroscopy
- Matrix Isolation FTIR (MI/FTIR)
- Gas chromatography-MI/FTIR (GC/MI/FTIR)
- Photoacoustic Spectroscopy (PAS)
- Laser Induced Breakdown Spectroscopy (LIBS)
- Laser Absorbance (Diode and Carbon Dioxide)
- Laser Induced Fluorescence (LIF)
- Multiphoton Ionization (MPI)
- Fluorescence
- Shpol'skii Spectrometry (SS)

The following sections will briefly describe the principles by which each of these techniques operate. The methods will also be categorized according to their spectral region of operation i.e. ultraviolet, infrared or consequence. A "consequence" spectroscopy method is one in which the absorption or emission of a photon is not monitored but a result of that absorption (such as photo-dissociation) is monitored. The methods will also be categorized as either OPM's or point monitors.

B.1 Ultraviolet Methods

Ultraviolet (UV) spectroscopy operates on the principle of electronic excitation of atoms or molecules. Thus, these methods are also sensitive to atomic species such as metals. The absorption strengths for these excitations are typically much larger than those in the infrared region. The region of the spectrum associated with this type of spectroscopy is about 200 to 400 nm.

B.1.1 Ultraviolet (UV) Absorbance Spectroscopy

UV absorbance spectroscopy is conventional absorption spectroscopy using the appropriate broad-band excitation source such as a Xenon lamp. The technique is well developed and requires about 1 minute to identify the concentration of a single species. Typically the UV has better sensitivity than the infrared because of the larger UV band strengths but not all compounds are observable in this region.

B.1.2 Fluorescence

This technique relies on the excitation of the molecule of interest to a known state by the absorption of a photon from a broad band light source such as a Xe arc. The photon is either emitted at the same frequency or more likely at a lower frequency. The emitted photons frequency is monitored by a spectrometer. The response times will generally be on the same order as those of the UV absorbance.

B.1.3 Laser Induced Fluorescence (LIF)

This technique is conceptually similar to the more general fluorescence described above but can be more species specific. LIF however uses a carefully tuned laser to excite the molecule of interest. This careful tuning allows for very specific excitations and allows for better compound identification. As with the fluorescence technique above the emitted photon can then be monitored as a function of frequency with a spectrometer of appropriate resolution. This gives the ability to both selectively excite and selectively detect the compounds of interest.

B.1.4 Shpol'skii Spectroscopy (SS)

The Shpol'skii effect is the result of a correlation between the molecule of interest and its neighboring solvent to narrow the spectral features of the molecule. Here, the molecule of interest is mixed with a carefully chosen alkane and frozen. The alkane is chosen so as to mimic the carbon bound structure of the compounds. Once frozen the sample may be interrogated by a laser and either absorption or emission monitored. This technique has seen some success when applied to PAHs and good spectra are available.

B.2 Infrared Methods

Infrared spectroscopy relies on excitation of the vibrational-rotational modes (and some pure rotational modes) of molecules. These infrared techniques are sensitive to molecules only and will not detect metals or even a class of molecules known as homonuclear diatomics (e.g. O₂, N₂, Cl₂, etc). The excitation strengths of these transitions are generally 10 to 100 times weaker than the electronic transitions in the UV. The spectral range is generally from about 200 to 4000 cm⁻¹.

B.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR allows for the collection of the entire infrared spectrum from about 4000 to 200 wave numbers in a few seconds. This technique offers the ability to look at all of the ambient air species which have infrared active bands. This method can be used in absorbance mode with the addition of an infrared source or in a passive emissions mode. Multipassing optics such as a white cell can also be added which can allow the FTIR to be used as an extractive white cell point sampler. In either case the molecular signature is obtained over a broad spectral range from which accurate identification of the species can be made. The advantage of taking the entire spectra is that if interfering species are present they will almost certainly not be present at all of the same frequencies throughout the IR and careful choice of analysis regions will allow for interference free detection. Unfortunately FTIR is also frequently limited in sensitivity because of the strengths of the IR bands available.

B.2.2 Matrix Isolation/Fourier Transform Infrared Spectroscopy (MI/FTIR)

This technique is an extension of the conventional FTIR described above. Here, the species are frozen (at about four degrees Kelvin) in a matrix of nitrogen gas. This freezing narrows the inherent spectral features and eliminates all excited state lines allowing for substantial reduction of interferences from adjacent spectra, it allows for an extended observation time, and for long signal averaging periods.

B.2.3 Gas Chromatography/Matrix Isolation/Fourier Transform Infrared Spectroscopy (GC/MI/FTIR)

GC/MI/FTIR is a combination of the MI/FTIR technique and an FTIR techniques. The addition of a gas chromatograph allows for the separation of species prior to quantitation thus removing possible spectroscopic interferences. This technique would be expected to have the lowest detection limits of the FTIR techniques. Like FTIR however, the method still suffers from the lower absorption strengths in the infrared but does have the advantage of long time scans to improve the signal to noise ratio.

