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AIR / SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES

Volume II - Estimation of Baseline Air Emissions at Superfund Sites

Interim Final

VOLUME II

ESTIMATION OF BASELINE AIR EMISSIONS
AT SUPERFUND SITES

INTERIM FINAL

by

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PREFACE

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

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

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

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

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Air Management Division, U.S. Environmental Protection Agency.

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OSHA	Occupational Safety and Health Administration, U.S. Department of Labor.
OVA	Organic vapor analyzer.
Particulate Matter	Airborne solid or liquid matter.
PEL	OSHA permissible exposure limit, expressed as ppm or mg/m^3 of substance in air.
ppb	Parts per billion.
ppm	Parts per million.
Probe	A tube used for gas phase concentration sampling or for measuring pressures at a distance from the actual collection or measuring apparatus.
Quality Assurance	A system of activities designed to assure that the quality control system is performing adequately.
Quality Control	A system of specific efforts designed to test and control the quality of data obtained.
RI	Remedial Investigation. Field investigations of hazardous waste sites to determine pathways and nature and extent of contamination.
RPM	Remedial Project Manager, equivalent to a site manager at non-NPL sites.
Sampling	The process of withdrawing or isolating a fractional part of the whole. In air or gas analysis, it is the separation or a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.
SARA	Superfund Amendments and Reauthorization Act. Modifications of CERCLA enacted on October 17, 1986.
Screening Technologies	Quick and simple methods for estimating baseline emissions.
Undisturbed Condition	The condition in which a hazardous waste site is discovered or may be left if a no-action remedial alternative is selected.
VOCs	Volatile organic compounds. An organic compound (containing carbon) that evaporates (volatilizes) readily at room temperature.

FIGURES

FIGURES (Continued)

GLOSSARY OF FREQUENTLY USED TERMS AND ACRONYMS

ACGIH   American Conference of Governmental Industrial Hygienists, 6500 Glenway Ave., Building D-5, Cincinnati, OH 45211.

Adsorption   A physical process in which molecules of gas, dissolved substances, or liquids adhere in an extremely thin layer to the surfaces of solid bodies with which they are in contact.

Air Monitoring   A gas phase sampling technique where ambient air is sampled. It can be used to develop emission rate estimates and is similar to indirect emission measurement except measurements usually are taken at greater distances from the waste site.

APA   Air Pathway Analyses. APA are designed to assess the potential for air emissions from a hazardous waste site.

BEEs   Baseline Emission Estimates. These are estimates of baseline emission rates from a hazardous waste site in its undisturbed conditions.

Calibration   Establishment of a relationship between the response of a measurement system obtained by introducing various calibration standards into the system. The calibration levels should bracket the range of levels for which actual measurements are to be made.

CERCLA   Comprehensive Environmental Response, Compensation and Liability Act of 1980. Modified by SARA in 1986. The Acts created a special tax that goes into a trust fund, commonly known as Superfund, to investigate and clean up abandoned or uncontrolled hazardous waste sites.

Co-disposal Site   A waste site that has received and mixed municipal and hazardous wastes.

Detection Limit   The minimum quantity of a compound which yields a "measureable response." Measurable response has many statistical definitions. Be careful to differentiate "instrumental detection limit," which refers to the minimum quantity of material introducible into a measurement system that can be detected, from "method detection limit," which means the minimum concentration of a compound in a sample which, when put through the entire sampling and analysis process, can be detected.

Direct Emissions Measurement   A measurement made directly on or above the waste to determine the emission rate of volatile species from a liquid or solid surface.

Disturbed Condition	Changes in a hazardous waste site as remediation takes place that usually involve increasing the emission rate of volatile species and particulate matter.
Emissions	The total of substances discharged into the air from a discrete source.
EPA	U.S. Environmental Protection Agency.
FS	Feasibility Study. Analysis and selection of alternative remedial actions for hazardous waste sites.
Fugitive Dust	Atmospheric dust arising from disturbance of granular matter exposed to the air; called "fugitive" because it is not released to the atmosphere in a confined flow stream.
Hazardous	Those wastes that are regulated or "listed" under RCRA (40 CFR Part 261) or wastes that are ignitable, corrosive, reactive, or toxic.
In-depth Technologies	Very detailed methods for measuring emissions. These technologies produce detailed, reliable data.
Indicator Species	Species found in hazardous waste that can be used to represent a group of species in determining emissions from a site.
Indirect Emissions Measurement	A gas phase sampling technology that measures ambient air concentrations at short distances down-wind of a hazardous waste site. Data are collected to satisfy specific needs of specialized models used to estimate air emissions.
Lagoon	In this manual, lagoon encompasses surface impoundments or impoundments designed to hold liquid wastes or wastes containing free liquids.
Landfill	For purposes of this manual, a landfill is a facility, usually an excavated pit, into which wastes are placed for permanent disposal.
mg/m3	Milligrams per cubic meter. This is a measure of mass per unit volume. The units mg/m3 are commonly used to describe concen-tra-tions of particulates, dusts, fumes, and mists.
NIOSH	National Institute for Occupation Safety and Health, Centers for Disease Control, Public Health Service, U.S Department of Health and Human Services.
NPL	National Priorities List. A list of waste sites for which EPA has assessed the relative threat of site contamination on soil, air, surface water, ground water, and the population at risk. Site listing is found under CERCLA (Section 105) and is updated three times a year.

ACKNOWLEDGEMENTS

SECTION 1
INTRODUCTION

The United States Environmental Protection Agency (EPA) is responsible for the assessment and cleanup of the National Priority List (NPL) sites under CERCLA and SARA. EPA's Remedial Program Managers (RPMs) are required to assess the potential for air emissions and air quality impacts caused by NPL sites prior to and during cleanup. To date, no standard approach for assessing the air pathway at NPL or other hazardous waste sites has been available. As a result, performing air pathway analyses (APA) has been less straightforward than evaluating other pathways such as the impacts on ground water or surface water quality. This manual assists RPMs in determining if an uncontrolled site has the potential for significant air emissions and, if so, how to characterize the baseline air emissions potential from the site.

This volume is one in a series of manuals prepared for EPA to assist its RPMs in the assessment of the air contaminant pathway and developing input data for risk assessment. Volume I (1) of the series provides overview and directional information for the RPM in the overall Superfund process. This manual (Volume II) provides guidance on developing baseline emission estimates from hazardous waste sites. Baseline emission estimates (BEEs) are defined as emission rates estimated for a site in its undisturbed state. Applications of BEEs are found in additional volumes: Volume III (2) provides guidance on estimating emissions from cleanup activities using these baseline emission estimates and other means; and Volume IV (3) provides guidance on ambient air monitoring and on dispersion modeling using baseline emissions or other source term data to predict ambient concentrations at locations of concern.

1.1 THE PROBLEM

CERCLA and SARA mandate the characterization of all contaminant migration pathways from the waste or hazardous material to the environment and

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evaluation of the resulting environmental impacts. However, air pathway analyses are often overlooked because many sites emit little or no perceptible air emissions in their baseline or undisturbed state. Exposure to the elements over time often causes surface materials to develop a type of surface crust which tends to impede volatile emissions. This type of surface can also reduce emissions of particulate matter. However, all sites have the potential to generate air emissions at some level during cleanup, and it is essential to anticipate these emissions. Emissions of potential concern include volatile and semi-volatile organics, acid gases, particulate matter, and toxics associated with windblown particulate matter such as metals, PCBs or dioxins.

A remedial investigation is typically necessary to either provide data on air emissions from the site directly, or to provide chemical and physical data that can be used as inputs to model the emissions. Remedial investigations (RIs) often include ambient air monitoring to assess baseline air quality impacts from the site, but measurements of emission rates or soil-gas concentrations are less widely employed. An introduction to these techniques is a major emphasis of this manual. Emission rate or soil-gas data can be useful for: 1) identifying "hot spots" e.g. areas of higher than average waste content or pockets of subsurface gases, 2) serving as model inputs (source terms) to estimate ambient air concentrations under meteorological conditions other than those encountered during the RI, and 3) estimating emissions during remediation. For this last use, the air emissions investigation during the RI stage would include emission measurements of both the undisturbed wastes and the exposed or disturbed wastes.

While not strictly part of baseline emission estimates, measurements of emissions from exposed or disturbed wastes can generally be performed during the RI using the same techniques presented in this manual for performing baseline emission measurements. These data along with the BEEs can be used in the procedures outlined in Volume III of this series to help to evaluate remediation options, design an engineering approach to the site mitigation, and determine whether air emission control technologies or an air monitoring program may be necessary as part of the remedial alternatives.

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1.2 THE OBJECTIVE

The overall objective of this manual is to assist RPMs or site managers in assessing the impacts on air quality from the site in its undisturbed condition. Specifically the manual is intended to:

- Present a protocol for selecting the appropriate level of effort to characterize baseline air emissions.

- Assist site managers in designing an approach for estimating baseline emissions.

- Describe useful technologies for developing site-specific baseline emission estimates (BEEs).

- Help site managers select the appropriate technologies for generating site-specific BEEs.

However, this manual has limitations:

- The manual is a decision making tool but it is not intended to relieve the site managers of their decision making responsibility.

- The protocol is not a "cookbook" for designing air pathway investigations or for determining BEEs.

- The determination of BEEs for a site will not by itself, yield an assessment of actual or potential air impacts, but it is a useful part of that evaluation process.

1.3 MANUAL ORGANIZATION

This manual (Volume II) provides general information on the potential for air contaminant emissions from hazardous waste sites in Section 2. Section 3 offers a protocol for determining if BEEs are required and how to develop

site-specific BEEs. Information on technologies used to obtain BEEs is provided in Section 4. Section 5 describes case studies in which BEEs were needed and/or determined for hazardous waste sites.

References are given in Section 6. An annotated bibliography of the information reviewed for this project is included as Appendix A. This literature was identified during a computer-assisted search of 15 databases and a telephone survey of regional EPA personnel, employees of EPA research offices, EPA contractors, university researchers, and referrals from those contacted. Appendix B identifies chemical and physical properties of waste material that may affect is emissions potential.

For this manual, all types of uncontrolled solid waste sites, land disposal sites in particular, will be referred to as "landfills" and all types of uncontrolled liquid waste sites will be referred to as "lagoons." The technologies described for application to landfills and lagoons may generally be applied to solid and liquid hazardous waste, respectively.

SECTION 2
AIR EMISSIONS FROM HAZARDOUS WASTE SITES

This section presents information on landfills and lagoons, the two general types of sites used in this manual to demonstrate methods for estimating the potential for air emissions. This section addresses potential emission sources and potential air quality impacts. Discussion of potential air quality impacts covers the general types of air quality impacts by waste site category, and the basic transport mechanisms involved with the movement of contamination from lagoons and landfills. Where not otherwise specified, the general term hazardous waste site is used to refer to both landfills and lagoons that contain hazardous wastes and/or substances. Figures 1 and 2 depict these two types of sites in generalized schematic drawings.

The site and contaminant characteristics discussed below are general background information for working with the protocol presented in Section 3. The information provided will assist the site manager in developing conceptual models of landfills and lagoons. Based on this conceptual understanding, the site manager can then develop strategies for assessing the potential impacts and for estimating potential air emissions from these sites. The references cited in this section and those listed in the annotated bibliography contain further background material.

2.1 GENERAL DESCRIPTION

2.1.1 Landfills

Landfills are facilities into which wastes are placed for permanent disposal, and usually are simply an excavated pit. Landfills may vary in size from a few tenths of an acre to several hundred acres and other landfill characteristics can also vary greatly from one site to the next. Most variations are attributable to the types of stored wastes, the operating practices and the age of the facility, and hence, its design.

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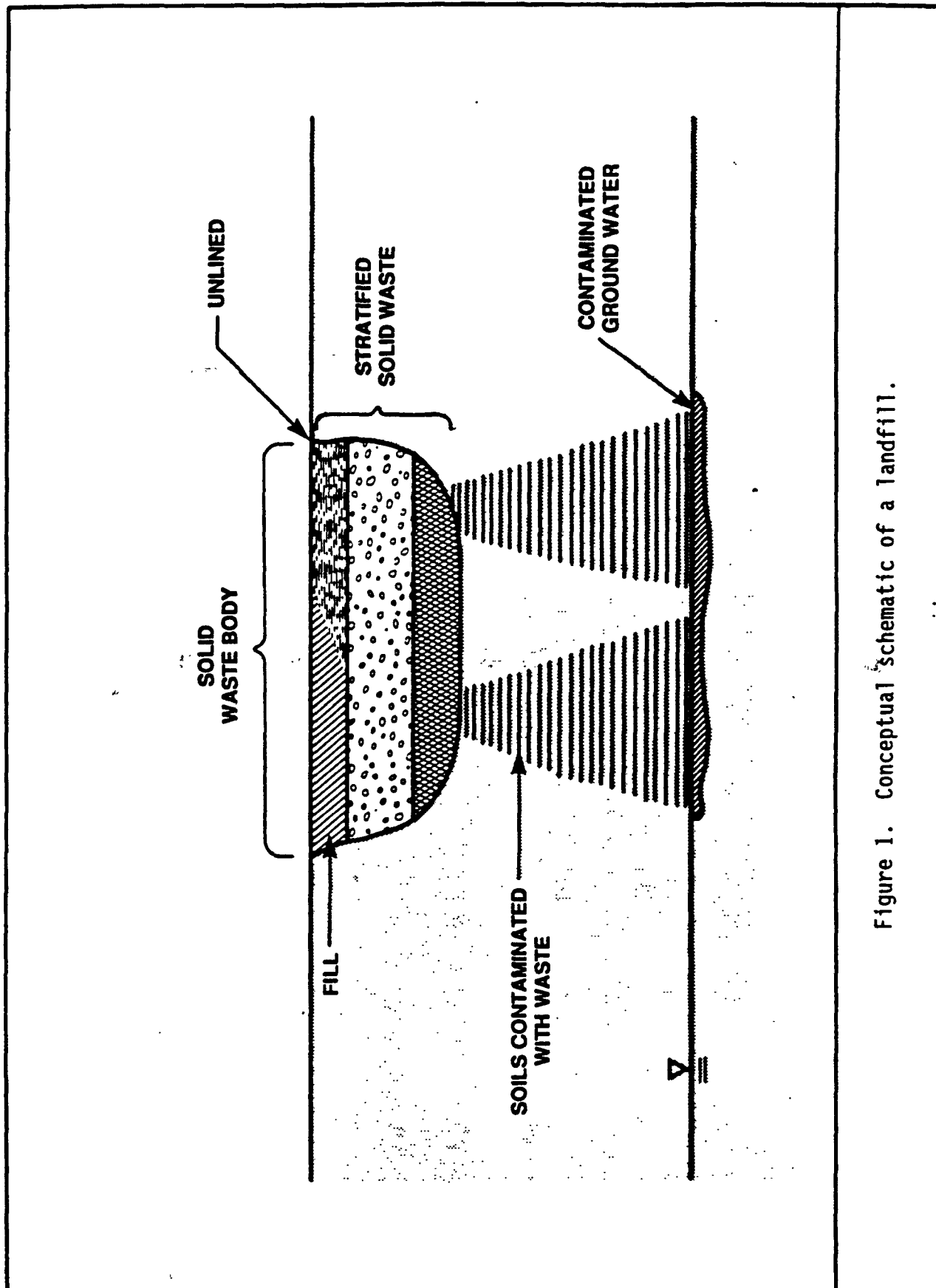
Figure 1. Conceptual schematic of a landfill.

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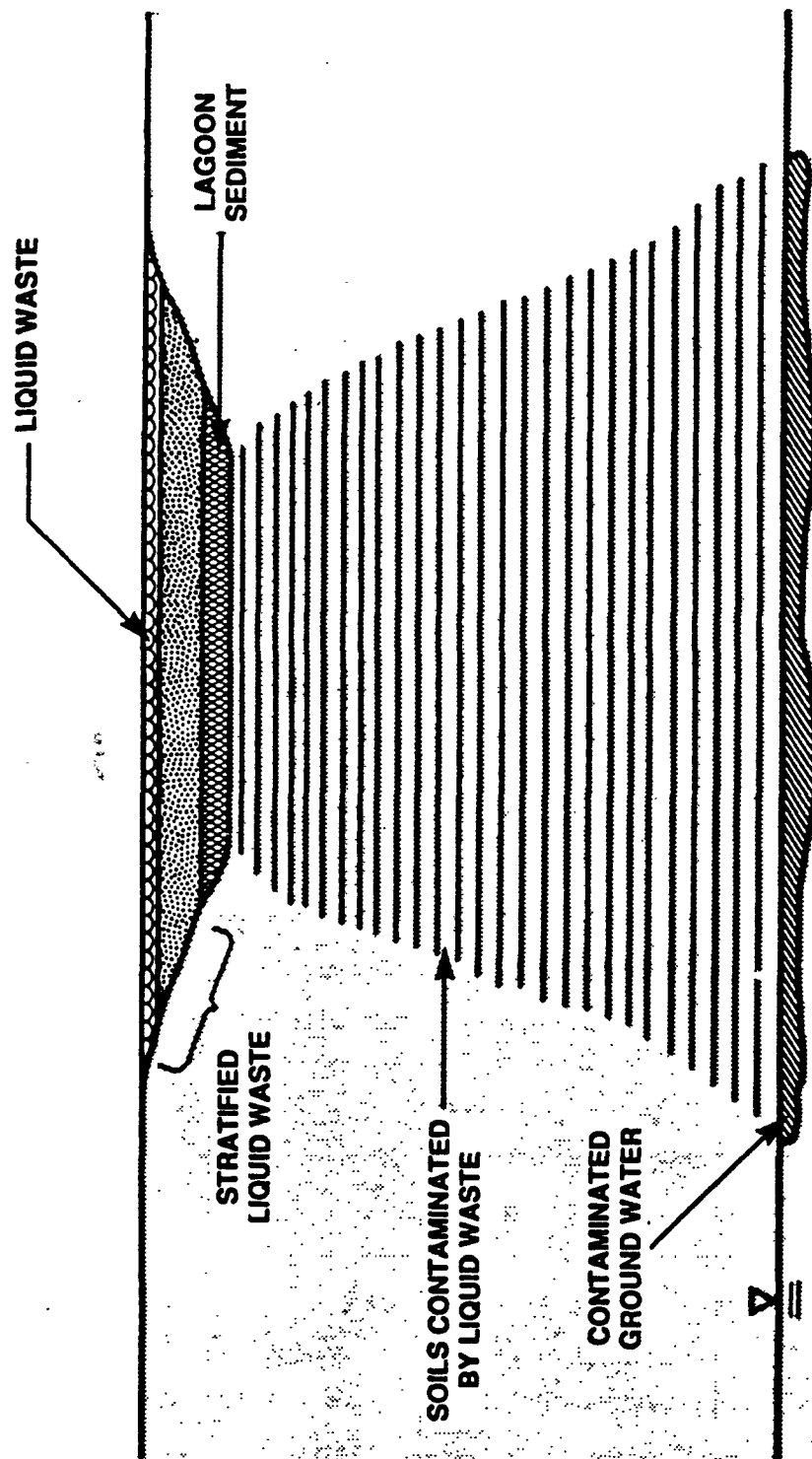
Figure 2. Conceptual schematic of a lagoon.

LIQUID WASTE

LAGOON SEDIMENT

STRATIFIED LIQUID WASTE

SOILS CONTAMINATED BY LIQUID WASTE

CONTAMINATED GROUND WATER

0488-035-2

Commercial landfills can be categorized by design criteria such as liners and gas-venting systems. Older landfills are usually unlined. Newer landfill designs may specify liner systems to retard transport of leachate and wastes into soils and ground water. Some landfills have built-in gas venting systems to prevent build up of landfill gases.

Landfills can be further differentiated by the types of waste they store. Commercial landfills are commonly classified as municipal or hazardous, depending on the types of waste accepted. Municipal landfills accept solid, semi-solid, and liquid nonhazardous wastes, including garbage, glass, plastics, paper, plant matter, ashes, some industrial wastes, and demolition and construction wastes.

Hazardous waste landfills accept hazardous sludge, liquids, semi-solids, residues, concentrates, or leachate or ash originating from a waste. Much of the hazardous waste originates from manufacturing, petrochemical, and chemical industries. Federal, state, and local regulations establishing minimum design standards and restricting types of acceptable landfill wastes have evolved over the last 25 years. In the past, mixtures of liquid and solid waste were common practice. Today, landfills can no longer accept liquid wastes or solids that contain free liquids unless they've been treated with fixatives and stabilizers to eliminate the free liquids prior to disposal.

Co-disposal landfills are sites that have received and mixed municipal and hazardous wastes. Any available disposal records may relate types of wastes and location/mixing within the landfill.

Most landfills that are selected as Superfund sites have undergone some form of closure. In some cases, currently operating facilities may have abandoned hazardous landfills at the same site. The appearance of a closed landfill will depend on when it was closed. Closure may mean that the site is covered with vegetation or that no waste is exposed. Telltale signals of covered waste are seeping leachate and odors. In the past, landfills were often sited in unpopulated areas close to the industry or industries

generating the wastes, but population growth and development may result in people living or working in close proximity to the site.

Superfund sites may differ in significant ways from the types of commercial landfills discussed above. In some cases, the site history will be one of relatively indiscriminate disposal of hazardous substances. The sites may contain buried drums or pockets of dumped/spilled wastes that are not uniformly distributed across the disposal area. Information on waste types, disposal practices, date of disposal, etc. may be limited or non-existent. However, the protocol and measurement techniques presented in this manual are sufficiently generalized that they can be applied to such uncontrolled sites. Conversely, the emission models presented here may be of only limited use for sites where the chemical and physical parameters that serve as model inputs are poorly defined.

Potential Site Conditions--

The site conditions encountered when investigating landfill sites will vary from site to site because of the siting, landfill design, landfill use, and difference in landfill operations among each of the sites. Figure 1 presents a conceptual schematic of a landfill site. The condition of the site cover material will vary greatly. It will depend, to a large extent, on the landfill's operational history. In the best situation, the landfill cover will extend over the entire land disposal area; the cover will have been constructed to minimize rainfall percolation into the waste body and regulated to minimize erosion of the cover. The degree to which the air, the surrounding native soils, and the ground water are protected from contamination from the wastes stored in the landfill will depend both on the landfill design and on the construction and operation of the waste storage facility. If the wastes have been disposed of into an unlined storage area, the likelihood of contamination of surrounding soils and eventual contamination of the ground-water beneath the landfill increases. If the landfill has been constructed at or below the ground-water table, the transport of pollutants into the ground water further increases. Waste material in the landfill may be stratified by age of disposal and/or settling of the more dense waste.

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Emission of air pollutants from landfills is dependent on the chemical and physical properties of the stored wastes and on the landfill design components which may have been implemented to reduce air emissions. Municipal landfills are sources of significant amounts of methane and carbon dioxide, and variable amounts of other non-methane hydrocarbons. Hazardous waste landfills often are sources of non-methane hydrocarbons, including volatile organic compounds (VOCs), semi-volatiles, and pesticides. Co-disposal sites combine the emission potentials of both municipal and hazardous waste sites. The methane gases generated often can increase the migration potential of the high concentrations of non-methane hydrocarbons by acting as a carrier medium during bulk flow transport of these contaminants. For this reason, co-disposal sites may generate very high emission rates compared to other types of landfills.

2.1.2 Lagoons

For purposes of this discussion, the term "lagoon" refers to the class of facility also known as surface impoundment or impoundment. This type of facility generally includes a natural topographic depression, a man-made excavation, or a diked area formed primarily of earthen materials. Lagoons are designed to hold liquid wastes or wastes containing free liquids. Lagoons include holding, storage, settling, and aeration ponds.

These waste sites may range in surface area from a few tenths of an acre to hundreds of acres. Man-made lagoons typically range in depth anywhere from 2 to 30 or more feet below land surface.

In some cases, for certain wastes, lagoons may be lined to minimize any fluid seepage. Clay, asphalt, soil sealant, and synthetic membranes are typical lining materials.

To prevent migration of pollutants into the native soils and ground water beneath the lagoon, lagoons are usually built above the naturally occurring water table and take advantage of any impermeable surface or subsurface soils.

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In areas with high ground-water tables, lagoons may be constructed on the land surface to minimize ground-water contact. Of course, use of liners and building above the water table will not prevent the release of contaminated air emissions from the surface of the lagoon, but these practices limit the possible routes of air emissions (see Section 2.2). Equally as important are operating practices and waste types in the lagoon. The importance of these factors tends to parallel the landfill discussion above, as does the importance of lagoon siting practices.

Potential Site Conditions--

Actual site conditions that will be encountered when investigating hazardous waste site lagoon sites will vary because of siting, lagoon design, lagoon usage, and differences in lagoon operations. Figure 2 presents a conceptual schematic of a lagoon site. The condition of the lagoon will depend, in large part, on the wastes stored there and the lagoon's operational history. Mixed wastes within the lagoon will often have separated into stratified layers. The lighter materials are near the surface, the denser liquids, sludges, and sediments have settled to the lagoon bottom. Contaminated soils around and beneath the lagoon are likely, as well as contamination of the underlying ground water.

2.1.3 <u>Equivalent Units</u>

NPL sites containing mixed wastes or having other types of inherent variability may require separate remedial options to be considered for each equivalent area. During the remedial investigation, the site should be theoretically divided into units of equivalent waste for estimating baseline emissions and evaluating potential emissions during remediation. For example, a site containing an abandoned landfill, sludge pits, and buried drums would have at least three distinct units and maybe more. If the type, concentration, or distribution of a given form of contamination varies, then further subdivision of the units should be considered. Similarly, if the soil media or proximity of receptors varies significantly across the site, then further subdivision of the units may be warranted.

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2.2 ROUTES OF EXPOSURE

Waste site characterizations performed during a remedial investigation are intended to determine potential or existing contaminant migration by the direct contact, surface water, ground water, and air pathways. Each pathway represents a potential route of exposure to the public and the general environment. Figures 3 and 4 show the potential routes for contaminant migration from landfills and lagoons, respectively. The focus of this manual is the air pathway, and several routes exist for contaminant emissions within this one pathway.

Emissions from surface wastes may occur as gaseous volatile organics and inorganics as gases, aerosols, and contaminated particulate matter. Where gas migration controls, (e.g., gas venting systems) have been installed, volatile emissions from the controls are likely to be higher than emissions from the site surface. The lateral migration of solid and liquid wastes into the surrounding soils and beneath the containment area can create large areas of contaminated subsurface soils. The contaminated soils also represent a source of potential air emissions via the transfer of contaminants into the air-filled spaces in the soil matrix. The contaminated soil gas can then transfer contaminants into the atmosphere at the surface soil/atmosphere interface.

The generation of leachate from landfills and lagoons can accelerate the pollutant migration into the ground water below and provide an additional source of air emissions resulting from the volatilization of dissolved contaminants in the ground water. The contaminated ground-water also can transfer contaminants into the soil gas and hence the atmosphere.

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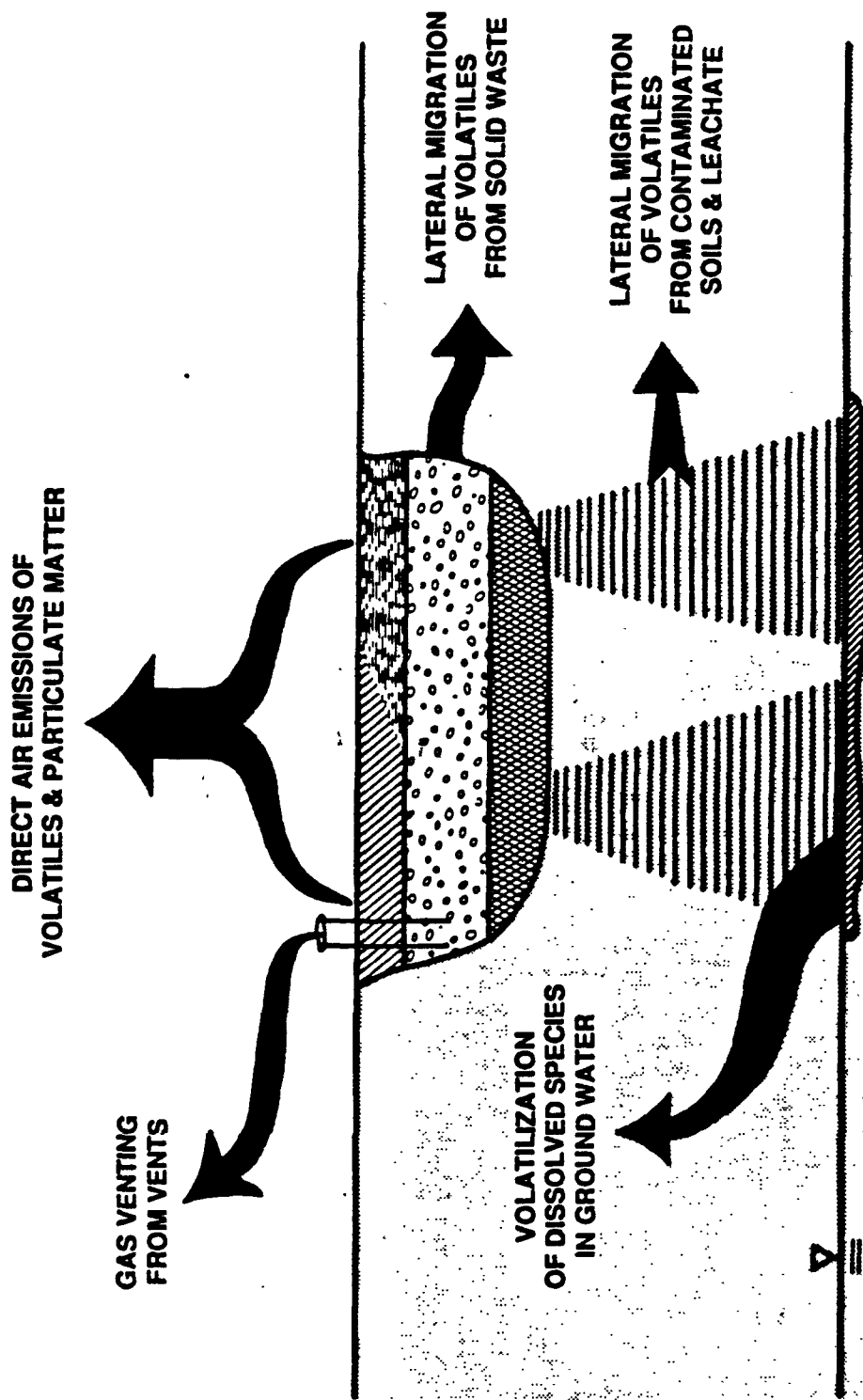
Figure 3. Conceptual schematic showing air contaminant pathways from a landfill.

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Figure 4. Conceptual schematic showing air contaminant migration from a lagoon.

DIRECT AIR EMISSIONS OF VOLATILES & AEROSOLS

LATERAL MIGRATION OF VOLATILES FROM LIQUID/SLUDGE WASTE

LATERAL MIGRATION OF VOLATILES FROM CONTAMINATED SOILS & LEACHATE

VOLATILIZATION OF DISSOLVED SPECIES IN GROUND WATER

2.2.1 Key Parameters and Critical Factors Affecting Emissions from Landfills

The generation of emissions from landfills depends on several key chemical and physical properties of the waste materials stored at these sites. Table 1 presents these key factors along with the qualitative effects these factors may have on baseline emissions. These data can be used to help estimate the potential air emissions from the site, given critical factors imposed by the site. A discussion of each parameter is outside the scope of this document, but in general, for volatile compounds the rate limiting step is the movement of vapors through the soil. Volatilization into the soil pore spaces and transfer from the soil-gas into the atmosphere once the soil/air interface has been reached, are usually quite rapid. Additional information about the key physical and chemical properties of the waste material are presented in Appendix B. Users should consult the references cited below and those listed in the annotated bibliography (Appendix A) for additional background material. General reading materials that may prove helpful include: Guidance Document for Cleanup of Surface Impoundment Sites,(4) Model Prediction of Volatile Emissions,(5) Air Pollution Assessment of Toxic Emissions from Hazardous Waste Lagoons and Landfills,(6) Air Quality Assessment for Land Disposal of Industrial Wastes,(7) Estimating Air Emissions from Disposal Sites,(8) and Air Pollution Problems of Uncontrolled Hazardous Waste Sites.(9)

2.2.2 Key Parameters Affecting Emissions from Lagoons

Figure 4 presents a generalized schematic of the volatilization process from lagoons. In general, the process consists of two steps: vaporization from the surface liquid layer into the boundary air layer and then mass transfer from the boundary layer to the bulk atmosphere. The rate of vaporization is dependent on factors such as the compound's concentration, Henry's Law constant, water solubility and the system temperature. Mass transfer into the bulk atmosphere is dependent on compound properties such as molecular weight and diffusion coefficient, and site-related factors such as

TABLE 1. IMPORTANT PARAMETERS IN DETERMINING AIR EMISSIONS
AND THEIR QUALITATIVE EFFECTS ON BASELINE EMISSION
ESTIMATES (BEEs)

Parameter	Qualitative Effect on BEEs[a]	
	Volatiles	Particulate Matter

Site Conditions

Size of Landfill or Lagoon	Effects overall magnitude of emissions but not rate per area.	Effects overall magnitude of emissions, but not rate per area.
Amount of Exposed Waste	High	High
Depth of Cover on Landfills	Medium	High
Presence of Oil Layer	High	High
Compaction of Cover on Landfills	Medium	Low
Aeration of Lagoons	High	High
Ground Cover	Medium	High

Weather Conditions

Wind Speed	Medium	High
Temperature	Medium	Low
Relative Humidity	Low	Low
Barometric Pressure	Medium	Low
Precipitation	High	High
Solar Radiation	Low	Low

Soil/Waste Characteristics

Physical Properties of Waste	High	High
Adsorption/Absorption Properties of Soil	Medium	Low
Soil Moisture Content	High	High
Volatile Fraction of Waste	High	Low
Semi-Volatile/Non-Volatile Fraction of Waste	Low	High
Organic Content of Soil and Microbial Activity	High	Low

[a] High, medium, and low in this table refer to the qualitative effect that the listed parameter typically has on baseline emissions.

temperature, pressure, and wind speed. Berms, wind breaks, and lagoon geometry affect the wind speed at the liquid surface and can thereby control the rate of mass transfer. In general, low molecular weight compounds are more volatile than high molecular weight compounds.

2.3 MAGNITUDE OF AIR EMISSIONS

The magnitude of baseline air emissions from landfills and lagoons is dependent on waste-specific chemical and physical factors and site-specific environmental factors. Limited data are available on measured air emission fluxes (rate per area) from previously studied waste sites (Table 2). These data can be used to give the site manager some idea of typical baseline emission estimation (BEEs) and a limited comparison of BEEs for different types of waste sites. Emission flux data for disturbed or exposed wastes are included to demonstrate the potential for increased emissions for volatiles during waste remediation.

2.4 EMISSIONS OF POTENTIAL INTEREST AT NPL SITES

The types of emissions at a hazardous waste site are dependent on the types of waste present, and these in turn are dependent on the types of industries and manuf-cturers that produced the waste. A listing of the typical wastes generated by 30 various industries and manufacturers can be found in the Handbook of Industrial Waste in California (11). The 25 most frequently detected compounds at 546 hazardous waste sites are summarized in Table 3 according to the type of media, i.e., groundwater, surface water, or air. The table shows the number of sites where each contaminant was detected and the contaminant's relative rank for each type of media. Another useful listing for selecting contaminants with the potential for emissions of concern, is the list of toxic compounds most commonly addressed by state and local regulatory agencies given as Table 4.

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TABLE 2. SUMMARY OF AVERAGE BASELINE EMISSIONS FOR VARIOUS EMISSION SOURCES

Waste Type	Source Type	Baseline Emission Estimate For TNMHC[a] (ug/m^2-min)	Disturbed or Exposed Waste Emissions For TNMHC (ug/m^2-min)
NPL/Hazardous Waste Sites	**Landfills**		
	Site A	360	190,000
	Site B	740	26,000
	Site C	29	170,000
	Lagoons		
	Site D	43	640,000
Industrial Waste	TSDF[c] Facilities		
	Active Landfills		
	Site E	---	44-150
	Site F	---	47
	Site G	---	9
	Inactive Landfills		
	Site H (covered)	<1.2	---
	Site I (covered)	<1.2	---
	Land Treatments		
	Site J	---	610-9600
	Lagoons		
	Site K	120	---
	Site L	570	---
	Site M	9-31[b]	---
	Site N	630	---

[a] TNMHC = Total Non-Methane Hydrocarbons.
[b] Different assessment techniques were used.
[c] Transfer, storage, and disposal facilities (RCRA) - Reference 10.