B.2.4 Laser Absorption (Carbon Dioxide and Diode)

These two lasers operate in the infrared region of the spectrum and their use would be similar to that of the FTIR in absorption mode. The two advantages here are 1) a high degree of spectral resolution which will allow the molecules to be more accurately identified over a smaller spectral range and 2) a larger signal to noise ratio due to the intensity of the laser light source and the possible use of harmonic detection. The main difference between a diode and CO₂ laser is that the diode produces a beam which is continuously tunable over approximately a fraction to 1 cm⁻¹ while the CO₂ laser produces discrete lines which cannot be easily shifted. In detecting a gas concentration the diode is chosen to coincide with an absorption of interest and swept across a feature for identification. For the CO₂ laser, lines must be chosen which inherently fall on or off of a spectral feature of the compound(s) of interest. The latter method clearly must be a

fortuitous, match the diodes can be forced. Laser absorption can be very sensitive and if sufficient scanning is possible (or enough lines are used) it can be very specific.

B.2.5 Gas Filter Correlation (GFC) Spectroscopy

This technique is a non-dispersive infrared method which relies on the determination of a species characteristic absorbance frequencies when compared to the correlation a reference cell which contains a sample of the species of interest. This technique, since it is non-dispersive, easily applied, is frequently applicable even in the presence of interferences, and has a very fast (approximately one second) response time. Unfortunately it is usually limited in sensitivity. The general working principle also requires a vapor phase sample of the compound of interest.

B.3 Consequence Spectroscopy

In consequence spectroscopy light intensity is not monitored but rather a consequence of absorption. An example of a consequence spectroscopic phenomena is photodissociation. Here, a molecule absorbs a photon which causes it to dissociate, the dissociation product is then monitored by some technique such as mass spectroscopy. In general, these techniques have low backgrounds and are therefore very sensitive to trace constituent quantitation.

B.3.1 Photoacoustic Spectroscopy (PAS)

This technique relies on the transfer of energy from electronic, vibrational, or rotational motions of the molecule to translational motion during a collision. The molecules of interest are excited with a laser at a known absorption frequency. The absorbed energy is then transferred to heat (i.e translational energy) through collisions with other molecules and atoms. This heat warms the gas, which if contained in a closed cell changes the pressure in the cell. The laser is usually modulated and the modulated pressure changes are then monitored with a sensitive microphone or density detecting interferometer. This method is very sensitive but must be used as a point sampler.

B.3.2 Laser Induced Breakdown Spectroscopy

This technique relies on the use of a very tightly focused laser beam. Lasers are a source of very large electric fields that when focused to a small point can strip electrons from molecules and force dissociation and frequently the formation of a plasma. This dissociation and plasma formation results in energy emission thereby creating its own excitation source. Nearby molecules will absorb this energy and later re-emit light. The emission of this light is monitored much in the same way as that of fluorescence spectroscopy.

B.3.3 Multiphoton Ionization (MPI)

MPI relies on ionizing the species of interest using laser photons. In general this requires the absorption of more than one photon thus the prefix "multi". Specific species can be ionized if the multiple absorption exactly coincides with specific internal states of the molecules. Here, instead of detecting light the ions are detected. Like fluorescence this can be a very specific and very sensitive approach if lasers of sufficient power and of appropriate wavelength are available.

B.4 Categorization of Methods

The techniques described in the previous sections are categorized for convenience in Table B-1 according to their spectral operating region (either UV, IR or consequence). Additionally, Table B-2 lists the techniques as either OPM's or point monitor. That is they are divided according to their ability to directly yield path-weighted concentrations.

Table B-1.

Spectral Regions of the Optical Remote Sensing Methods

Ultraviolet	Infrared	Consequence
UV Absorbance	GC/MI/FTIR	LIBS
Fluorescence	MI/FTIR	PAS
LIF	FTIR	MPI
SS	Laser Absorbance	
	GFC	

Table B-2.

Open-Path and Point Monitoring Capability

Method	Open-Path Monitors	Point Monitors
UV Methods		
UV Absorbance	X	X
Fluorescence	X	X
LIF	X	X
SS		X
IR Methods		
GC/MI/FTIR		X
MI/FTIR		X
FTIR	X	X
Laser Absorption	X	X
GFC	X	X
Consequence Methods		
PAS		X
LIBS		X
MPI		X

APPENDIX C
GLOSSARY OF TERMS

APPENDIX C

GLOSSARY OF TERMS

Attempts have been made recently to standardize the terminology used in the field of optical remote sensing. These preliminary compilations of terminology, while well intentioned, are not completely consistent with the equivalent terminology used in fields such as spectroscopy, physics, and astronomy. Consistent terminology is essential to avoid miscommunication and confusion. The following glossary of terms was prepared for this document; future revisions will be necessary as a consensus terminology is developed by EPA and other researchers.

Absorbance ($A(v)$)	The negative base ten logarithm of the transmittance. While absorbance is related to optical depth or log base of transmittance, the difference is a constant factor of 0.434.
Active System	An optical remote sensor that interacts in an active way with the species being monitored. For example, absorption spectroscopy using a laser or broadband source propagated through the sample.
Angstroms	A unit of length equivalent to 10^{-10} meters. Commonly used to measure light wavelength in the ultraviolet and visible regions of the electromagnetic spectrum.
Background Spectrum	Collection of the intensity of the light beam as a function of wavenumber or wavelength in the absence of the absorbing molecules. This is ratioed to the intensity observed in the presence of absorbers to calculate the transmittance.
Band Pass Filter	Optical filter that allows a selected region or band from a light source to pass while restricting light of both longer and shorter wavelength.
Bandwidth	The width of a reported spectral feature (e.g. bandpass). It is defined in terms of either the full width at half the peak maximum (FWHM) or half the width of the peak at half the peak maximum (HWHM).
Bistatic Configuration	A measurement configuration using a transmitter and receiver by some distance. For example, placement of an optical transmitter and receiver at opposite ends of a monitored path.

Broad Band Source	Electromagnetic radiation source that emits light over a broad range of frequencies as opposed to a monochromatic or single frequency source. Broad band sources are used in UV-DOAS, FTIR's and GFC's.
Conventional Point Monitor	(CPM)- point monitor such as a canister or a sorbent tube, or other device commonly used as a point monitor of gas concentrations, but not an ORS system used as a point monitor.
Differential Absorbance Lidar	(DIAL)- Lidar using two pulsed lasers (or two wavelengths of a single laser), one tuned to an absorbing frequency and the other tuned close but off that absorbing frequency. The difference in the detected backscatter signal between the two lasers is a measure of the gas concentration and common variations allow for correction of the signal for natural attenuation losses.
Differential Optical Absorbance Spectroscopy	(DOAS)- technique used to remove the effects of scattering and continuum absorption so that concentration may be obtained. This technique involves the measurement of the difference between absorption within a spectra feature and the wing of that absorbing feature taken as non-absorbing.
Effective Concentration	Quantity derived from a path-weighted measurement by dividing by the pathlength and has the equivalent absorbance as if that concentration was homogeneously distributed across the path. Expressed in ppm, ppb, $\mu\text{g}/\text{m}^3$, molecules/ cm^3 , etc.
Electromagnetic Spectrum	(EM)- the total of all the possible frequencies of electromagnetic radiation.
Emissions Flux	(J)-the measurement of the mass of emissions per second per unit area crossing the beam path. Knowledge of the area of a plane parallel to the beam path which the light monitors allows determination of the rate of emissions across the beam path.
Emissions Spectroscopy	The monitoring of light emitted (or lost) from a species rather than light removed from a well characterized beam of radiation by the species.

Frequency	The measurement in time of the crest of a sinusoidal wave passing a particular point in space (see Figure C-1). Numerically equal to the propagation velocity divided by the wavelength.
Fourier Transform Infrared (FTIR) Interferometer	An ORS system capable of open path and point monitoring. Uses an interferometer and mathematically manipulates the output to generate an infrared spectrum. Typically identifies compounds by using reference spectra. Can quantitate tens of compounds in minutes.
Gas Filer Correlation (GFC) Spectrometer	A special case of correlation spectroscopy capable of both open path and point monitoring. Uses correlation of the spectrum measured from an unknown to that of a reference cell to evaluate gas concentration. Has a response time on the order of 1 second.
Hertz	(Hz)-has units of reciprocal seconds. The unit of frequency equal to the reciprocal of period or time per cycle.
Homonuclear diatomics	A class of molecules containing two identical atoms (examples include Cl ₂ , F ₂ , N ₂ , O ₂). Homonuclear diatomics can not, under normal circumstances, be detected by infrared radiation. The molecules can absorb under high pressure conditions but then do so in a structureless fashion.
Infrared (IR) Region	Region of the electromagnetic spectrum from approximately 1 μm (10,000 cm^{-1}) to 1 mm (100 cm^{-1}). The subregion of the infrared used by an FTIR for detection of the species typically encountered in environmental monitoring applications is from approximately 250 μm (400 cm^{-1}) to 2.5 μm (4000 cm^{-1}).
Intensity	The amount of power per unit area delivered to the detector at a specific wavelength or wavenumber.
Interferogram	Direct output of an interferometer and is a complex function caused by the interference of light.