TABLE 3. MOST FREQUENTLY REPORTED SUBSTANCES AT 546 NATIONAL PRIORITY ᴸLIST SITES

Substance Identified at Hazardous Waste Disposal Sites	Sites[a]	Ground Water Sites (Rank)[b]	Surface Water Sites (Rank)[b]	Air Sites (Rank)[bc]
Most Frequently Occurring				
1. Trichloroethylene	179	127 (1)	49 (3)	8
2. Lead	162	77 (4)	84 (1)	7
3. Toluene	153	81 (3)	40 (4)	16
4. Benzene	143	84 (2)	36 (5)	18
5. Polychlorinated Biphenlys (PCBs)	121	29 (21)	54 (2)	6
6. Chloroform	111	70 (6)	24 (11)	1
7. Tetrachloroethylene	90	57 (7)	17 (14)	3
8. Phenol	84	43 (9)	28 (8)	3
9. Arsenic	84	45 (8)	35 (6)	2
10. Cadmium	82	28 (16)	28 (9)	31
11. Chromium	80	34 (14)	33 (7)	1
12. 1,1,1-Trichloroethane	79	58 (6)	20 (12)	3
13. Zinc and Compounds	74	28 (17)	27 (10)	2
14. Ethylebenzene	73	36 (12)	14 (20)	7
15. Xylene	71	32 (15)	8 (25)	9
16. Methylene Chloride	63	36 (13)	17 (15)	2
17. Trans-1,2-Dichloroethylene	59	42 (10)	17 (16)	1
18. Mercury	54	27 (20)	20 (13)	4
19. Copper and Compounds	47	17 (24)	16 (18)	6
20. Cyanides (Soluble Salts)	46	16 (25)	16 (19)	2
21. Vinyl Chloride	44	28 (18)	10 (23)	4
22. 1,2-Dichloroethane	44	25 (21)	17 (17)	2
23. Chlorobenzene	42	23 (23)	9 (23)	0
24. 1,1-Dichloroethane	42	28 (19)	8 (24)	0
25. Carbon Tetrachloride	40	25 (22)	12 (21)	2

[a] Number of sites at which substance is present. Substances may be present in one, two, or all three environmental media at all sites at which it is known to be rpesent. Therefore, the number of sites at which each substance is detected in environmental media may not equal the number in this column.

[b] Not all ranks will be represented in all media because not all chemicals found in media are among those found most frequently at site.

[c] Volatile organics not otherwise specified were reported as being detected most often (rank 1) in the air medium.

Source: <u>Air Quality Engineering Manual for Hazardous Waste Site Mitigation Activities.</u>[12]

TABLE 4. TOXIC POLLUTANTS MOST COMMONLY ADDRESSED BY STATE AND LOCAL AGENCIES

Acetaldehyde	Hexachlorocylopentadiene
Acrolein	Hydrazine
Acrylonitrile	Hydrogen Sulfide
Allyl Chloride	Lead
Arsenic	Lindane
Asbestos	Maleic Anhydride
Benzene	Manganese
Benzidine	Mercury
Benzo(a)pyrene	Methyl Bromide
Benzyl Chloride	Methyl Chloride
Beryllium	Methyl Chloroform
Bis(chloromethyl)ether	Methylene Chloride
1,3-Butadiene	beta-Naphthylamine
Cadmium	Nickel
Carbon Tetrachloride	Nitrobenzene
Chlordane	n-Nitrosodimethylamine
Chlorobenzene	Nitrosomorpholine
Chloroform	Parathion
Chloroprene	Perchloroethylene
Chromium	Phenol and Chlorinated Phenols
Cresol	Phosgene
1,4-Dichlorobenzene	Polychorinated Biphenyls (PCBs)
3,3-Dichlorobenzidine	Polycyclic Aromatic Hydrocarbons (PAH)
Dimethyl Sulfate	Propylene Oxide
1,3-Dioxane	Radionuclides
Dioxins	Styrene
Epichlorohydrin	1,1,2,2-Tetrachlorethane
Ethylene Dibromide	Tetrahydrofuran
Ethylene Dichloride	1,1,2-Trichloroethane (vinyl trichloride)
Ethylene Oxide	Toluene
Ethylenimine (azridine)	Trichoroethylene
Formaldehyde	Vinyl Chloride
Heptachlor	Vinylidene Chloride
	Xylene

Source: Reference 12.

2.5 SUMMARY OF POTENTIAL RECEPTORS

Receptors can be divided into three broad categories:

•On-site workers;
•Off-site populace; and
•Non-human receptors.

The on-site workers are in the closest proximity to the hazardous waste site and are potentially subject to the most acute exposure to hazardous substances. The use of personal protective equipment, real-time field instruments, personnel monitoring, site controls, and designated work zones are designed to ensure that field personnel are properly protected against the hazards present at the work site.

The off-site (and any on-site) population in close proximity to the hazardous waste site is another receptor of primary concern. These people are often acutely aware of the hazardous waste site and the potential for contaminant exposure. Section 3 provides an approach for estimating emissions which can subsequently be used to predict the airborne contaminant concentration for downwind receptors to assist in the establishment of appropriate action levels. Use of this protocol, coupled with an effective monitoring and modeling program, will provide useful information for the site's community relations program.

Non-human receptors also may be a concern at some hazardous waste sites. Disturbance of the site may lead to exposure through inhalation of contaminated air or exposure through ingestion of or direct contact with contaminants deposited on plant and inert surface. The possibility of inhalation exposure may affect feral or domesticated animals downwind of the site. This also impacts humans in that animal exposure to pollutants can lead to contamination accumulation in the food chain.

Certain gaseous pollutants (e.g., ozone, oxides of sulfur and nitrogen), if present in high concentrations, also can affect plant and animal growth. Deposition of airborne contaminants may cause stressed vegetation, release pesticides and herbicides, or impact the value/usability of agricultural crops. Also, deposition of metals or other pollutants in surface waters may impact marine life. Copper and some other metals can cause fish kills at very low concentrations.

SECTION 3
PROTOCOL FOR BASELINE EMISSION ESTIMATES

This section presents a protocol for developing baseline emission estimates (BEEs). This protocol is a component of an air pathway analyses (APA) program to assess potential air quality impacts from hazardous waste site landfills and lagoons. While not all sites will require BEEs, the first three steps in the protocol should be implemented to see if BEEs are necessary for a given site. The protocol is a recommended guideline; the level of effort that is required or the need to develop BEEs for individual sites must be determined on a case-by-case basis.

3.1 PROTOCOL STEPS FOR DEVELOPING BEEs

Figure 5 diagrams a protocol for developing BEEs. The protocol was developed to help the site manager to determine baseline emission rates and absolute emissions. These values can be used as inputs to dispersion models to assess the air impacts for receptor locations of interest. The activities identified in this flow chart are consistent with the steps of the CERCLA remedial investigation process that involve the assessment of the air contaminant migration pathway. Although the protocol was developed for NPL sites, it also applies to assessing air emissions from other hazardous waste sites. The flow chart is applicable to all sites, regardless of the type of site (landfill, lagoon, waste pile, etc.), type of waste, or the potential for the site to generate air emissions. Each step of the protocol is described below.

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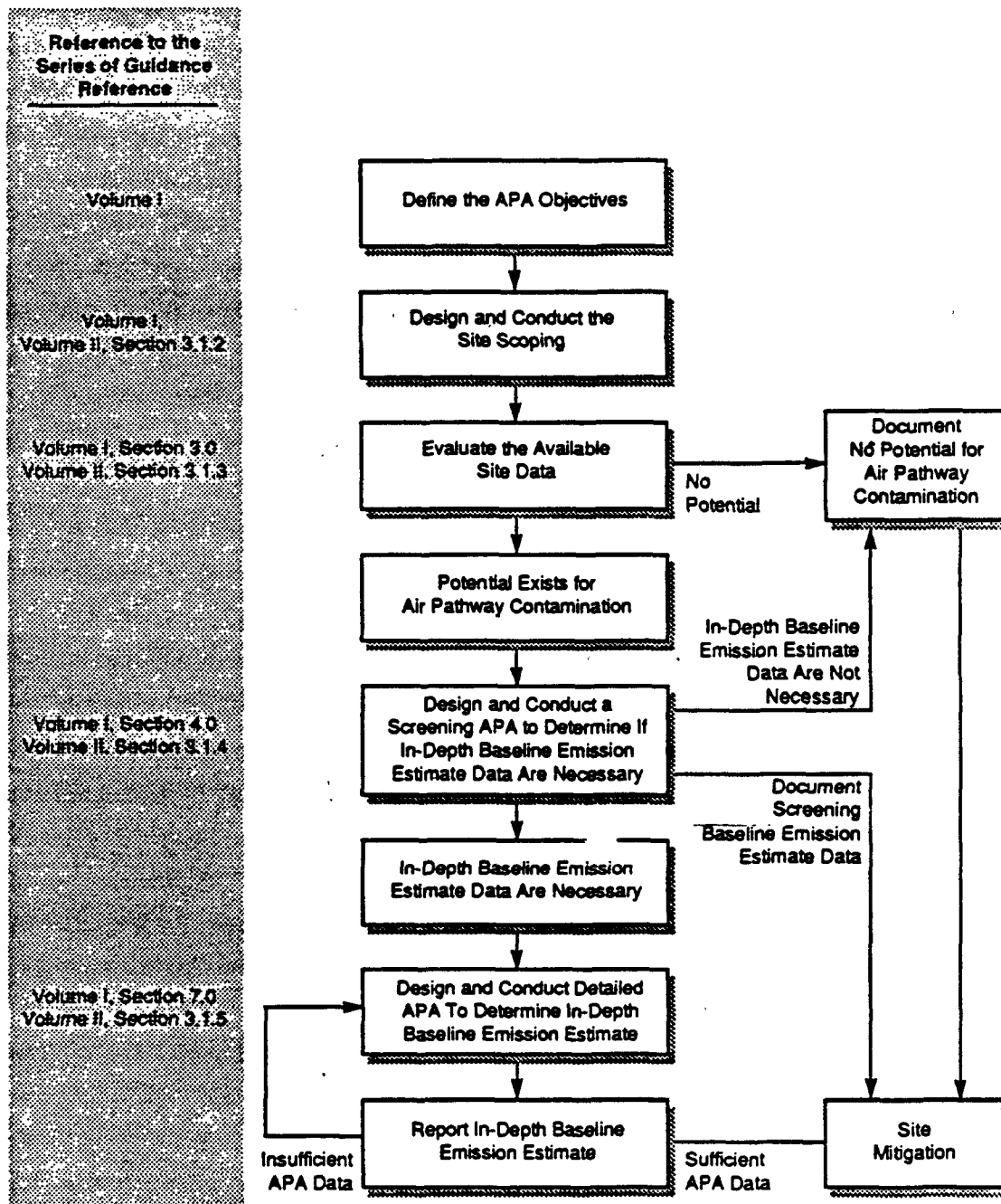
Figure 5. Flowchart of activities for developing screening and in-depth baseline emission estimates.

3.1.1 Define the APA Objective

CERCLA and SARA legislation highlight the basic objectives for all remedial investigations. Simply stated,.these objectives are to provide data that are "necessary and sufficient" to characterize the "nature and extent" of contamination on site. In addition, they mandate that "all potential migration pathways for contaminations" require characterization. As the first step of the protocol to assess baseline emissions, site-specific objectives should be developed; this will generally occur simultaneously with the performance of Steps 2 and 3 (data collection :and review) of the protocol. The site manager should consider the following issues when formulating site-specific objectives:

- **What information is already available?** As described in Section 3.1.2, available information should first be reviewed before developing final site-specific objectives. This preliminary review of information will provide necessary background information and aid in identifying data gaps.

- **What pathways must be considered?** Except in rare cases, all pathways, namely air, soil, and water, must be considered.

- **What is technically possible?** Site and situational factors that may adversely affect the air pathway investigation should be identified to avoid establishing unrealistic objectives. These factors can range from complexity in site geology/hydrogeology and complex terrain to the feasibility of detecting the contaminants of interest.

- **What time deadlines exist?** Schedule constraints can affect the nature of the investigation and must be balanced with technical concerns.

- **What data quality objectives are required?** Data must be of a known accuracy and precision for use in evaluating the air pathway.

- **What program is most cost effective?** The type, level, and extent of contamination per migration pathway will primarily determine how the available resources are apportioned. It is also necessary to collect, integrate, and consider a variety of types of data, including technical information, institutional issues, political issues, public protection, community relations issues, and community concerns.

- **What contaminants must be considered?** The investigation will typically involve identifying and characterizing the extent of the contamination. Concentrations of individual or summed indicator compounds are often selected to represent the extent of total contamination. Site-specific objectives should neither identify specific indicator compounds nor require characterization of all compounds.

Table 5 provides examples of objectives related to baseline emissions estimates. The first step in developing site-specific APA objectives is to collect and review readily available site historical records. The potential for air emissions can be inferred from the review of preliminary site information. While baseline emiss'ons may be low, during remediation sites have the potential for air emissions of particulate matter (semi-volatile organics, metals, and other inorganic contaminants) and enhanced volatile organic emissions.

Among the types of information that can be reviewed and used to develop site-specific APA objectives are: waste characteristics; distribution of the waste; orientation of the general public to the emission source concerns; technical feasibility; and program resources. The first three items are discussed below.

TABLE 5. EXAMPLES OF APA OBJECTIVES FOR BEEs

- Characterize the air emissions potential for volatile species and particulate matter from the undisturbed site.

- Characterize the air emissions potential for volatile species and particulate matter from the disturbed site.

- Identify contaminants of concern.

- Provide baseline emission estimates that can be used to assess the health risk and the need to mitigate.

- Provide baseline emission estimates that can be used to assess the need for on-site or fenceline ambient monitoring.

- **Waste Characteristics.** Knowledge of the industrial process or the waste source involved can suggest the types of chemicals or agents that may be in the waste. For example, volatile emissions are likely from waste sites with organic solvents or petroleum waste. Wastes in liquid form tend to have higher baseline emissions than wastes in solid form. In addition, identifying common decomposition products of the chemicals identified in the waste may be useful. It is helpful to categorize potential air contaminants by their generic volatility: volatiles, semi-volatiles, and non-volatiles. Examples of the types of compounds in each category are listed in Table 6. The categories group together compounds with similar physical behavior in the atmosphere and thus are useful for predicting emissions potential.

- **Distribution of the Waste.** The relative position of the waste can influence the potential for air emissions and, thus, the APA objectives. The amount and nature of overburden strongly influences the baseline emissions at a site. Semi-volatiles and non-volatiles present near the surface can be emitted as windblown particulate matter. Waste piles may have relatively high emissions of both volatile organics and particulate matter due to their geometry and surface area to volume ratio.

- **Location of the Affected Population and Community Concerns.** The population potentially at risk from exposure to toxic air emissions from the site must be identified and the exposure characterized. The close proximity of residential areas may require the addition of measurement and monitoring activities for health and safety purposes that are beyond what is necessary to develop BEEs for the site. Thus, the site-specific objectives may include a component related to determining the potential impact on the nearest population (e.g., air monitoring at the site boundary).

TABLE 6. POTENTIAL AIR CONTAMINANTS BY GENERIC TYPE OF CONTAMINANT

Volatiles (>1 mm mercury vapor pressure)

- All monochlorinated solvents; also trichloroethylene, trichloroethane, tetrachloroethane

- Most simple aromatic solvents; benzene, xylene, toluene, ethylbenzene

- Some normal alkane; up to decane

- Inorganic gases; hydrogen sulfide, chlorine, sulfur dioxides

Semivolatiles (1-10⁻⁷ mm mercury vapor pressure)

- Most polychlorinated biphenyls; dichlorobenzenes, aroclors, dieldrin

- Most pesticides; aniline, toxaphene, nitroaniline, parathion, phthalates

- Most complex alkanes; dodecane, octadecane, hexacosane

- Most polynuclear aromatic's; napthalene, phenanthrene, benz(a)anthrencene

Non Volatiles or Particulate Matter (<10⁻⁷ mm mercury vapor pressure)

- Larger polynuclear aromatics; chrysene, coronene

- Metals; lead, mercury, chromium

- Other inorganics; asbestos, arsenic, cyanides

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The APA objectives should be documented and circulated for peer review by staff members that have knowledge of the site, APA, and the site mitigation process. The review process may also help identify site characterization data needs. Developing site-specific objectives is an iterative process; more than one round of data gathering, review, and discussion may be needed to develop satisfactory objectives.

3.1.2 Site Scoping

The second step in the development of BEEs is collecting available information about the site. This should be a quick, straightforward information search, involving but not limited to the collection of records, reports, shipping manifests, newspaper clippings, and information from interviews with people living close to or affiliated with the site. For NPL sites, data should be available from the preliminary assessment and site inspection conducted prior to inclusion on the NPL. The type of information to be collected parallels, for the most part, the factors considered in creating the objective. These include:

- Source of the waste (type of industry);

- Composition of the waste (organic-volatile/semi-organic; inorganic-metals, others; biological; radioactive);

- Distribution of the waste and cover material limiting volatilization and uptake of particulate matter from the waste;

- Distance from the waste to the property fenceline; and

- Representative meteorological data.

3.1.3 Evaluate Available Site Data

The existing site information should be evaluated to determine the potential for air pathway contamination. Examples of types of contaminants and situations to be evaluated are provided in Table 7. If it is determined through this assessment that the site poses no potential for air pathway contaminant migration, then no further evaluation of the baseline emissions is required. The site manager must record the basis for this decision and include these data in the site investigation documentation. In most cases, insufficient information will be available at this stage, and further work will be warranted. If air emissions are a potential concern, the next step of the protocol (site screening study) should be implemented to provide additional information to make a judgement regarding the potential for air emissions from the site. At this point the site-specific APA objectives should be reviewed to ensure they are still realistic, attainable, and applicable.

3.1.4 Design and Conduct the Site Screening Study

Designing a site screening study to assess the air emissions potential involves the selection of an air emissions measurement/assessment technology. The four broad categories of measurement/assessment technologies include:

- Direct emissions measurement;
- Indirect emissions measurement;
- Air monitoring/modeling; and
- Emissions (predictive) modeling.

Each technology can be further categorized according to its level of complexity as screening (quick and simple) or in-depth (very detailed).

The activities necessary to design and conduct the site screening study are:

TABLE 7. EXAMPLES OF TYPES OF CONTAMINANTS AND SITUATIONS THAT MAY
INDICATE A POTENTIAL FOR AIR PATHWAY CONTAMINATION

Situation/Condition	Volatiles	Particulate Matter	Comment
• Site Odors, Neighborhood Complaints	✓		Indicates moderate to high levels of BEEs.
• Observation of Dust Clouds During Wind		✓	Check soil cover and look for waste piles.
• Evidence of Metal Corrosion	✓	✓	Look for corrosive agents.
• Vent pipes	✓		Check records to determine if the site is a codisposal facility.
• Seeps of Waste	✓		Probable buried wastes.
• Weathered Waste Surface	✓	ˏ	Emissions of disturbed waste may be very high.
• Aged and Layered Waste	✓	·	Likely that volatiles are higher in underlying lay chemicals possible.
• Aerated Lagoons	✓	✓	Increased emissions.
• Exposed Waste	✓	✓	Increased emissions.
• Industrial Wastes	✓		Waste mixtures likely, check for particular solvent types, aromatic and halogenated organic solvents.
• Petroleum Wastes	✓		Tar/wastes with volatile emissions likely.
• Industrial Wastes/ Paint Wastes	✓		Organic volatiles likely.