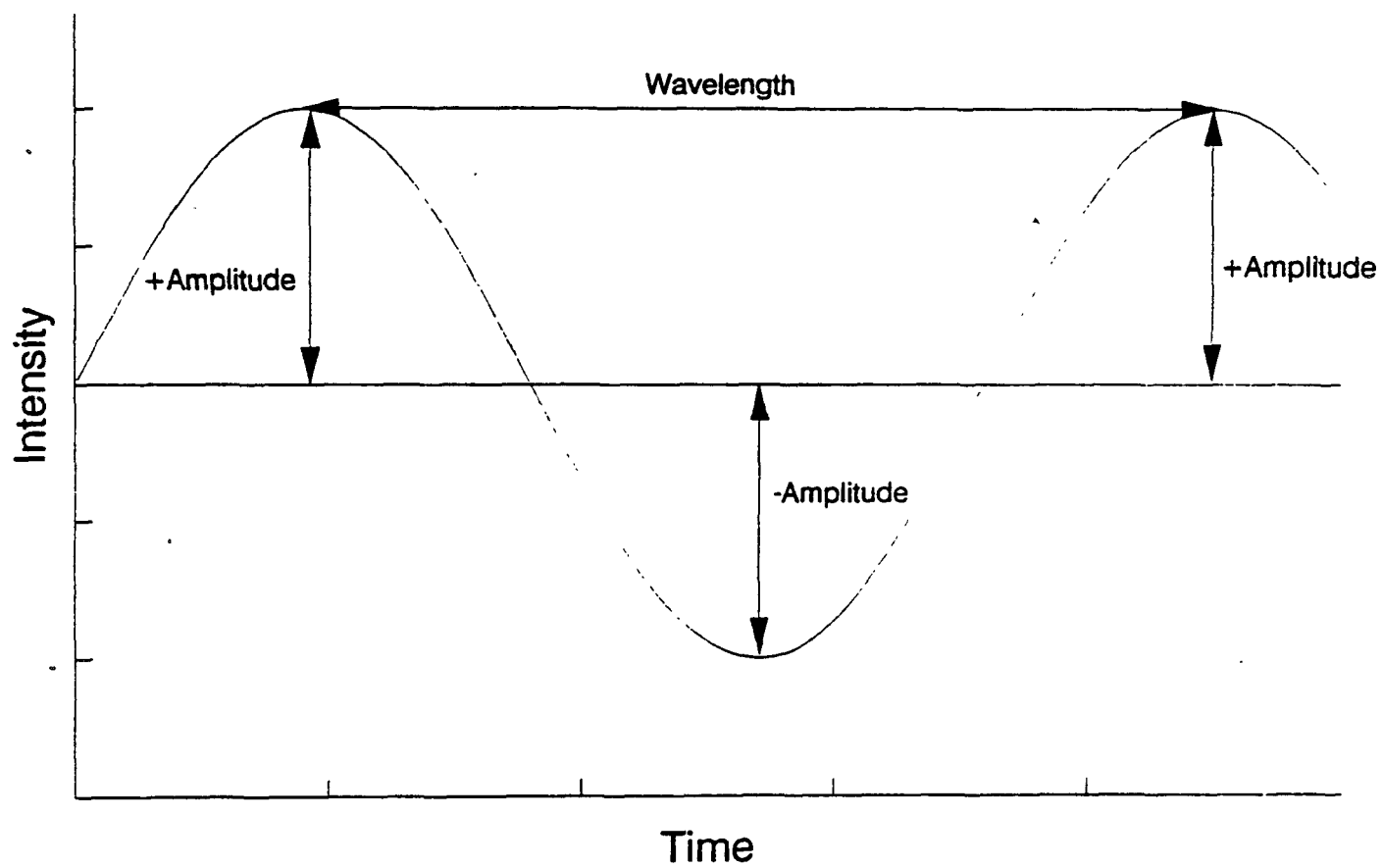


Figure C-1. Sinusoidal Wave Pattern

Interferometer	Opto-mechanical device at the heart of the FTIR. Provides modulates light to produce a complicated interference pattern caused by the constructive and destructive interference of a light beam with itself.
In-situ monitoring	Monitoring without the need of a sampling method (such as a canister of sorbent tube) with real time or near real time data turn around.
Lambert-Beer Law	Often called Beer's Law, it governs the relation between absorbance and concentration. For perfectly resolved spectra the law states that the absorbance is linear in concentration. This is only approximately true and significant deviation can be noticed for non-perfectly resolved data. This law is approximately true for low concentrations, and for weak absorbancies.
Laser	An acronym for Light Amplification by Stimulated Emission of Radiation. It is a device which can produce very coherent and nearly monochromatic radiation with very high intensities.
Monitoring systems	Any combination of sampling and analytical methods applied to monitoring.
Monochromatic Source	Light source which produces only a single frequency or color of light. A laser is a close approximation to the monochromatic source.
Monostatic	A configuration in which the source and receiver are effectively co-located. Co-location or near co-location of the transmitter and receiver is possible for OPM by using a reflecting optic such as a retroreflector at the opposite end of the path. If source and receiver are integrated into a single unit, it is typically referred to as a transceiver.
Nanometer	Measure of length equivalent to 10^{-9} meters. Generally used to refer to light wavelength in the ultraviolet and visible regions of the electromagnetic spectrum.

Open Path Monitor	(OPM) - any optical remote sensor configured so that it monitors in the open air. No sample cell is used and the output is usually a path-weighted concentrations or effective concentration. Open path monitoring may be conducted either indoors or out of doors.
Optical Remote Sensor	(ORS) - any optical instrument which is used for detection of pollutants or meteorological parameters. Subsets of ORS's include open path monitors, radars, lidars, and spectroscopic point monitors (SPM's).
Passive System	Optical remote sensing system monitors without actively interacting with the sample. An example in environmental monitoring are FTIR's used in emission measurements without an artificial source.
Path length	The distance that the light travels from source to detector.
Path-weighted concentration	The effective concentration times the pathlength expressed in units of ppm*meters, ppb*meters, $\mu\text{g}/\text{m}^2$ or molecule/ m^2 , etc. This nomenclature is consistent with that used in physics and astronomy for measurements of concentrations that are not necessarily homogeneously distributed.
Point monitoring	Monitoring at a specific point in space. Subsets of this monitoring include conventional point samplers and spectroscopic point samplers.
Scattering	An elastic or inelastic deflection of a photon off of its linear course. This type of scattering maybe compound or size, or orientation specific.
Sinusoidal Motion	Periodic motion of a wave often used to represent one form of light. Represented mathematically by $x = A \sin(2\pi ft)$ where x is the position, A is the amplitude at the crest of the wave f is the frequency and t is the time. (See Figure C-1.)
Transceiver	An optical device that shares the same optics for both beam launch and beam reception.
Ultraviolet (UV) Region	Region of the electromagnetic spectrum from approximately 200 to 400 nanometers.

UltraViolet-Differential Optical Absorbance Spectroscopy	(UV-DOAS)- extrapolation of a typical laboratory ultraviolet absorbance technique to account for the processes of Mie scattering and continuum absorption which occur in the ambient air.
Visible (Vis) Region	Region of the electromagnetic spectrum from approximately 400 to 750 nanometers. Often grouped with the ultraviolet region for spectroscopic purposes.
Wavelength	Measure of the distance between crests in a sinusoidal wave pattern (see Figure C-1). Typically has the units of length expressed in micrometers for the infrared region, nanometers or angstroms for the visible and ultraviolet regions.
Wavenumber	A quantity which is proportional to energy and has units of reciprocal centimeters. Typically used when referring to infrared spectra.

APPENDIX D
TRANSECT METHOD

APPENDIX D

TRANSECT METHOD²

The transect technique, also referred to as plume mapping, measures the concentration of the emitted species at several downwind locations aligned perpendicular to the anticipated plume centerline. The in-depth transect technique is an indirect emission measurement approach that has been used to measure fugitive particulate and gaseous emissions from area and line sources. This technique has been successfully tested at a variety of waste sites, including landfills. Figure D-1 illustrates the transect sampling array.

The transect technique uses horizontal and vertical arrays of samplers to measure concentrations of species within the effective cross-section of the emission plume. The volatile species emission flux is then obtained by spatial integration of the measured concentrations over the assumed plume area. For volatile species, the emission flux is calculated as:

$$J_i = \frac{U}{A_s} \int \int A_p C_i (h,w) dh dw$$

where:

J_i	=	emission flux of component i ($\mu\text{g}/\text{m}^2\text{-sec}$);
U	=	wind speed (m/sec);
A_s	=	surface area of emitting source (m^2);
A_p	=	effective cross-sectional area of the plume (m^2);
C_i	=	concentration of component i at point (h,w) corrected for upwind background ($\mu\text{g}/\text{m}^3$);
h	=	vertical distance coordinate (m); and
w	=	horizontal distance coordinate (m).

For particulates, the emission flux is calculated as:

$$J = \frac{1}{t A_s} \int \int A_p \frac{m(h,w)}{a} dh dw$$

where:

J	=	emission flux ($\mu\text{g}/\text{m}^2\text{-sec}$);
t	=	sampling time (sec);
A_s	=	surface area of emitting source (m^2);
A_p	=	effective cross-sectional area of plume (m^2);
m	=	mass of particulates collected after correction for background concentration (μg);
h	=	vertical distance coordinate (m);
w	=	horizontal distance coordinate (m); and
a	=	intake area of sampler (m^2).