(Continued)

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TABLE 7. (Continued)

Situation/Condition	Volatiles	Particulate Matter	Comment
• Industrial Wastes Works or Plating		√	Metal-contaminated particulate matter likely.
• Municipal Wastes	√		Methane/carbon dioxide volatiles likely; look for industrial waste.
• Hospital Wastes	√	√	Solvent used likely; biological hazards and radioactive waste possible.
• Chemical Product	√	√	High concentrations of specific chemicals likely.
• Site "Walk-Overs"	√		Gas detection results indicate the presence of gas species and the potential for emissions.
• Site "Walk-Overs"		√	Visual inspection and particle counting/detection results indicate the potential for particulate matter emissions.

- Determine the feasibility of obtaining the screening data. (Identify any site factors that may limit this activity.)

- Select appropriate tracer species, screening technologies, and applicable equipment/instrumentation.

- Design the site inspection technical approach and test plan, including the Quality Assurance/Quality Control Program. Make sure that all units of a combined site are studied.

- Circulate the site screening approach for review and ensure the screening addresses the site-specific objective(s).

- Modify the site screening program, as necessary.

- Conduct the site screening study and document the findings.

- Determine if the site screening study was adequate to characterize the air contamination migration pathway and if detailed BEE data are necessary. If detailed BEEs are necessary, initiate the in-depth site characterization study. If not, document the site inspection survey results and the basis for discontinuing the APA.

One preliminary step is to evaluate those key factors that affect the air emissions of volatiles and particulate matter. The factors were presented in Section 2 and are summarized in the check-list presented in Figure 6. This figure can be used to summarize site information and facilitate the decisions regarding selecting and implementing screening technologies. If the site contains a waste type that has the potential to create air emissions, the most important factors which determine the baseline emissions are typically site conditions and weather conditions. Once the checklist (Figure 6) has been completed and some knowledge of the factors affecting air emission processes is gained, the site manager must select appropriate indicator species and select air emission screening technologies, equipment, and instrumentation.

Parameter	General Affect Volatiles	General Affect PM	Site Information	Effect on Emissions — Volatiles Increase	Volatiles Decrease	Effect on Emissions — Particulate Matter Increase	Particulate Matter Decrease
SITE CONDITIONS							
Amount of Exposed Waste	High	High					
Depth of Soil	Med	High					
Presence of Oil Layer	High	High					
Compaction of Cover	Med	Low					
Aeration of Lagoons	High	High					
Ground Cover	Med	High					
WEATHER CONDITIONS							
Wind Speed	Med	High					
Temperature	Med	Low					
Relative Humidity	Low	Low					
Barometric Pressure	Med	Low					
Precipitation	High	High					
Solar Radiation	Low	Low					
SOIL/WASTE CHARACTERISTICS							
Physical Properties	High	High					
Sorption of Soil	Med	Low					
Soil Moisture	High	High					
Volatile Fraction	High	Low					
Semi/Non-Volatile Fraction	Low	High					
Organic Content of Soil	High	Low					

Figure 6. Checklist of factors affecting air emissions per unit. The site manager should use this to summarize site data on critical factors to determine how these factors may affect the air emissions potential.

Indicator species are species found in the waste that can be used to represent a group of species in determining emissions. If little is known about which specific species are present at the site, select an indicator that represents a family or class of species so that gross data on emissions can be obtained and then later refined. Table 8 provides information that will aid in this selection process. The ideal indicator species or class of species is:

- Present in the air emissions in a fixed ratio;

- A non-reactive or stable species;

- Present at levels above analytical detection limits;

- Unique to the site (not in background air samples);

- Representative of the "worst case" toxicity for compounds at the site; and

- Applicable for existing measurement and monitoring technologies; and

- Of known toxicity and exposure criteria.

A list of candidate indicator species can be developed from those species previously identified in analysis of the waste or by identifying broad-band type indicators that represent the type of waste identified in the scoping. Candidate species should match as closely as possible the characteristics of an ideal indicator species. The two main required characteristics are presence in the air emissions from the site and the ability to measure/monitor the species using commercially available methods and instruments. Examples of broad-band, class and indicator species are given in Table 9.

TABLE 8. FACTORS TO CONSIDER IN SELECTING AN INDICATOR SPECIES FOR STUDY

1) Homogeneity of waste and representativeness of proposed indicator species;

2) Variety of types of air contaminants (organic, inorganic, biohazard, radioactive);

3) Physical state of air contaminants (gas, liquid, solid);

4) Level of air contaminant emission;

5) APA objectives;

6) Feasibility of air monitoring for proposed indicator species;

7) Availability of standard sampling/analytical/monitoring techniques;

8) Potential interferences for the proposed indicator species; and

9) Health effects.

TABLE 9. EXAMPLES OF BROAD-BAND, CLASS, AND INDICATOR SPECIES

BROAD BAND	CLASSES OF COMPOUNDS	INDICATOR SPECIES
Volatile Organics	Aliphatics	Alkanes, Total Hydrocarbons as Pentane
	Aromatics	Benzene, Xylene, Toluene
	Halogenated Species	Trichloroethene, Trichloroethane, Vinyl Chloride
	Oxygenated Species	Ethanol, Formaldehyde
	Sulfur Containing Species	Mercaptans, Thiophenes
	Nitrogen Containing Species	Benzonitrile
Volatile Inorganics	Acid Gases	Sulfur Dioxide, Hydrogen Chloride
	Sulfur Containing	Hydrogen Sulfide
Semi-Volatile Organics	Polynuclear Aromatics (PAH)	Napathalene, Benzo-(a)Pyrene
	Polychlorinated Biphenols (PCBs)	PCBs As Aroclor 1254
Non-Volatiles	Metals	Lead, Chromium, Zinc

In addition to selecting indicator species, the site manager must select the most suitable air emissions screening technology. Screening technologies are summarized in Table 10 and described in Table 11. Air emissions measurement/assessment technologies are described in detail in Section 4. The four categories of screening technologies are described below.

- **Direct Emissions Measurement.** Concentration measurements can be made of the air directly above the waste, either the "head space" or air space of a sampler placed on the waste, or the head space of a sample bottle half-filled with waste material. The screening provides a relative measure of the emission potential of various wastes/locations. High concentrations of volatile species (C_i) in the head space can indicate high potential for air emissions from the site. Likewise, low concentrations can indicate low potential for air emissions. The advantage of these screening technologies is that they are relatively quick, easy and inexpensive to perform. They also can have the highest sensitivity (i.e., detect the contaminants even at low concentrations), since they measure concentrations at the source. The techniques are only applicable to volatile gas species. These data can be used to estimate emission factors to indicate the potential for air emissions.

- **Indirect Emissions Measurement.** This class of technologies can be used for any type of contaminant such as volatiles and/or particulate matter. It is probably the most common screening technology used, though it is usually not used to develop emission estimates. Screening measurements can be made upwind and downwind and directly above waste material using real-time instruments to estimate potential for air emissions. Air concentration measurements made at short distances (<40 meters) downwind of the waste can be used to indicate the potential for air emissions from the site. Downwind measurements should be corrected for any instrument bias and upwind interferences. Meteorological factors

TABLE 10. SCREENING TECHNOLOGIES APPLICABLE TO SITE SCREENING APA
FOR LANDFILLS AND LAGOONS*

- Direct Emissions Measurement

  - Head Space Sampler (Refer to 4.1.1)
  - Head Space Analysis of Bottled Sample (Refer to 4.1.2)

- Indirect Emissions Measurement

  - Upwind/Downwind (Refer to 4.2.1)
  - Mass Balance (Refer to 4.2.2)
  - Real-time Instrument Survey (Refer to 4.2.3)

- Air Monitoring/Modeling

  - Upwind/Downwind (Refer to 4.2.1)

- Emissions (Predictive) Modeling

  - Any model using literature values and assumed concentrations.
  - Thibodeaux-Hwang (Landfills)
  - Mackay (Lagoons)

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*See Section 4 for more detail.

TABLE 11. SUMMARY TABLE OF INFORMATION ON THE VARIOUS CLASSES OF ASSESSMENT TECHNOLOGIES AND SCREENING ASSESSMENT TECHNOLOGIES

Class of or Assessment Technology	Application	Advantages	Disadvantages
• Direct Emission Measurement	Landfills and Lagoons, especially if identification of BEEs per unit on a combined site is required.	High precision and accuracy, measures undisturbed or disturbed BEE without modeling, can distinguish between units if combined site.	Heterogeneous waste will require higher number of measurement points for representative BEE.
Head Space Sampler	All landfills; lagoons (non-aerated) with flotation device.	Representative of volatile emissions potential.	Sampling devices required.
Head Space Sample in a Bottle	All landfills and lagoons where you have a sample of the waste.	Rapid Screening technology that is easy to perform.	Can lose a significant fraction of the volatile species.
• Indirect Emission Measurement	Larger landfills and lagoons and sites with waste handling activities, combined sites.	Assess BEE from an area source, regardless of homogeniety and site activity. Can be used for inaccessible sites.	Limitations imposed by modeling, techniques are influenced by meteorological conditions, may not be able to distinguish between units of a combined site or up-wind interference.
Upwind/Downwind	Landfills and Lagoons (any area source).	Broadly applicable and can provide an estimate of emissions.	Single point ambient measurements may not represent the emission source.

(Continued)

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TABLE 11.   (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
Mass Balance	Lagoons and some landfills.	Limited resources are required.	Requires concentration data over time, inherent insensitivity due to low mass of volatile species.
Real-time Instrument Survey	Landfills and lagoons (any area source).	Rapid, real-time data that can be used to indicate emissions potential.	Highly variable, quality control program for analyzers required.
• Air Monitoring/ Modeling	Landfills and lagoons (any area sources).	Typically provides data that represents air concentrations the community is exposed to (fenceline).	Limitations imposed by modeling, techniques are influences by meteorological conditions, analytical sensitivity may be a limiting factor.
Upwind/Downwind	Landfills and Lagoons (any area source).	Broadly applicable, provides community ambient concentration data.	Low concentrations with high variability, measurement subject to meteorlogical influences.

(Continued)

TABLE 11. (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
• Emissions (Predictive) Modeling	Landfills and lagoons, especially applications with site-specific information.	Provide rapid, inexpensive assessment, particularly where only a few species are of concern. Model inputs can be assumed or taken from literature if site-specific data is not available.	Accuracy, precision dependent on qulaiyt of site-specific data or assumptions. Most models have limited validation.

can influence the air concentration of volatiles and particulate matter so field notes must include on-site observations and meteorological conditions during testing.

- Air Monitoring/Modeling. Air monitoring and modeling technologies are equivalent to the indirect emissions measurement technologies except that the samples are collected at greater distances from the waste, typically at the fenceline or property line, and the sampling locations are not as clustered. If meteorological data are collected concurrently, these data can be used to validate dispersion model estimates and estimate the potential for contaminants to reach off-site receptors. However, they may be limited by the sensitivity of the instrumental measurement used and the dispersion and dilution of the air emission. Unless estimates of off-site impact potential are needed, fenceline monitoring is not recommended for the screening study.

- Emissions (Predictive) Modeling. Emissions modeling can be used if the preliminary assessment has provided fairly detailed information that can be input into a model. The model estimates can usually be improved by using air emissions data from the site. The Thibodeaux-Hwang model is appropriate as a screening technology for landfills, and the Mackay model is appropriate for lagoons. Modeling has the obvious advantage of being an off-site activity.

Once an appropriate screening technology and associated equipment/ instruments are selected, a technical approach to applying the technology should be developed. The Data Quality Objective For Remedial Response Activities (13) can provide assistance in designing the site screening. Again, each unit of a combined site must be studied independently. This may involve the use of different screening technologies for the various site units.

Quality control should be an integral part of any screening study, and direction in developing and documenting a quality assurance project plan can be obtained from the interim Guidelines and Specifications For Preparing Quality Assurance Project Plans.(14) One very useful exercise in the design of the screening study is a "dry-run" survey, including a mock exercise involving data use. This will help in determining if the technical approach will satisfy the intended objective of obtaining an estimate of the potential for air emissions from the site.

After design is completed, the site screening approach should be circulated for review and then modified, as necessary.

Once the site screening has been completed, the screening data should be evaluated to determine if further data (in-depth measurements) are required for the site characterization. Screening data may consist of a concentration number representing volatile content (headspace sampler or analysis of headspace above the waste in a bottled sample) or a preliminary BEE (indirect emission measurement/model estimate, air monitoring/model estimate, predictive model estimate). The equations in Figure 7 show how these data should be organized. Note that the BEE should be an addition of all of the site units if the units are studied individually. Any emissions data for disturbed waste should not be included in the BEE and do not have to be summed separately since the site mitigation planning will probably use the disturbed site emission estimates on a unit basis in developing mitigations for "operable units."

Absolute criteria against which to compare these BEE data are not available. Estimated ambient levels (determined from the BEEs) can be compared to state ambient air toxic levels and to EPA cancer risk values if available.

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Undisturbed Site BEE

$$\text{Unit}_1 \quad C_1 \qquad\qquad\qquad\qquad\qquad\qquad (\text{Eq. } 1)$$

$$\text{Unit}_1 \quad UEE_{i,t,a} \qquad\qquad\qquad\qquad\qquad (\text{Eq. } 2)$$

where, Unit_1 = a waste site or a discrete component of a waste site (combined site with multiple units);

C_1 = concentration of species above the undisturbed waste in a sampler; or concentration of species in the air above or downwind of the undisturbed waste;

i = species or group of species;

t = time duration of emission measurement;

a = area of exposed waste per unit; and

$UEE_{i,t,a}$ = site emission estimate for species; for unit U (mass/time-area) for exposed waste surface (expressed per unit surface area).

For sites with multiple units, the BEE expression is:

$$BEE = \text{Unit}_1 \text{ Emissions } +$$
$$\text{Unit}_2 \text{ Emissions } + \text{Unit}_3 \text{ Emissions}... \qquad (\text{Eq. } 3)$$

or

$$BEE = U_1 EE_{i,t,a} + U_2 EE_{i,t,a} + U_3 EE_{i,t,a}... \qquad (\text{Eq. } 4)$$

where, $U_1 EE_{i,t,a}$ = undisturbed site emission estimate for Unit_1.

Figure 7. Undisturbed site BEE equations.

If high levels of air emissions from the site are possible and more detailed information is required to meet the APA objectives, then site characterization should be conducted using in-depth technologies to develop representative BEEs. If, however, little or no potential for air emissions surfaces from the data or if screening BEEs provide enough information for a site manager to evaluate air emissions, in-depth BEEs development may not be necessary in the site characterization.

3.1.5 Design and Conduct the In-Depth Site Characterization

The activities to design and conduct an in-depth study are similar to those described in Section 3.1.4 for the screening APA except that in-depth assessment technologies rather than screening technologies are-used. The steps are:

- Determine the feasibility of obtaining the detailed BEEs.

- Select appropriate detailed technologies, indicator species, and applicable equipment/instrumentation.

- Design the site characterization technical approach and test plan, including the QA/QC program.

- Circulate the detailed technical approach and test plan for review and ensure it addresses the site-specific objective(s).

- Conduct the site characterization program and document the findings.

- Determine if the BEE data are sufficient and adequate for site mitigation decisions. If adequate, document them; if inadequate, evaluate the data needs and reiterate, as necessary. Re-evaluate and document.

In-depth technologies for developing BEEs are summarized in Table 12 and presented in detail in Section 4. Information that may be useful in selecting the appropriate assessment technology is summarized in Table 13. In general, direct emissions measurement technologies offer several advantages over the other technology categories and are considered to be the preferred technologies for most sites. With the exception of the wind tunnel, the direct measurement technologies applicable to landfills and lagoons are limited to volatiles. These technologies generate BEEs as a function of the site conditions and can be used with a variety of analytical techniques. Measurements at the source (waste) will be the highest in concentration compared to the other measurement techniques. The direct emission measurement technologies are not suited to sites that are heterogeneous.

For those applications where the waste is not homogeneous, is inaccessible, or consists of multiple sources which need not be individually studied, the indirect technologies are preferable to direct technologies. Total site air emissions can be obtained and used to estimate BEEs and disturbed waste emission data. Indirect technologies are susceptible to meteorological influences and require analytical techniques with greater sensitivity than those used for direct measurements. Also, upwind interferences can create problems.

Air monitoring/modeling technologies are similar to indirect technologies, but used farther downwind. They have the same applicability and limitations, except that even lower air concentrations can be expected farther downwind. This approach is not generally recommended unless fenceline data are required for other needs. Air monitoring/modeling technologies are discussed in detail in Volume IV of this series of guidance manuals.

Emissions (predictive) modeling can be used; however, site-specific data, particularly diffusion coefficient data, are often necessary to obtain representative BEEs. These data may be difficult and expensive to gather.

TABLE 12. IN-DEPTH TECHNOLOGIES APPLICABLE TO SITE CHARACTERIZATION
FOR LANDFILLS AND LAGOONS

- Direct Emissions Measurement

  - Surface Emission Isolation Flux Chamber (Refer to 4.1.3)
  - Portable Wind Tunnels (Refer to 4.1.4)
  - Soil Vapor Probe (Refer to 4.1.5)
  - Soil Vapor Monitoring Well (Refer to 4.1.6)
  - Downhole Emission Flux Chamber (Refer to 4.1.7)
  - Vent Sampling (Refer to 4.1.8)

- Indirect Emissions Measurement

  - Concentration Profile (Refer to 4.2.4)
  - Transect (Refer to 4.2.5)

- Air Monitoring/Modeling

  - Concentration Profile (Refer to 4.2.4)
  - Transect (Refer to 4.2.5)
  - Exposure Profile (Refer to 4.3.1)

- Emissions (Predictive) Modeling

  - Any model using site-specific values
  - RTI. (Landfills)
  - Thibodeaux, Parker, and Heck (Lagoons)

TABLE 13. SUMMARY TABLE OF INFORMAITON ON THE VARIOUS CLASSES OF
ASSESSMENT TECHNOLOGIES AND IN-DEPTH ASSESSMENT TECHNOLOGIES

Class of or Assessment Technology	Application	Advantages	Disadvantages
• Direct Emission Measurement	Landfills and lagoons, especially if identification of BEEs per unit on a combined site is required.	High precision and accuracy, measures undisturbed or disturbed BEE without modeling, can distinguish between units if combined site.	Heterogeneous waste will require higher number of measurement points for representative BEE.
Emission Isolation Flux Chamber (Volatiles)	Landfills-active, inactive, soil contamination, waste piles; Lagoons (nonaerated) with flotation on device.	High precision and accuracy, measures undisturbed or disturbed BEE without modeling, can distinguish between units if combined site.	Heterogeneous waste will require higher number of measurement points for representative BEE.
Soil Probe (Volatiles)	Landfills-active, inactive, soil contamination, waste piles; Lagoons-berms around lagoons, heavy sludges.	Can obtain a subsurface distrubed BEE 1-to-10 feet below land surface without excavation.	Heterogeneous waste will require higher number of measurement points for representative BEE.
Downhole Emission Flux Chamber (Volatiles)	Landfills-active, inactive, soil contamination, waste piles; Lagoons-berms around lagoons, heavy sludges.	Can obtain a subsurface disturbed BEE 1 to 100 feet or more below land surface with a hollow stem auger drill rig.	Layered or stratified waste will require BEE for each discrete layer.

(Continued)

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TABLE 13.   (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
Vent Sampling (Volatiles)	Waste repositories with passive or active venting system, common at municipal, and co-disposal landfills.	Simple BEE measurement procedure.	Often difficult to measure low gas flow rates which causes imprecision and inaccuracy, include sampling schedule that identifies ddiurnal variations/other factors that influence gas production.
Crack Sampling (Volatiles)	Covered landfills or subsurface contamination.	Identifies gross estimate of emissions from covered landfills.	Only provides an estimate of emissions rate, must include sampling at other locations to assess emissions potential.
Wind Tunnel Measurement (Volatiles and/or Particulate Matter)	Specialized for particulate emissions from waste piles and solid surfaces, landfills, lagoons (non-aerated) with flotation on device.	BEE for particulate matter and/or volatiles as a function of wind speed.	Heterogeneous waste will require higher number of measurement points for representative BEE, additional support equipment needed to produce simulated wind speed.

(Continued)

TABLE 13. (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
• Indirect Emission Measurement	Larger landfills and lagoons and sites with waste handling activities, combined sites.	Assess BEE from an area source, regardless of homogeniety and site activity. Can be used for inaccessible sites.	Limitations imposed by modeling, techniques are influenced by meteorological conditions, may not be able to distinguish between units of a combined site or up-wind interference.
Concentration Profile (Volatiles)	Lagoons, Landfills-large solid waste site and contaminated soil.	Specialized measurement and modeling technique, high precision and accuracy for an indirect technique.	Must meet meteorological conditions of technique, not well suited for small waste areas, sophisticated support equipment required.
Transect (Volatiles/ Particulate Matter)	Lagoons, Landfills-large or small sites.	Specialized measurement and modeling technique, can be used for particulate matter from waste handling.	Must meet meteorlogical conditions of technique, technique influenced by meteorological conditions.
• Air Monitoring/ Modeling	Landfills and Lagoons, complete site emissions, monitoring at downwind distances greater than indirect emission measurements.	Typically provides data that represent air concentrations the community is exposed to (Fenceline).	Limitations imposed by modeling, techniques are influenced by meterological conditions, analytical sensitivity may be a limiting factor.

(Continued)

TABLE 13. (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
Concentration Profile (Volatiles)	Not typically used for downwind measurements.	None.	Modeling may not predict emissions from data taken downwind.
Transect (Volatiles/ Particulates Matter)	Lagoons, Landfills (any waste site or waste handling treatment for total site emissions).	Generally applicable to most situations.	Limitations imposed by modeling, techniques are influenced by meterological conditions, analytical sensitivity may be a limiting factor.
• Emissions (Predictive) Modeling (Volatiles/ Particulate Matter)	Landfills and lagoons, especially applications with site-specific information.	Provide rapid, inexpensive assessment, particularly where only a few species are of concern. Model inputs can be assumed or taken from literature if site-specific data are not available.	Accuracy, precision dependent on quality of site-specific data or assumptions. Most models have limited validation.
AP-42 Dust Emissions for Vehicles (Particulate Matter)	Road Dust	Established EPA-approved model.	Accuracy depends on quality site-specific data.

(Continued)

TABLE 13. (Continued)

Class of or Assessment Technology	Application	Advantages	Disadvantages
Covered Landfill Models (Volatiles)	Covered Landfills	Provide rapid, inexpensive assessment. Models can be selected based on available input data. Can account for bio-gas generation at co-disposal sites.	Accuracy, precision, dependent on qualiyt of input data. Do not account for losses to other pathways.
Open Dump Models (Volatiles)	Open Landfills	Account for non-steady state emission (i.e., declining emission) over time.	Accuracy, precision dependent on quality of input data. Do not account for losses to other pathways. Do not account for bio-gas generation.
Lagoon Models (Volatiles)	Lagoons, with or without generation.	Provide rapid, inexpensive assessment. Models can be selected based on available data.	Accuracy, precision dependent on quality of input data. Do not account for losses to other pathways. Assume constant source strength over time.

In addition, demonstrating the validity of the models for specific applications may be difficult. It is emphasized that site-specific data are required for site characterization; the use of literature data should be limited, if possible.

Once the in-depth site characterization has been designed and conducted, the BEEs should be evaluated and documented. Data should be organized like the screening assessment data generating the detailed undisturbed site BEE (Eq. 4). These equations are identical to the screening assessment equations but are generally better estimates of the emissions potential since more sophisticated technologies are used.

If the baseline emission estimates are considered necessary and sufficient to satisfy the project needs, then the field studies for the APA are complete and these data are documented. If the BEEs are considered inadequate or additional APA data are required, then follow on-site characterization should be designed and conducted.

3.2 USE OF THE BEEs IN THE MITIGATION PROCESS

Figure 8 illustrates how the BEEs fit in the CERCLA mitigation process. Data uses for non-NPL sites will probably be very similar to those identified in Figure 8. BEEs generated in the remedial investigation can be used in two ways. First, BEE data provide information regarding the potential air quality impact and health risk(s) posed by the site should the no-action remedial alternative be selected. Essentially, this is the air impact that can be expected from the site over time if the site is left alone. Thus, the BEEs used in this way may help justify the decision to mitigate the site. These data may also indicate the need for an immediate removal action to protect the public from possible air contaminants.
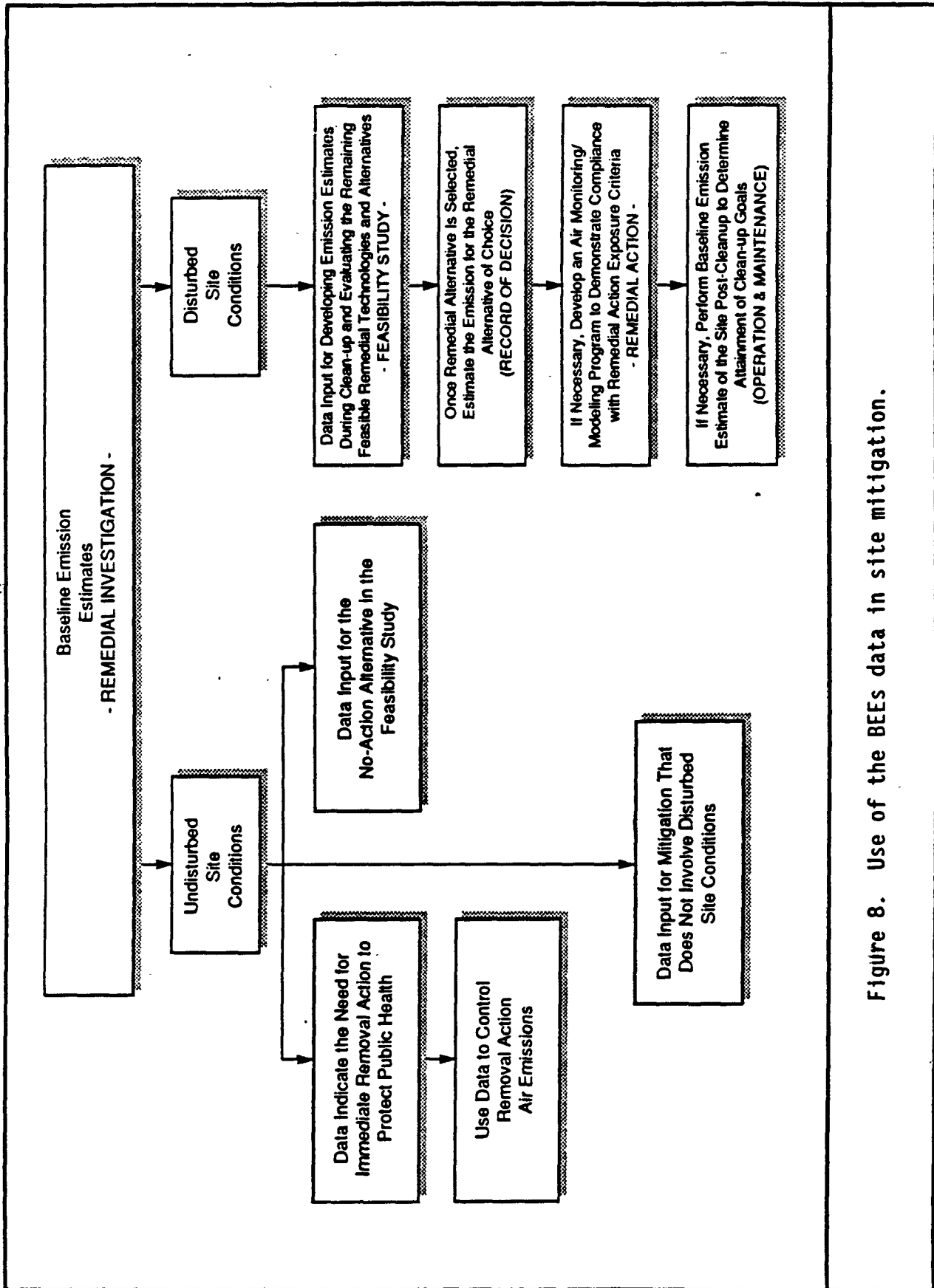
Figure 8. Use of the BEEs data in site mitigation.

Second, data for the disturbed site are necessary to estimate short-term impacts to air quality and risks to on-site workers and neighboring residents during cleanup. These data assist in the evaluation of remedial alternatives considered in the feasibility study. Remember that this protocol is designed specifically to develop BEEs (and disturbed emission estimates). These data, along with dispersion modeling, can be used to assess off-site impacts to air quality. Assessing off-site impacts is one of the topics addressed in Volume IV.

SECTION 4
AIR EMISSION MEASUREMENT TECHNIQUES

Section 4 describes recommended air emission assessment technologies for landfills and lagoons. The recommended technologies are organized into four generic categories: direct emission measurement technologies, indirect emission measurement technologies, air monitoring/modeling technologies, and emissions (predictive) modeling technologies. Each category is further divided into two classes: screening technologies, and in-depth assessment technologies. The screening technologies provide some level of air emission assessment but may not accurately represent the site's potential for air emissions. The in-depth assessment technologies are much more rigorous and generally provide a more accurate estimate of the potential for air emissions from the site. Screening technologies are typically used in the site inspection stage of the RI, whereas in-depth assessment technologies are typically used during site characterization.

Where possible, "preferred" technologies are identified and recommended for use. However, the preferred technology will not always be the best choice of assessment technology for every application. The intent of identifying preferred technologies is to assist the RPM or site manager by identifying those technologies that are preferable from a technical standpoint for the majority of sites.

4.1 DIRECT EMISSION MEASUREMENT TECHNOLOGIES

A general discussion of direct measurement technologies is followed by descriptions of the individual techniques. The direct emission measurement technologies presented in this section are:

Screening Technologies--
4.1.1   Head Space Sampler
4.1.2   Head Space Analysis of Bottled Sample

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In-Depth Technologies--

4.1.3   Emission Isolation Flux Chamber
4.1.4   Portable Wind Tunnels
4.1.5   Soil Vapor Probes
4.1.6   Soil Vapor Monitoring Well
4.1.7   Downhole Chamber
4.1.8   Vent Sampling

Direct emission measurement technologies are often the preferred technologies for investigating the air pathway. The technologies generally consist of isolating or covering a small section of the site surface or subsurface using a chamber or enclosure. The concentration of emissions produced by the isolated surface is measured within the chamber or from an outlet line. These concentration measurements, along with other technology-specific parameters, are then used to calculate an emission flux or relative concentration valve. The emission flux (rate per area) can generally be related to an emission rate for the entire source.

The types of volatile or particulate species that can be measured by the technologies are essentially unrestricted; their measurement depends on the sampling media selected and analysis technique rather than the emission measurement technology. However, few of the technologies are applicable to both volatile and particulate emission rate measurement. Selection of sampling media and analysis techniques is outside the scope of this document, but is addressed in Volume IV of this series. The direct emission measurement technologies can be used to determine the emission rate variability of a site by performing multiple measurements at selected locations across the site. In addition, these technologies allow for the evaluation of individual waste areas at the site so that the investigation can focus on those areas with the greatest potential emissions.

The cost of the direct emission measurement technologies varies considerably. However, most of the technologies are cost-effective, allowing for several measurements in a given day. Real-time instruments can be used with all the direct technologies to provide immediate data for decision-making

during the sampling program, and for the relative ranking of the emission rate at locations across the site. This procedure can be used to reduce the number of samples requiring laboratory analysis by screening for those samples with significant concentrations.

Direct emission measurement technologies, as a class of assessment technologies, are generally preferable to other classes of technologies because they have been proven to be a cost-effective approach for obtaining emission rate and concentration data and they avoid the necessity of modeling to develop BEEs. Direct emission measurement technologies and equipment are generally relatively simple and straightforward.

4.1.1 Head Space Samplers (Screening Technology)

Head space samplers are in-situ screening technologies that use a chamber to isolate part of the emission source surface.(15,16,17) The quantity or concentration of vapors and/or gas emitted from the surface that build up in the chamber over a period of time is measured, rather than measuring a rate. The head space sampler technology was a predecessor to the emission isolation flux chamber described in 4.1.3.

Head space samplers may be operated in one of two modes, referred to as static and dynamic modes. In the static mode, the sampling enclosure is placed over the emitting surface for a given period of time.(15) The enclosure may be purged initially with clean air or nitrogen. Surface emissions then enter the chamber from the exposed surface and are allowed to concentrate in the chamber before sample collection.

A time-integrated emission flux for the static mode is calculated as:(15)

$$E_i = (C_i \; V_E)/(t \; A) \hspace{2cm} \text{(Eq. 5)}$$

where E_i = emission flux for component i (ug/m^2-sec);
         C_i = concentration of component i (ug/m^3);
         V_E = volume of the enclosure (m^3);

t = length of time enclosure is in place (sec); and

A = surface area enclosed by chamber (m^2).

The build-up of gas species within the chamber improves the sensitivity of the method relative to ambient air sampling. However, the accuracy of the calculated emission rate is dependent on the duration of sampling relative to the time required to reach steady-state concentrations within the chamber. For long sampling periods, the concentration gradient of the soil/air interface is reduced and the emission flux is underestimated. Also, instantaneous changes in the flux cannot be measured.

In the dynamic mode, the sampling enclosure also is placed over the emitting surface for a given time period and the chamber may be initially purged with clean air or nitrogen. However, collected emissions are continuously withdrawn from the enclosure.(15) The chamber can be operated with a second port allowing ambient air to enter the chamber to prevent a negative pressure within the chamber. The emitted species is concentrated on sampling media or may be continuously monitored. When the sample is concentrated on the sampling media (i.e., sorbent), the emission flux is calculated as:(15)

$$E_i = (C_i \, V_s)/(A \, t) \qquad \text{(Eq. 6)}$$

where E_i = emission flux for component i (ug/m^2-sec);
C_i = concentration of component i (ug/m^3);
V_s = total volume of sample withdrawn (m^3);
t = length of sampling interval (sec); and
A = surface area enclosed by chamber (m^2).

An advantage of the dynamic mode is that the sampling duration and air sampling rate can be varied to adjust the volume of air sampled in order to achieve the required analytical sensitivities. The disadvantage of operating in the dynamic mode is that as the atmosphere within the enclosure is withdrawn, the emission flux value may be affected. This can occur by the addition of bulk flow of the soil gas into the chamber or, alternately, air

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entrainment occurring within the enclosure because of leakage at the enclosure's bottom edge, or by air moving through the soil at the enclosure's bottom edge. If a second port is used to allow atmospheric air to enter, a means of removing volatiles from the atmospheric air must be used.

The major advantage of the technology is that the emissions process does not have to be fully evaluated to employ the technology. Determining whether the emission rate is controlled by diffusion through the soil cover, volatilization at the surface/air interface, etc., to employ the technology is not necessary. Site-specific conditions, such as depth of soil cover or soil porosity, do not have to be determined to employ the technology. Although desireable, knowledge of the waste composition and exact spacial boundaries of the waste are not necessary to use the technology to assess the air pathway. However, both of these factors will help in the selection of appropriate emission concentration measurement instruments or sampling techniques and the selection of sampling locations.

Applicability--

The emission isolation flux chamber is preferred to head space samplers except where the emission flux is expected to be extremely low. Under these conditions, use of head space samplers in static mode for long intervals (possibly days) may allow emission fluxes to be measured by the head space sampling technology where other technologies may fail to produce a measurable emission flux.

Head space samplers are applicable to emission flux measurement from all forms of solid area sources including landfills, open dumps, and waste piles, and for homogenous, quiescent lagoons. The technology can be used at open and closed landfills, with or without internal gas generation. The technology can be used to assess emission rates from cracks in the surface cover and from vents that have minimal or no volumetric flow. The technology is applicable both for undisturbed and disturbed site conditions.

Limitations--

As previously mentioned, head space samplers may enhance (dynamic mode) or suppress (static mode) the emission flux. The dynamic mode also may be subject to air entrainment resulting in deceptively low emission flux values. The technology does not assess the effects of wind speed on the emission flux. For lagoons, removal of air from the chamber will induce a pressure change unless make-up air is able to enter the chamber. The chamber will require some type of support of flotation system, and this may be affected by waves or agitation.

Head space samplers are not applicable to the measurement of particulate emission fluxes. Also, the technology has not been reported as a validated technology.