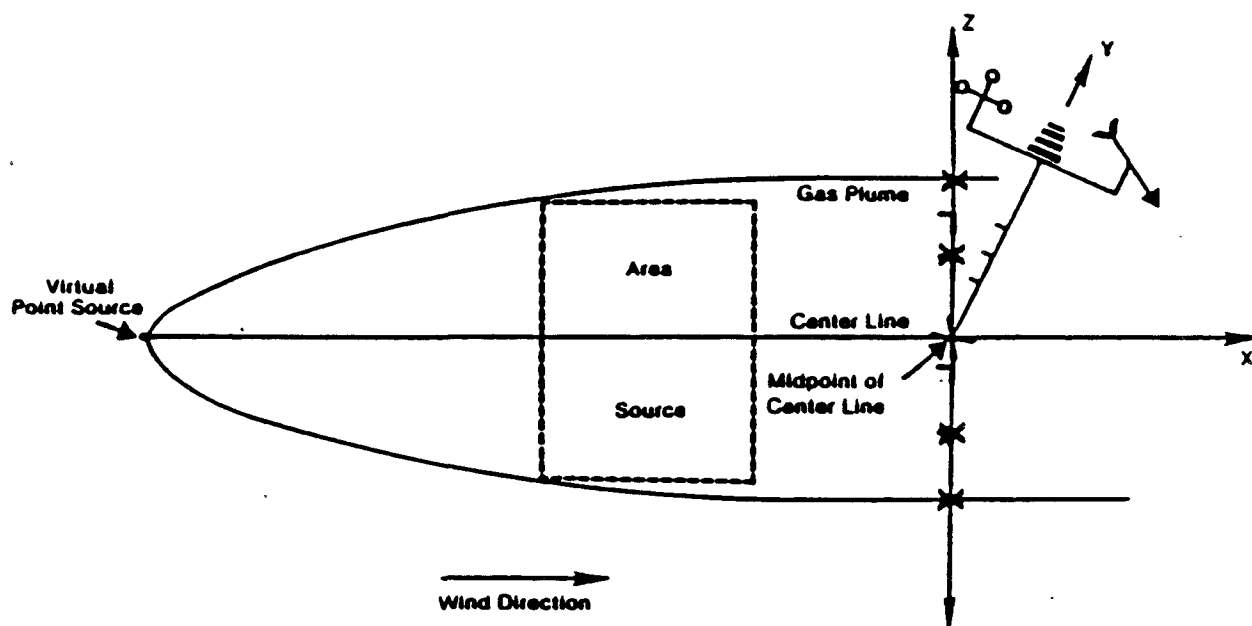


Figure D-1. Example of transect technique sampling.

The cross-sectional area of the source (A_s) term can be eliminated from both equations, if only the total site emission per time is required. An alternative equation for volatile species, based on diffusion theory and measurements is:

$$Q(t)_i = \sum_1^n \pi X_i K_i \sigma_y \sigma_z C \bar{U}$$

where:

$Q(t)_i$	=	emission rate of species i (gm/sec);
X_i	=	peak concentration of species i (Gaussian Fit Curve);
K_i	=	conversion factor gm/ppm for species i;
σ_y	=	lateral extent of Gaussian plume;
σ_z	=	vertical extent of Gaussian plume;
C	=	instrument response factor;
π	=	3.141; and
\bar{U}	=	mean wind speed.

All parameters are obtained from field measurements. (In some instances, σ_z is estimated from σ_y). As for the C-P technique, users should see the cited literature for further guidance on the data reduction procedures. The key point to note is that the equations are relatively complex. Furthermore, terms such as σ_y and σ_z will require curve-fitting of the data and will typically have a large associated uncertainty.

The sampling equipment consists of a central 3.5-meter mast supporting three equally spaced air sampling probes, and single wind direction, wind speed, and temperature sensors at the top; and five 1.5 meter masts with single air sampling probes. The central mast is aligned downwind along the expected plume center-line. Two masts are placed on each side of the central mast perpendicular to the plume centerline at equal spacings; and one mast is used to collect air samples at an upwind location. The spacing of the associated masts is selected to cover the expected horizontal plume cross-section, as defined by observation and/or profiling with real-time analyzers. Additional sampling locations, both vertically and horizontally, can be added as required to provide sufficient coverage of the plume cross-section. Prior to sample collection, meteorological parameters must be monitored to determine if sampling conditions meet the predetermined meteorological criteria.

The transect technique is somewhat less susceptible to changing meteorological conditions than the concentration profile technique, but it does not account for the vertical dispersion of the emitted species due to their varying molecular weights. A more complex array of samplers can be employed to overcome this shortcoming, if necessary. The transect is often the preferred technique because the technique is applicable to a variety of some types and the resulting data can be more useful since the data are collected across the plume area.

Applicability

The transect technique is applicable to emission rate measurement from all forms of area sources, including lagoons, landfills, open dumps, and waste piles.

The technique can be used for both volatile and particulate matter emission rate assessment. The technique is applicable both for undisturbed and disturbed site conditions, and for testing of emission control techniques. The technique is applicable to emissions measurement during all phases of the RI/FS process and can therefore, provide directly comparable data throughout the process, including post remediation monitoring.