4.1.2 Headspace Analysis of Bottled Samples (Screening Technology)

Headspace analysis of bottled sample is a preferred technology for field screening of wastes and soils to determine their relative emissions potential. In this method, liquid, soil, or waste from the site surface or subsurface is collected. The material is immediately placed in a sampling container, typically 1-liter or a 40 mL volatile organic analysis (VOA) vial with septa; and the container sealed. Transferring the soil or waste immediately after collection into the sample container to prevent loss of volatiles is the key to successful use of the technology. The container is allowed to stand for a given period of time, typically 5 to 30 minutes. The container lid is then cracked open and the probe of a field instrument is inserted to determine if soil-vapors are present. Syringes can be used to withdraw gas samples via parts of the VOA vial septa for more sophisticated analysis techniques. Typical field instruments used include portable flame ionization detectors, photoionization detectors, combustion meters, and colorimetric tubes.

A second type of headspace analysis involves analyzing the headspace gas or extracted solids of a soil waste core. To obtain a sample to measure the headspace, an undisturbed core is collected using an auger or by driving a

tube into the ground. The sample is then sealed in a sample container with minimal headspace.

The core sampler shown in Figure 9 consists of a brass core sleeve which is pressed into the soil to a sufficient depth to fill the sampler but not compress the sample. After excess soil is removed, the sleeve is sealed with a Teflon-lined cap. The samples are stored at room temperature. Headspace gas is removed from the core by a syringe and analyzed by GC.

Applicability--
The headspace analysis is an excellent screening technology for all types of soil or waste which have a volatile component. Some experimentation may be required to determine the optional time to allow for volatilization to occur before measurement. The technology can be used to identify surface contamination boundaries, select sampling locations for detailed technologies, and identify health and safety concerns.

Limitations--
The technology does not provide for calculation of an emission rate, but rather identifies soils and wastes which are potential source of air emissions. The technology generally only provides qualitative data on species type, however, species specific data can be obtained if suitable analytical techniques are selected. The technology is not applicable to particulate emissions.

The technology is best suited for measuring adsorbed organics, although it can also be effective with free organics in the pore space if the material is rapidly transferred to the sample container, or if tube or core samplers are used.

Preferred Technology--
Headspace analysis of bottled samples is one of the two preferred technologies for the emission screening study. This direct approach is preferred because it is simple to implement and effective at identifying volatile content, which represents volatile emissions potential. Chemical

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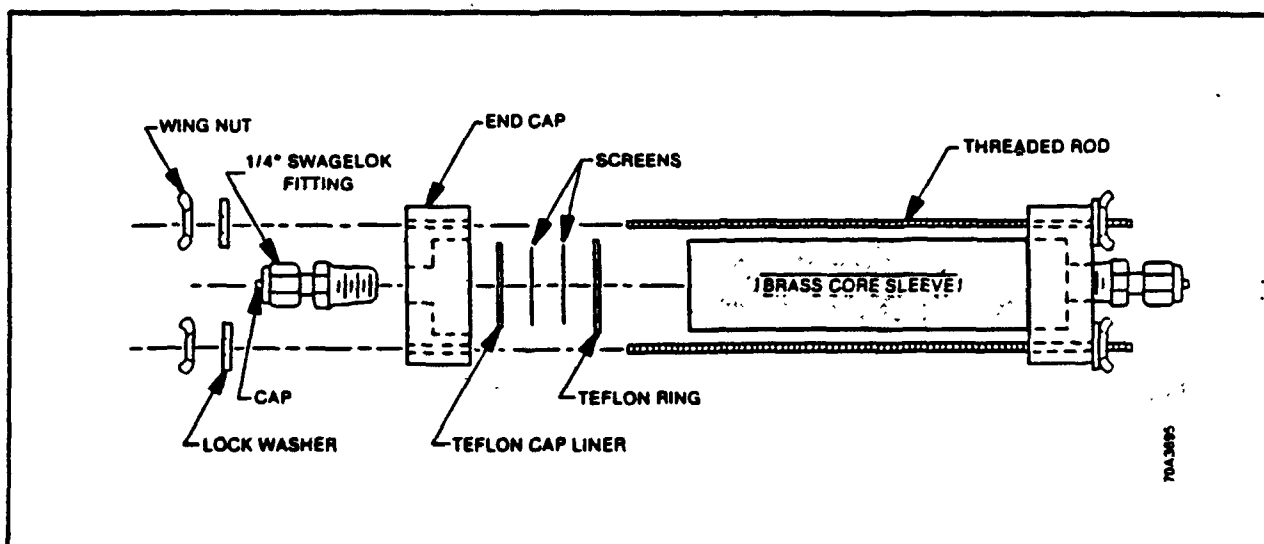
Figure 9. Schematic diagram of a soil core sample sleeve.

analysis of the waste will identify the potential for contaminated particulate matter emissions. Thus, the headspace analysis and the analysis of the waste can provide effective screening of emissions potential. The other preferred screening technology is an indirect technology, simple upwind/downwind sampling.

4.1.3 Emission Isolation Flux Chamber (In-Depth Technology)

The emission isolation flux chamber is one of the preferred in-depth technologies for the direct measurement of volatile species emission rates.(18-23) The technology uses a surface enclosure (flux chamber) to isolate a known surface area for emission flux (rate per area) measurement. The emission isolation flux chamber for solid surfaces is illustrated in Figure 10 and for liquid surfaces in Figure 11.

Emissions enter the open bottom of chamber from the exposed surface. Clean, dry sweep air is added to the chamber at a metered rate. Within the chamber, the sweep air is mixed with emitted vapors and gases by the physical design of the sweep air inlet. The sweep air creates a slight wind velocity at the emitting surface, preventing a build up of the emission concentration in the boundary layer directly above the surface. The exit port is used for measurement of the concentration of the air with the chamber or for sampling and subsequent analysis. A pressure relief port in the enclosure prevents pressure build up within the chamber that might otherwise occur when sampling liquid surfaces. A positive or negative pressure in the enclosure could affect the emission event and, thus, the assessment of the emission flux. For lagoons, a support or flotation system is necessary.

The technology directly measures essentially an instantaneous emission flow (flux) from that surface. The emission flux is calculated from the surface area isolated, the sweep air flow rate, and the emission concentration. Statistical methods are used to determine the number of measurement locations required to characterize the emission from an area source. These methods are based on the surface area of the source and the variability (precision) of the measured emission rate at randomly selected
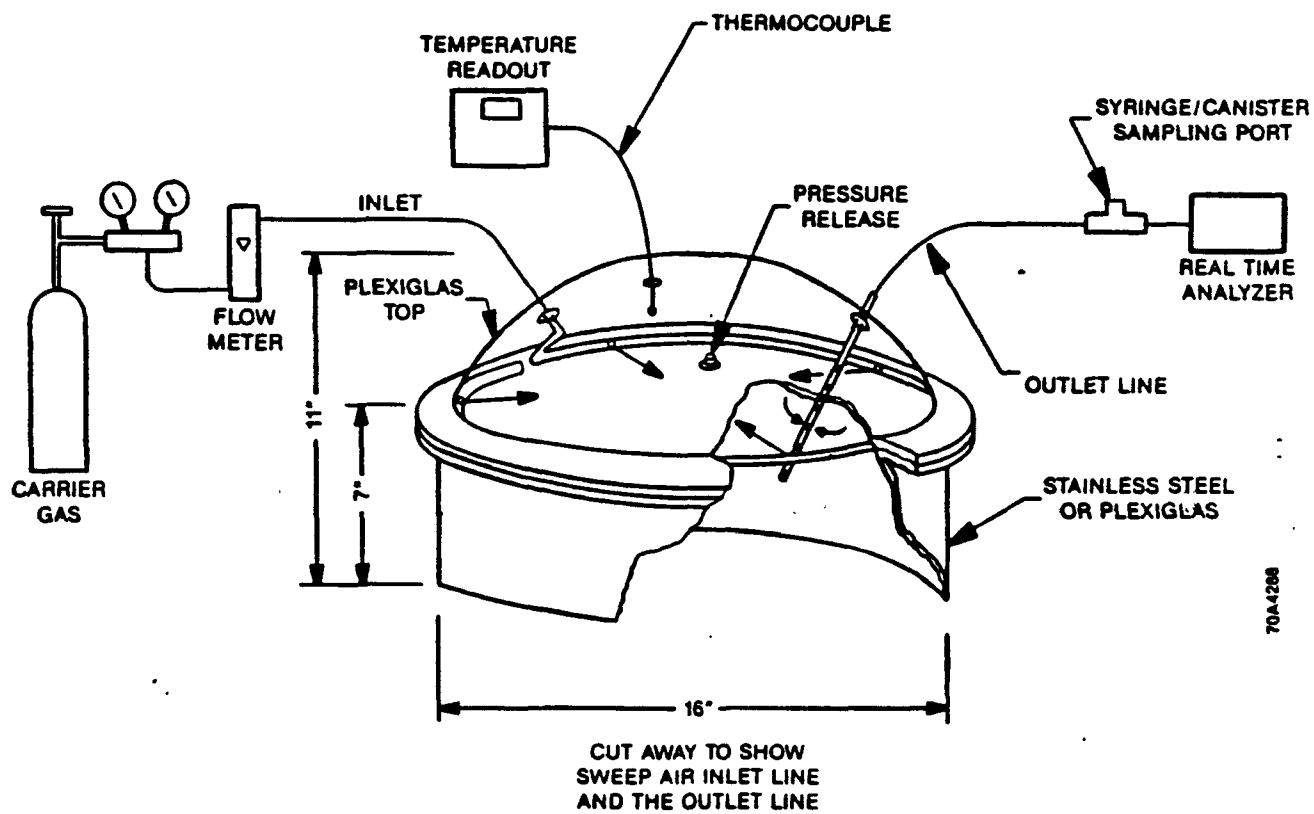
Figure 10. A cutaway diagram of the emission isolation flux chamber and support equipment.
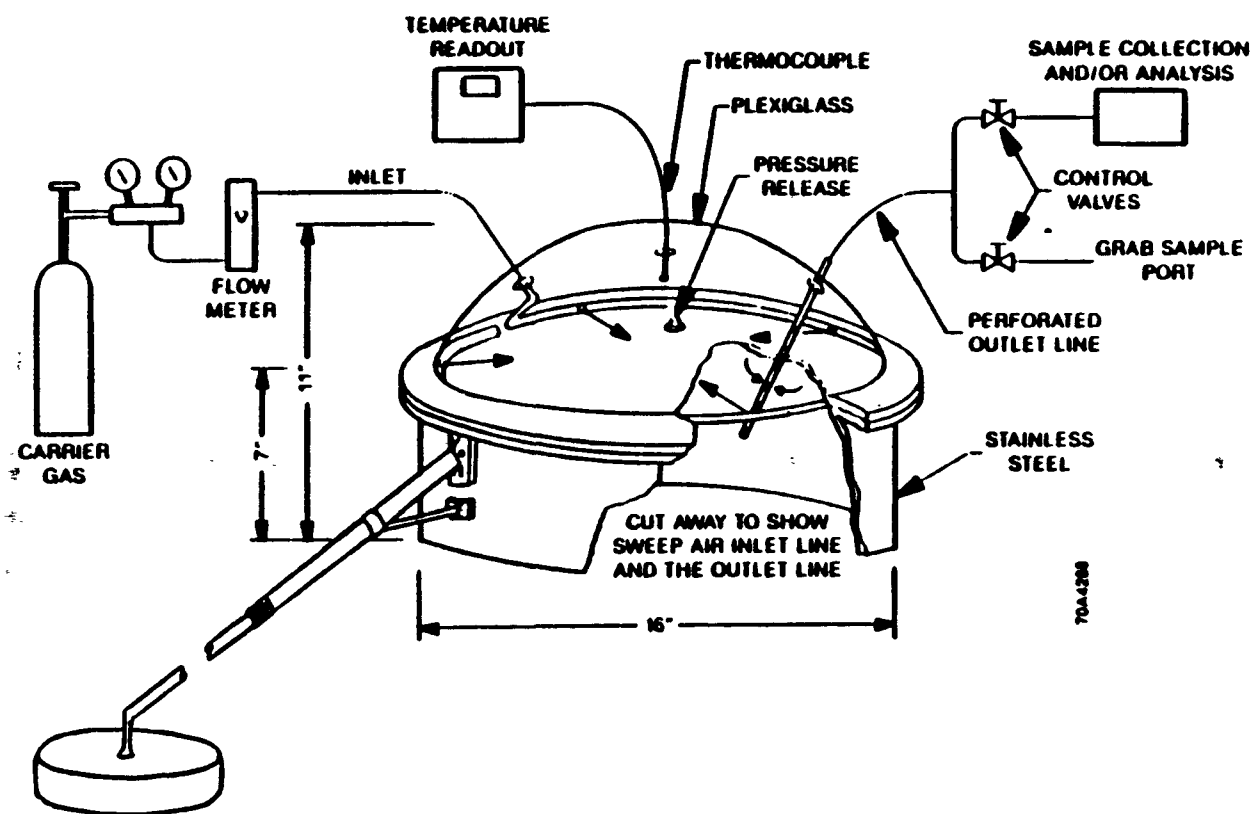
Figure 11. A cutaway diagram of the surface emission isolation flux chamber and support equipment for liquid surfaces.

locations across the site. Use of the emission isolation flux chamber is
described in the draft "Measurement of Gaseous Emission Rates from Land
Surfaces Using an Emission Isolation Flux Chamber User's Guide (23)." The
emission isolation flux chamber was validated for EPA (using standard methods)
for measuring volatile emissions from landfills.(22,23)

The emission flux is calculated as (23):

$$E_i = (C_i \, Q)/A \qquad\qquad (Eq.\ 7)$$

where E_i = emission flux of component i $(ug/m^2\text{-min})$;

   C_i = concentration of component i at chamber outlet (ug/m^3);

   Q = sweep air flow rate into chamber (m^3/min); and

   A = surface area enclosed by chamber (m^2).

Applicability--

 The emission isolation flux chamber is applicable to emission flux
measurement from all types of area sources including lagoons, landfills, open
dumps, and waste piles. The technology can be used at open and closed
landfills, with or without internal gas generation. The technology can be
used to assess emission rates from cracks in the surface cover and from vents
that have minimal or no volumetric flow.

 The technology is applicable both for undisturbed and disturbed site
conditions, and for the testing of emissions control technologies. The
technology can be used to satisfy data needs for all phases of the RI/FS
process, as well as post-remediation monitoring and, therefore, can provide
directly comparable data throughout the process.

Limitations--

 The emission fluxes of volatile species may be enhanced or suppressed
since the flux chamber alters the environmental conditions (e.g., wind speed)
at the sampling locations. The technology does not assess the effects of wind
speed on the emission rate.

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The technique is not particularly well suited to large emission sources with a high degree of heterogeniety. Comparison of sample data and variability estimates can determine the number of sampling locations needed to determine representative area emissions. Also, the technique is not applicable to the measurement of particulate emission fluxes.

Preferred Technology--

The emission isolation flux chamber is a preferred technology for developing in-depth BEEs. As discussed, the advantages generally out-weigh the limitations of the technique. The technique is well documented in the user's guide and well characterized.

4.1.4 Portable Wind Tunnels (In-Depth Technology)

Wind tunnels are in-depth technologies used to directly measure the emission rate of erodible material. They also can be used to measure the emission flux of volatile compounds. In either application, measurements can be made under varying wind conditions to examine the effect of wind speed on emissions. The required equipment consists of portable, open-bottomed enclosures used to isolate a known surface area, a blower used to simulate wind conditions, and sampling devices.

The Cowherd wind tunnel, shown in Figure 12 is a portable wind tunnel developed for "in situ measurement of emissions from representative test surfaces under predetermined wind conditions"(24). The tunnel was developed to measure particulate matter emissions from open waste piles. "The open-floored test section of the portable wind tunnel is placed directly over the surface to be tested. Air is drawn through the tunnel at controlled velocities. The exit air stream from the test section passes through a circular duct fitted with a sampling probe at the down-stream end. Air is drawn through the probe isokinetically by a high-volume sampling train"(24). The sampling train consists of a trapper probe, cyclone precollector, parallel-slot cascade impactor, backup filter, and high volume motor. Air flow is provided by a blower located downstream of the sampling train.
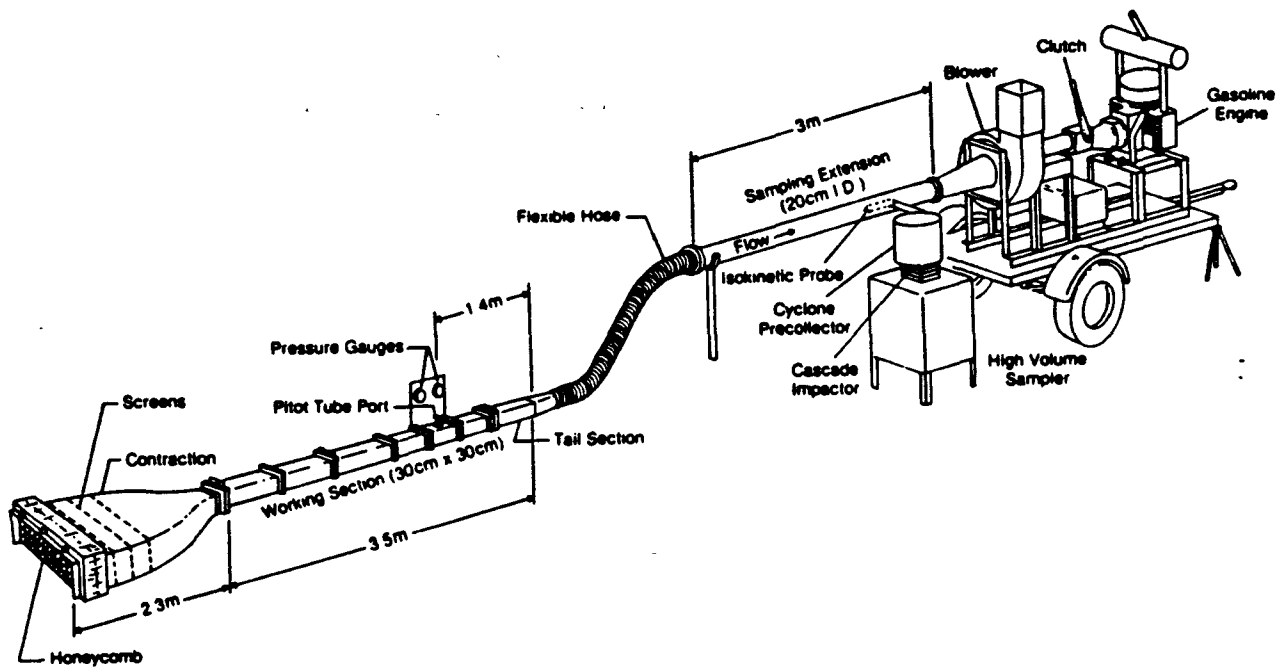
Figure 12.   Illustration of MRI wind tunnel.

The authors state that, "although a portable wind tunnel does not generate the larger scales of turbulent motion found in the atmosphere, the turbulent boundary layer formed within the tunnel simulates the smaller scales of atmospheric turbulence. It is the smaller scale turbulence which penetrates the wind flow in direct contact with the pile surface and contributes to the particle entrainment mechanisms"(24).

The emission flux is calculated from the isolated surface area, emission concentration, simulated wind speed, and time period during which particulates are collected. Because the emission concentration is collected over time, the technology measures the overall (time integrated) emission rate rather than the emission flux. Varying the simulated wind speed between measurements allows for development of a weighted average emission rate. This is preferred to using an average wind speed because the total erosion may be greatly influenced by infrequent periods of high wind speed.

The loss of erodible material is calculated as (24):

$$E_i = (C_i \; Q \; t)/A \hspace{3cm} \text{(Eq. 8)}$$

where

E_i = emission rate of component i (g/m^2);

C_i = average particulate concentration of component i in tunnel exit stream (g/m^3);

Q = tunnel flow rate (m^3/sec);

t = duration of sampling (sec); and

A = exposed test area (m^2).

Elimination of the time factor in the calculation will provide an emission flux on a unit area per time basis (g/m^2-sec). The average particulate concentration (C_i) may be reduced to account for background dust levels by sampling under light wind conditions and subtracting the resulting average concentration from C_i values generated during simulations of higher wind conditions.

The Astle wind tunnel, shown in Figure 13, is a form of surface enclosure developed for "measurement of odor source strength"(25); but it also may be applicable to volatile emissions measurement. This portable wind tunnel consists of an open-bottom enclosure that is placed over the emitting surface. Ambient air is blown through the chamber at typical wind speed rates (e.g., 1 to 15 mph) and collected near the enclosure outlet. Test results for volatile emission rate measurement were not identified in the literature.

The emission flux is calculated from the simulated wind speed, emission concentration, and surface area isolated. Varying the wind speed between measurements allows for development of a weighted average emission rate. The measurement is essentially instantaneous.

The emission flux calculation is (25):

$$E_i = (C_i \, Q)/A \qquad \text{(Eq. 9)}$$

where E_i = emission flux of component i (ug/m^2-sec);

C_i = concentration of component i (ug/m^3);

Q = air flow rate through tunnel (m^3/sec); and

A = surface area enclosed by the tunnel (m^2).

.Applicability--

Wind tunnels are applicable to emission measurements from all forms of solid area sources, including quiescent lagoons, landfills, open dumps, and waste piles. The technology can be used at open and closed landfills, with or -without internal gas generation. The technology is applicable both for undisturbed and disturbed site conditions.

Limitations--

The portable wind tunnels do not account for macro-atmospheric effects on the emission flux. Repeated measurement at a given location may deplete the reservoir of erodible material.
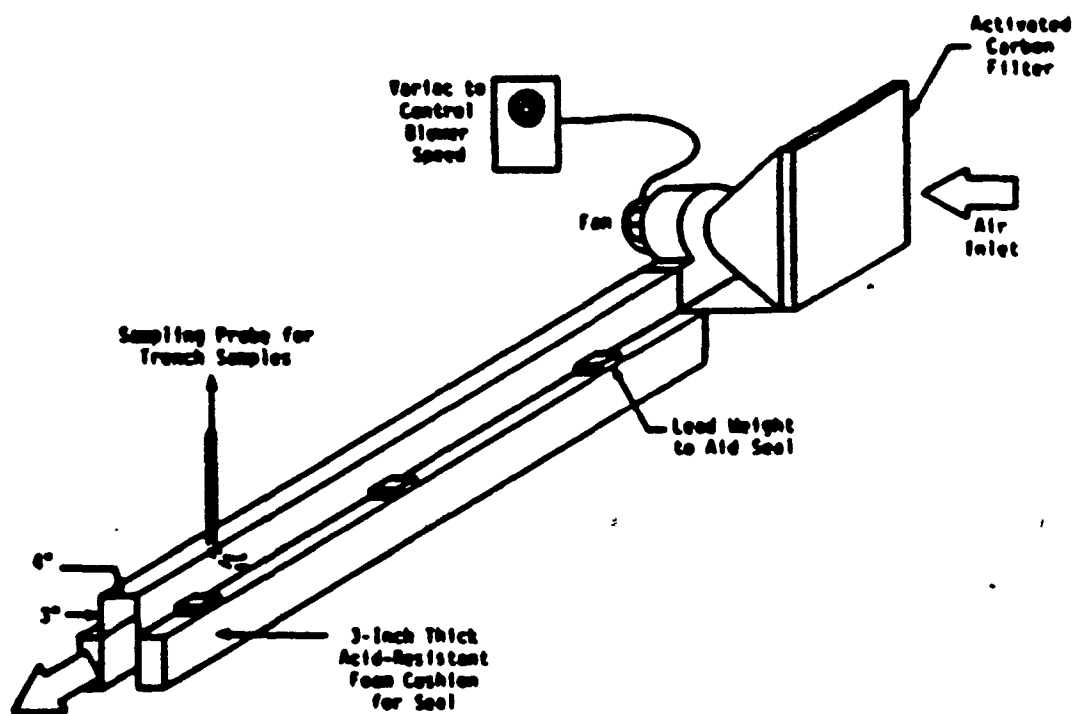
Figure 13. Schematic of portable wind tunnel.

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4.1.5 Soil Vapor (Ground) Probes (In-Depth Technology)

Soil vapor or ground probes are a preferred in-depth technology for mapping the horizontal extent of soil gas plumes in near-surface soils (26,27,28). The technology directly measures the emission rate potential from a small area of exposed subsurface soils. One variation of a ground probe is shown in Figure 14. Probes with small chambers or openings at the probe end have also been used (see Figure 15). Reference 27 includes descriptions of a wide variety of ground probe designs.

The probe assembly is driven into the ground to the desired sampling depth. Emissions enter the probe from the exposed subsurface soil, depending on the design via existing openings or by raising the pipe away from the drive tip. Generally, either a small aliquot of soil gas is collected to avoid disturbing the soil gas equilibrium or a known amount of soil-gas is pumped from the probe. The concentration measured is used as a relative indicator of contamination and potential emissions. Clean, dry sweep air can be added to the probe at a metered rate if a relative emission "flux" is desired. No true flux can be measured since the exact surface area of exposed waste is not known.

The major advantage of the technology is that it allows for rapid mapping of the horizontal extent of soil gas plumes in near-surface soils. Generally, mapping is performed by measuring the soil gas concentration without use of sweep air. The mapping can be used to determine the approximate subsurface boundaries of buried waste or immiscible liquids floating on the water table. Ground probes are very useful for investigating the migration of soil vapors as part of the air pathway analyses.

It is not necessary, although desirable, to know the waste composition to use the technology. Knowing the waste composition will help in the selection of appropriate instrumentation or sampling apparatus.
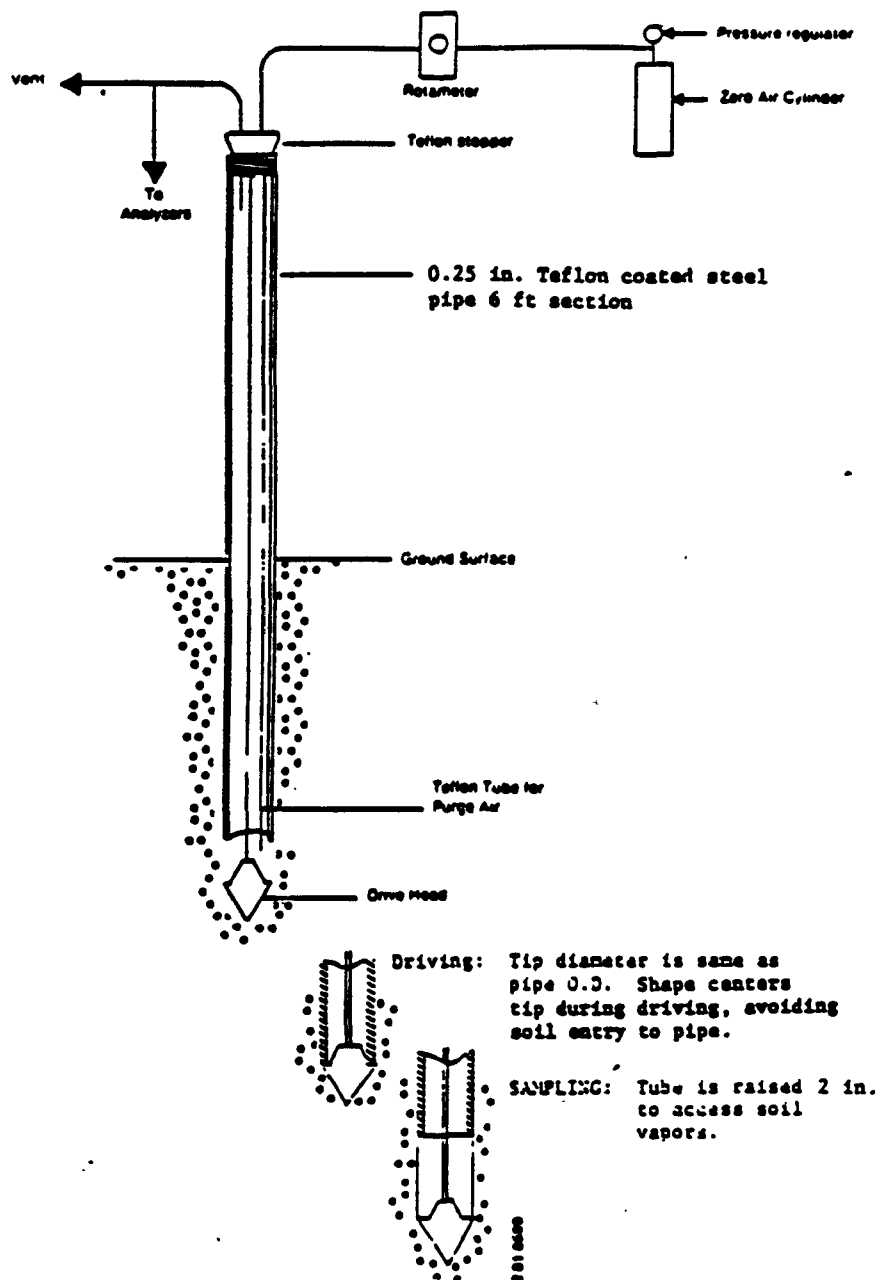
Figure 14. Schematic diagram of a simple ground probe.

syringe

3 way valve

Tenax GC trap

fitting

pounding plate

pipe

tubing

coupling

air holes

point
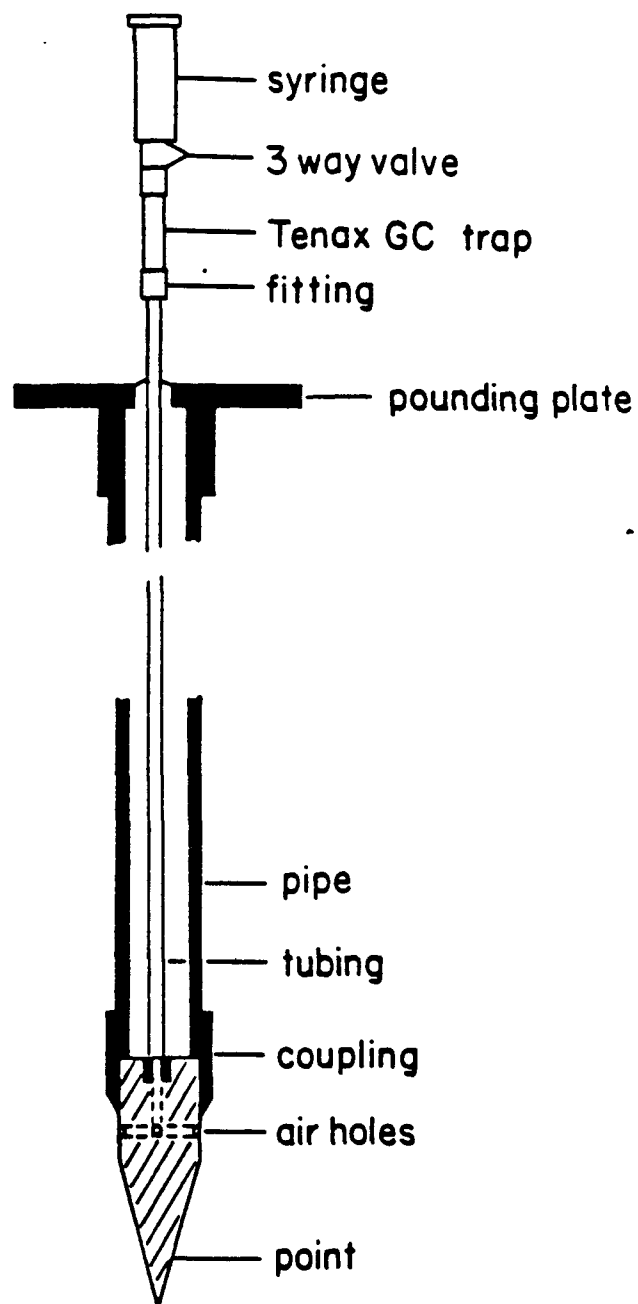
Figure 15. Ground probe design with minimal internal volume.

Applicability--

The technology can be used to map soil gas plumes to indicate approximate waste boundaries or soil gas migration routes. Ground probes are also applicable to the measurement of potential volatile emissions from disturbed subsurface soil and waste. The technology measures the emissions that would occur if the subsurface soil or waste were disturbed by excavation. The technology also can be used to measure the soil gas concentration by operating the probe without sweep air. Soil gas concentration measurements can be used as an input to predictive models, as discussed in Section 4.4.

The technology is applicable for estimating emissions from solid waste sites, including open and closed landfills, with or without internal gas generation, open dumps, and waste piles. The technology also can be used to estimate emissions below the edges of tanks, buildings, ponds, etc., by driving the probe into the soil at an angle. In addition, ground probes can be hand- or machine-driven. Hand-driven probes allow measurements to be performed in areas where surface access by machines is not available.

Limitations--

Ground probes do not measure the undisturbed emission rate or flux from a waste site. Rather, the technology measures the potential emissions that would occur during site disturbance.

Use of ground probes is generally limited to near-surface soils, typically less than 12 feet deep. However, the operational depth will depend on site and equipment characteristics which limit the ability to insert the probe. Ground probes do not measure particulate emission rates.

4.1.6 Soil Vapor Monitoring Wells (In-Depth Technology)

Soil vapor monitoring wells (29) are used to measure the emission flux from subsurface soil and waste and to monitor soil vapor concentrations and the effects of soil vapor remedial actions. The in-depth technology uses a monitoring well consisting of a screened chamber installed during drilling activities. As such, the soil vapor monitoring well is a permanent or

semi-permanent structure. Figure 16 illustrates a typical soil vapor monitoring well.

Soil vapor monitoring wells are installed through the annulus of a hollow-stem auger. The well consists of an enclosed, screened chamber with sampling lines leading to the surface. The chamber is enclosed in a sand pack. The well casing is used to provide support during well construction and protection for the sampling lines, but soil vapors and gases do not contact the well casing. Soil vapors and gases enter the soil vapor monitoring well through the chamber screen. Within the chamber, the vapor and gases are mixed with clean, dry sweep air. The resulting mixture is withdrawn through the exit port to measure the emission concentration and/or for sampling and subsequent analysis. The sweep air flow rate is selected to approximate the instrumentation or sampling apparatus flow rate.

Because the measured emission concentration is directly related to an emissions event from an isolated surface over an essentially instantaneous time period, the technology can be used to estimate the emission flux from the isolated soil surface. The estimated emission flux is calculated from the assumed surface area isolated, the sweep air flow rate, and the emission concentration.

The emission flux is calculated as (26):

$$E_i = \frac{C_i Q}{A}$$ (Eq. 10)

where E_i = emission flux for component i (ug/m²-min);
         C_i = concentration of component i (ug/m³);
         Q = sweep air flow rate (m³/min); and
         A = exposed surface area (m²) = πdh
              d = screen diameter (m); and
              h = height of sand pack (m).

Typically, soil vapor monitoring wells are used to measure the soil vapor concentration, rather than the emission flux. The soil vapor concentration is measured by operating the well without sweep air.

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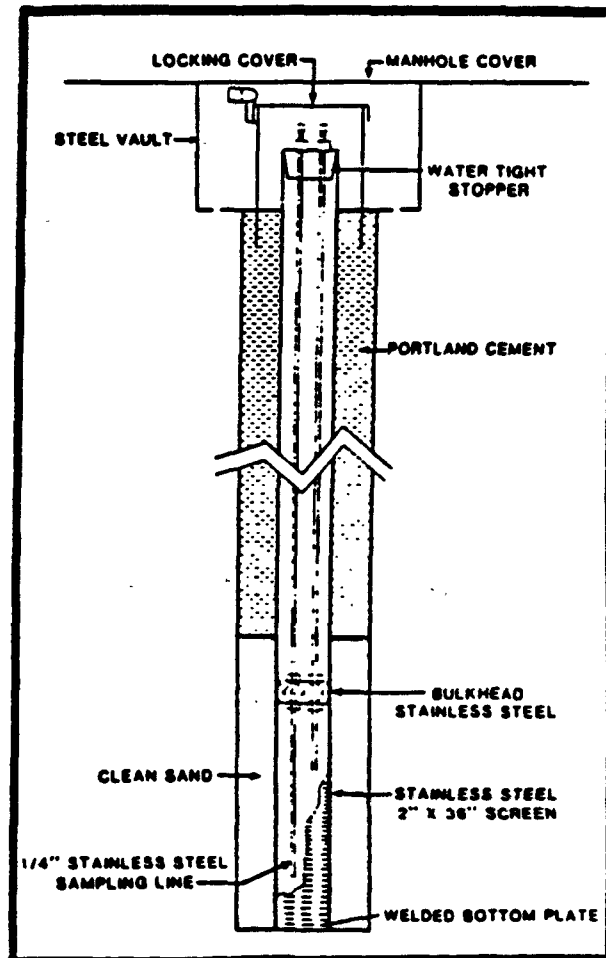
Figure 16. Vapor monitoring well constructions. (Not to scale)

The technology is not dependent on knowledge of the emissions process or the waste composition, although knowledge of the waste composition will help in selecting appropriate instrumentation and/or sampling apparatus.