While the method assumes a relatively homogeneous site and a well mixed plume, these conditions are not necessarily required to use the method. The placement of sufficient sampling stations across the plume can allow the technique to be used at a heterogeneous site, or where the distance downwind for equipment set up is limited. However, data collected under these conditions should be carefully evaluated before use.

Limitations

The technique requires that meteorological conditions during sampling, particularly wind speed and direction, match the predetermined conditions used to select the sampling locations. The center mast should be on the approximate plume centerline. The technique may not adequately collect emissions from point sources within an area source, such as cracks in landfill covers or vents, unless the plume is fairly well mixed at the sampling locations. The technique provides only limited vertical profiling of the plume. The technique is not applicable during quiescent or unstable wind conditions; it may produce false negative results during these conditions.

Preferred Technique

The transect technique is a preferred indirect emission assessment technique. The technique has been used for several different types of area sources and is documented in the literature. The applicability of the technique, the conditions required for sampling, and the moderate level of equipment and manpower needs suggest this technique as a preferred technique relative to other indirect approaches.

APPENDIX E

CASE EXAMPLES OF THE USE OF OPM SYSTEMS AT SUPERFUND SITES

APPENDIX E

CASE EXAMPLES OF THE USE OF OPM SYSTEMS AT SUPERFUND SITES.

Over the past few years, OPMs have been employed at various Superfund sites during various remediation activities. Some of the funding for such applications has come from the Superfund Innovative Technology Evaluation (SITE) program. This section briefly discusses the application of OPMs to five sites. An FTIR system was used as the sole OPM for the majority of sites. One site, however attempted use of an FTIR, UV-DOAS, and a LIDAR. The five sites and the OPM system(s) used are:

Site	OPM System
New Castle, Delaware	FTIR
Shavers Farm, Georgia	FTIR
Middlesex County, New Jersey	FTIR, LIDAR, UV-DOAS
Lipari Landfill, New Jersey	FTIR
Abbeville, Louisiana	FTIR

The discussion below covers some of the compounds of interests, the pathlengths available, the goals of the monitoring and the phase of the remediation process during which the OPM was used. The information may be useful for assessing analagous situations of similar sites. Some of the configurations are well documented and the official report documents provide additional information.

New Castle, Delaware - FTIR¹⁹

The site at New Castle, Delaware was a heavily industrialized area in which an FTIR was evaluated under the Superfund Innovative Technology Evaluation (SITE) program. The FTIR (was a Nicolet 730 spectrometer modified by Tecan Remote, Inc.) was configured in a monostatic manner using a transceiver, a retro-reflector and an unmodulated source. The FTIR and transceiver were mounted in a van so changes in wind direction could be accommodated.

Two types of measurements were conducted. The first was a comparison of the FTIR and a CPM method (i.e. canisters) at the industrial complex. These measurements were conducted with a pathlength of 250 meters; the site imposed a physical limitation that precluded longer pathlengths without multipassing. The second set of measurements were conducted at a landfill that was several square miles in area. The pathlengths used were 250 meters and 500 meters, depending on the monitoring goal.

The authors concluded that the FTIR as configured was capable of meeting the needs of some monitoring activities provided the concentration levels were above 50 ppb. The authors make the claim that changing the optical system would improve the detection limits but no specific changes were recommended. The change, as discussed below, would be to reconfigure the FTIR so that source modulation could be conducted before launch of the beam.

Shavers Farm, Georgia - FTIR²⁵

The Shavers Farm site in northwestern Georgia was undergoing excavation remedial activities and the compounds of interest were benzaldehyde and benzonitrile. The FTIR system was (Nicolet Model 730 FTIR modified by MDA Scientific, Inc.) configured in a *monostatic method* using a *retro-reflector*. This system however was upgraded so that the light was modulated before launch. The FTIR was mounted in the back of a truck. The path lengths were on the order of 500 meters.

Measurements were made on two paths each of 500 meters. The meteorological conditions however were such that the FTIR was predominantly upwind of the excavation and neither benzonitrile nor benzaldehyde were detected. Laboratory detection limits for benzonitrile were reported as 186 ppm*meters in a 15 cm cell giving a theoretical effective concentration detection limit of 372 ppb, i.e. significant emissions would have to take place to be detected. However, the remedial activity was in its latter stages and there were few "hits" even using canister sampling. The authors do make the point however that at least the upper limit of the concentration present can be assigned.

The authors credit the modulation of the light source with significantly reducing the background radiation and thereby decreasing the detection limits. A QA program which was implemented on site was also described. While the program was specific to their instrument, it does offer an approach to QA that can be modified if no specific QA guidance is available.

Middlesex County, New Jersey - FTIR - Lidar - UV-DOAS²⁶

This site saw the application of three OPMs to the pre-remediation phase. The three systems were the FTIR (Nicolet 740 spectrometer) a UV-DOAS from the University of Denver, and a carbon dioxide, differential absorbance Lidar (DIAL) system. The monitoring took place over several days and several pathlengths. The compounds of interest included toluene, benzene, chloroform, 1,2-dichloroethane and 1,1,1-trichloroethane.

The UV-DOAS system was of the monostatic variety with a transceiver and a retroreflector. The UV-DOAS was mounted on a tripod and placed external to the van. The DIAL system used two CO₂ lasers (ELS-Lasersafe). The first laser was tuned to a specific absorption wavelength of a compound and the second tuned to a wavelength just off that absorbance. The differential absorbance of the two wavelengths was used to determine the concentration present.

Only one monitoring event showed the presence of any of the target compounds. Toluene was detected by the FTIR at a path-weighted concentration of 20 to 23 ppm*meters. Surprisingly, the UV-DOAS, which has a lower-limit of detection, used over nearly the same path detected no toluene. The 20-23 ppm*meters concentration is below the detection limits of the DIAL system. The authors used various monitoring locations to exploit the advantages of the systems within the goals of pre-remediation phase and some of these configurations may shed some light on how to proceed under similar scenarios.

Lapari Landfill, New Jersey - FTIR¹⁷

FTIR monitoring (using a MDA Scientific, Inc. Model 282000) was conducted at the Lapari Landfill during the installation of extraction wells. These wells were part of a pump and treat remedial operation. The FTIR was configured along the perimeter of the site and path-weighted concentration measurements fed into a program to up date emissions rates. The emissions rates were calculated using Turner's Gaussian Equation as given in Section 4.4. The emissions rates were then used to calculate plume centerline concentrations.

A tracer study was conducted to measure the vertical dispersion, σ_z . The tracer gas used was SF₆, which has a very strong (1 ppm*meter) infrared absorbance and is not normally present in the ambient air in significant concentrations. The dispersion was first estimated using measurements of sigma theta and textbook stability class curves. Next, the tracer gas was released at a known rate and σ_z calculated using equations similar to those in Section 4.4. The tracer gas dispersion values did not agree with those obtained from the stability class estimates despite the measurement of sigma theta.

The vertical dispersion, σ_z , must be known to estimate total dispersion. It can be measured directly using LIDAR/SODAR, inferred from tracer gas studies, or estimated from the lateral dispersion term, σ_y , and the atmospheric stability. Dispersion is an important parameter in predicting (back calculating) source terms and subsequently estimating downwind concentrations of emitted contaminants. If the dispersion is overestimated by a factor of 2 then the calculated source term (emission rate) is decreased by a factor of 2. Therefore, an accurate knowledge of σ_z (and σ_y) is important to accurately assess air impacts. The authors therefore recommend use of the tracer gas study to determine site specific vertical dispersion.

The issue of accurate dispersion estimates is particularly critical if the compounds are below the detection limits of the monitoring system. This was the case at the Lapari site as no compounds on the analyte list were detected. However, it was determined that even at the detection limit, the emission rate of the compounds of interest was not sufficient to exceed action levels. Therefore, OPM did provide useful information at this site.

Abbeville, Louisiana - FTIR¹⁸

The FTIR (MDA Scientific, Inc. Model 282000) was applied during a pilot scale excavation and dewatering operation to monitor emissions of benzene, toluene, ethylbenzene and xylenes emissions. Several pathlengths were used depending on specific monitoring locations. Tracer studies were carried out by using carbon tetrafluoride (CF_4) which has a detection limit of .03 ppm*meters.

During the pilot-scale operation, no target compounds were detected by the FTIR. However, octane and iso-octane were being emitted in detectable concentrations. These compounds were then used as surrogates. The target compounds were expected to follow the meteorological behavior of the surrogates and analysis proceeded accordingly. Emissions of methane were also detected.

This study demonstrated the use of surrogate compound detection for emission rate assessment. A tracer gas study was conducted to determine the emission source strength (see Equation 4-18). This relation was found to be an acceptable approach for determining emission rates provided the source exhibits ground-level, non-buoyant behavior.

APPENDIX F
OPEN PATH MONITOR VENDORS

Appendix F

Open Path Monitor Vendors

VENDOR	PHONE NUMBER
Air Instruments and Measurements	(818) 813-1460
ANARAD	(805) 963-6583
Bomem	(418) 877-2944
Denver University	
Insittec Measurement Systems	(510) 837-1330
Mattson Instruments, Inc.	(608) 831-5515
MDA Scientific, Inc.	(800) 323-2000
MIDAC Corporation	(714) 645-4096
Nicolet	(608) 271-3333
Opsis Inc.	(203) 698-1810
Optech Inc.	(416) 661-5904
Simens (U. K.)	44 202 782000