Applicability--

Soil vapor monitoring wells are applicable to the estimation of the potential emission flux from subsurface soil and waste. The technology does not measure the undisturbed emission flux, but rather estimates the emission flux that would occur during site disturbance. Therefore, the technology is suitable for determining emissions potential for remedial alternative evaluation. Soil vapor monitoring wells also are applicable to the monitoring of soil vapor concentrations and vapor migration, and are the preferred method for monitoring the effects of soil vapor extraction systems. -

The technology is applicable to the estimation of emission fluxes and concentrations from open and closed landfills, with and without internal gas generation, and open dumps. The technology also is applicable to measurement of emission concentration from immiscible liquids floating on the water table.

Limitations--

Soil vapor monitoring wells do not measure the undisturbed emission flux, but rather the flux that would occur during site disturbance. The technology is not applicable to the measurement of particulate emission fluxes. Determining the actual exposed surface area is an assumed or estimated value.

4.1.7 Downhole Emissions Flux Chamber (In-Depth Technology)

The downhole emissions flux chamber is one of the preferred in-depth technologies for direct measurement of potential volatile emissions from subsurface soils (30). The technology uses a flux chamber to measure emission fluxes from subsurface soils exposed by drilling operations. The chamber isolates a known area of soil at a desired depth within the annulus of a hollow-stem auger. Figure 17 depicts the downhole emissions flux chamber.
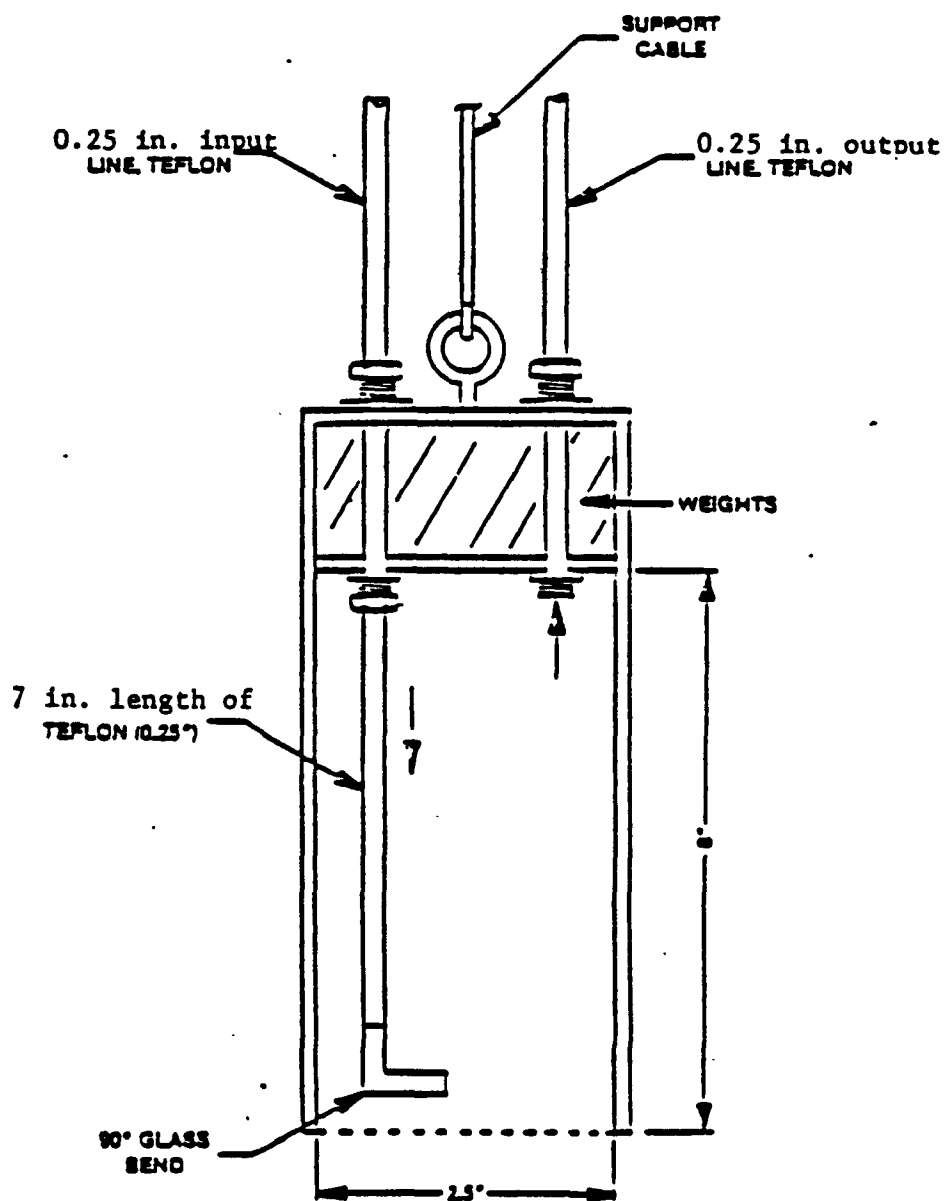
Figure 17. Schematic diagram of the downhole emissions flux chamber.

Emissions enter the chamber from the exposed surface. Clean, dry sweep air is added to the chamber at a metered rate. Within the chamber, the sweep air is mixed with emitted vapors and gases by the physical design of the air inlet. The mixture of sweep air and emitted vapors and gases is withdrawn through the exit port for measurement of the emission concentration or for sampling and subsequent analysis. The sweep air flow rate must match the flow rate of the analytical instrumentation or sampling apparatus that is used to withdraw sample gas.

Because the measured emission concentration is directly related to an emissions event from an isolated surface over an essentially instantaneous time period, the technology directly measures the emission flow (flux) from the surface. The emission flux is estimated from the assumed surface area exposed, the sweep air flow rate, and the emission concentration.

The emission flux is calculated as (30):

$$E_i = \frac{C_i Q}{A}$$ (Eq. 11)

where E_i = emission flux of component i (ug/m^2-min);

C_i = concentration of component i (ug/m^3);

Q = sweep air flow rate (m^3/min); and

A = exposed surface area (m^2).

The major advantage of the technology is that it allows the investigation of subsurface areas without excavation.

Although desireable, knowledge of the waste composition is not necessary to use the technology to assess the air pathway. However, knowledge of the waste composition will help in the selection of appropriate emission concentration measurement instruments.

Applicability--

The downhole flux chamber is applicable to measurement of the potential emissions from subsurface soil and waste. The technology estimates the emission flux that would occur if the subsurface soil or waste were exposed by excavation. Therefore, the technology is most suitable for determining emissions potential for remedial alternatives evaluation and/or site disturbances. The technology also can be used to measure the soil gas concentration by operating the chamber without sweep air. However, for shallow depths, ground probes are preferred for gas concentration measurements (see Section 4.1.5).

The technology is applicable for estimating emission fluxes from all materials that can be investigated using hollow-stem auguring techniques. The technology can be used at open and closed landfills, with or without internal gas generation, and at open dumps.

Limitations--

The downhole emissions flux chamber does not measure the baseline emission flux from a waste site. Rather, the technology measures the potential emission rate that would occur during site disturbance.

The emission flux of volatile species may be enhanced or suppressed if the sweep air flow rate does not closely match the flow rate of the sample gas extraction system. The downhole flux chamber cannot be used to measure particulate emission rates.

Preferred Technology--

The downhole emissions flux chamber is a preferred technology for developing emissions estimates for subsurface disturbed waste. Most investigations involve subsurface sampling using a hollow-stem auger and drill rig and downhole flux chamber work can be incorporated in the investigation.

4.1.8 Vent Sampling (In-Depth Technology)

Vent sampling for emissions measurement have been well documented elsewhere (32), and will not be discussed in detail here. Vent sampling is performed when the waste site contains vents with measurable flow rates (i.e., active venting, not passive venting), such as vent systems at some landfills. The in-depth technology requires measuring the emission concentration and the volumetric flow rate, typically as the exhaust velocity and cross-sectional area of the vent. Volumetric flow rates for vents (or ducts) can be obtained using the procedures given in 40 Code of Federal Regulations (CFR) Part 60. Those procedures indicate how to determine the exhaust velocity and appropriate sampling location. The emission rate for a vent is calculated as (31):

$$E_i = C_i \, U \, A \qquad\qquad \text{(Eq. 12)}$$

where

E_i = emission rate of component i (ug/sec);

C_i = concentration of component i (ug/m^3);

U = gas velocity through vent (m/sec); and

A = cross-sectional area of vent (m^2).

Applicability--

Vent sampling is applicable to any waste site that contains active or passive venting systems. However, active venting systems are not typical of uncontrolled hazardous waste sites. Vent sampling can be applied to landfill vents, tanks, building vents, machinery, and equipment. Where present, vents may be a major source of air emissions from the site.

Limitations--

Vent sampling using standard stack sampling technology is not applicable when the vent has minimal or no flow. For these situations, the emissions isolation flux chamber technology is preferred, provided that the chamber's cross-sectional area is larger than the vent's. When the vent is too large for use of the flux chamber, emission rate estimates may be based on head space concentration measurements at the vent outlet and diffusion in air modeling.

4.2 INDIRECT EMISSION MEASUREMENT TECHNOLOGIES

A general discussion of indirect measurement techniques is followed by a description of specific techniques. The indirect emission measurement technologies presented in this section are:

Screening Technologies--

4.2.1 Upwind/Downwind

4.2.2 Mass Balance

4.2.3 Real-Time Instrument Survey

In-Depth Technologies--

4.2.4 Concentration-Profile (C-P)

4.2.5 Transect

4.2.6 Boundary Layer Emission Monitoring

Indirect emission measurement technologies generally consist of measuring the atmospheric concentration of the emitted species and then applying these data to an equation (air model) to determine the emission rate. Many of the equations were developed to determine downwind concentrations resulting from stack emissions. For area emission sources, the source is treated as a virtual point source or line source.

The in-depth technologies are very similar as all involve clusters of ambient air samplers. The C-P technique involves a vertical array of samplers directly over the source. The transect technique involves vertical and horizontal arrays of samplers within the downwind plume. The boundary layer technique is a simplified version of the transect technique and involves several downwind samplers each at a different height.

A disadvantage of indirect emission measurement technologies is that the results are highly dependent on meteorological conditions. The indirect technologies require meteorological monitoring to properly align the sampling systems and to analyze the data following sample analysis. Changing meteorological conditions significantly affect the efficiency of collecting

useful data. Unacceptable meteorological conditions may invalidate much of the data collected, requiring an additional sampling effort. The technologies also may produce false negative results if the emitted species are present in low concentrations which are below the sampling and analysis detection limits, or if upwind sources cannot be fully accounted for. The technologies also may not be feasible at some sites where the source area is excessively large, or where insufficient space exists downwind of the source to set up the sampling array without disturbance of the air flow pattern by obstructions (e.g., buildings, tanks).

The types of volatile and particulate species that can be measured by the technologies are essentially unrestricted, they depend on the sampling media selected and analysis technique rather than the emission measurement technology. Sampling media and analysis techniques are not discussed here.

Indirect emission measurement technologies generally do not provide significant data on the emission rate variability for different locations across a site. This is because the emission concentration is measured downwind of the site after some atmospheric mixing. The technologies generally do not allow for the evaluation of individual contaminated areas at the site unless the areas are separated from one another and are not located upwind of one another.

The costs of the indirect emission measurement technologies vary considerably. The screening technologies are relatively simple and straight-forward to implement, and require minimal labor and analytical costs. The in-depth technologies are complex and require considerable equipment, labor, and analysis costs. All of the technologies are subject to data loss or sampling delay due to inappropriate meteorological conditions.

4.2.1 Upwind/Downwind (Screening Technology)

The upwind/downwind technology is an indirect screening technology (33). As the name implies, in this approach one or more monitors are located upwind of the area source and a second monitor or set of monitors are located

downwind. The monitoring stations include detectors or samplers for the species of interest as well as devices for measuring wind speed and direction. The upwind monitor serves as a blank or background sampling location. Concentration is measured primarily along the downwind axis only. The average surface emission flux for a particular trajectory is equal to the increase in column concentration (downwind minus upwind) divided by the transit time across the source. Transit time is a function of the distance between the source and downwind location, and the average wind velocity.

$$E.R.i = (C_D - C_U) \, \pi \sigma_y \, \sigma_z \, \bar{U} \qquad \text{(Eq. 13)}$$

where $E.R.i$ = emission flux of species (ug/m^2-sec);

C_D = downwind concentration of species i (ug/m^3);

C_U = upwind concentration of species i (ug/m^3);

π = 3.141 ...

σ_y = lateral extent of Gaussian plume;

σ_z = vertical extent of Gaussian plume; and

$\bar{U}$ = mean wind speed (m/sec).

Applicability--

The upwind/downwind technology is applicable to emission flux measurement from all forms of area sources, including lagoons, landfills, open dump, and waste piles. The technology can be used at open and closed landfills, with or without internal gas generation. The technology is applicable both for undisturbed and disturbed site conditions, and for testing emission control technologies. The technology can be used for both volatile and particulate emission flux assessment.

Limitations--

Upwind/downwind requires that meteorological conditions during sampling, particularly wind speed and variability, match the predetermined conditions used to select the sampling locations. The sampling locations must be on the approximate plume centerline.

The technology also assumes that the site is fairly homogeneous and that the plume is well mixed at the downwind sampling location. Therefore, the technology may not be applicable to heterogeneous sites. The technology also may not adequately collect emissions from point sources within an area source, such as cracks in landfill covers or vents, unless the plume is well mixed at the downwind sampling location. The technology is not applicable during quiescent or unstable wind conditions, and may produce false negative results during these conditions.

Preferred Technology--

The upwind/downwind screening technology is a preferred indirect assessment technology. The technology is similar to a simple real-time inspection survey, however, it is superior in that it specifies data collection consistent with a model that can be used to estimate emissions from a variety of area sources.

4.2.2 Mass Balance (Screening Technology)

Mass balance technology can be used to indirectly determine emission rates by accounting for material in and out of a system and assuming the difference is lost as air emissions (31). The use of mass balance for baseline emission estimates at uncontrolled landfill or lagoon sites was not identified, but it might be applicable to waste lagoons that have minimal leaching losses. To apply the technology at an uncontrolled site, the concentration of the species contained in the lagoon (or landfill) would be measured infrequently over time, and the emission rate would be estimated as the loss of species over time.

Applicability--

The technology would be best suited for homogenous sources containing highly volatile wastes. Application of the technology to "fresh waste", when emission rates are typically highest, is more feasible than application to "weathered" waste. The technology does not appear applicable to particulate matter emission assessment.

Limitations--

The technology is generally unsuited to uncontrolled waste sites because of the source types and since losses of material are difficult to identify due to the precision of the sampling and analytical methods. In addition, the mass balance technology does not distinguish between material lost to other pathways.

4.2.3 Real-Time Instrument Survey (Screening Technology)

Real-time instrument surveys are a preferred screening technology for determining the volatile emissions potential for hazardous waste sites. The survey consists of inspecting the site with real-time instruments to determine the average species concentration in the air layer directly above the site, and to identify "hot spots" with above average emission concentration. Real-time instrument surveys can also include taking headspace concentration measurements in cracks and vents. They can be used for both volatile species and particulate matter, but it is typically used for volatile species emission.

The site is inspected by placing the inlet of the real-time instrument at a specified height above the surface, typically 2-3 inches to several feet above the site surface. The site is walked on a 25-foot grid as shown in Figure 18, although the grid may be adjusted to accommodate site size. Upwind measurements are made before and after inspecting the site by measuring the ambient air at 5-feet above the site at an upwind location. Sampling should be performed during quiescent wind conditions (i.e., average wind speed less than 5 miles per hour).
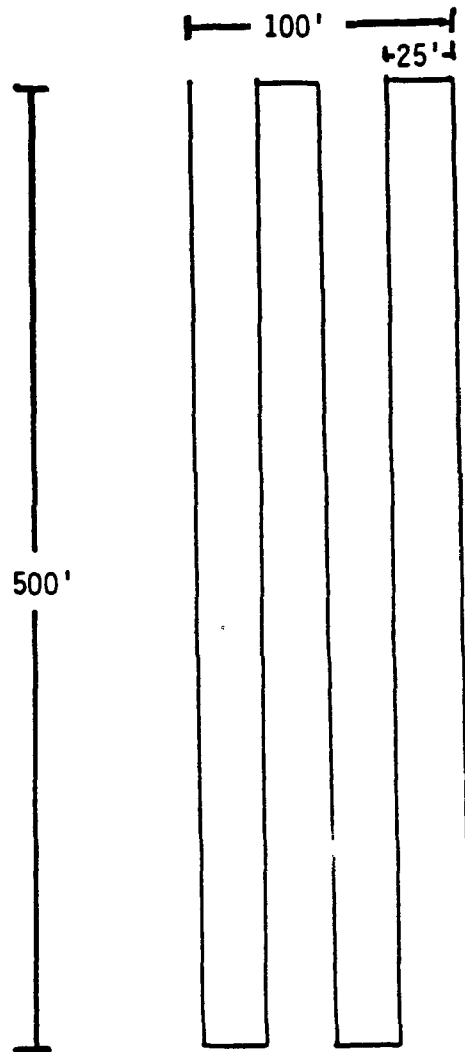
Figure 18. Real-time instrument survey.

Applicability--

The real-time instrument survey is applicable to all types of hazardous waste sites, assuming sampling personnel can reach all areas of the site.

Limitations--

The technology does not provide for calculation of an emission rate, but rather determines the site's potential for air emissions including particulate matter emissions can be measured using aerosol/dust counting devices.

4.2.4 Concentration-Profile (In-Depth Technology)

The concentration-profile (C-P) technology measures the concentration of the emitted species at logarithmically spaced heights at a downwind location on the anticipated plume centerline (21,34). This technology has been tested under a variety of waste site conditions and has been shown to produce valid results. Figure 19 illustrates the C-P sampling approach.

The C-P technology was developed by L.J. Thibodeaux and co-workers at the University of Arkansas under an EPA contract. The technology is based on measurements of wind velocity, volatile species concentration, and temperature profiles in the boundary layer above the waste body. These measurements are used to estimate the vertical flux of the volatile species as (31):

$$E_i = \left[\frac{D_i}{D_{H_2O}}\right]^n \, S_v S_i K^2 / \phi_m^2 S_c \qquad \text{(Eq. 14)}$$

where E_i = emission rate (flux) of organic species i (g/cm²-sec);

D_i = molecular diffusivity of organic species i in air (cm²/sec);

D_{H_2O} = molecular diffusivity of water vapor in air (cm²/sec);

n = exponent for diffusivity ratio;

S_v = logarithmic slope of the air velocity profile (cm/sec);

S_i = logarithmic slope of the concentration-profile for organic species i (g/cm³);
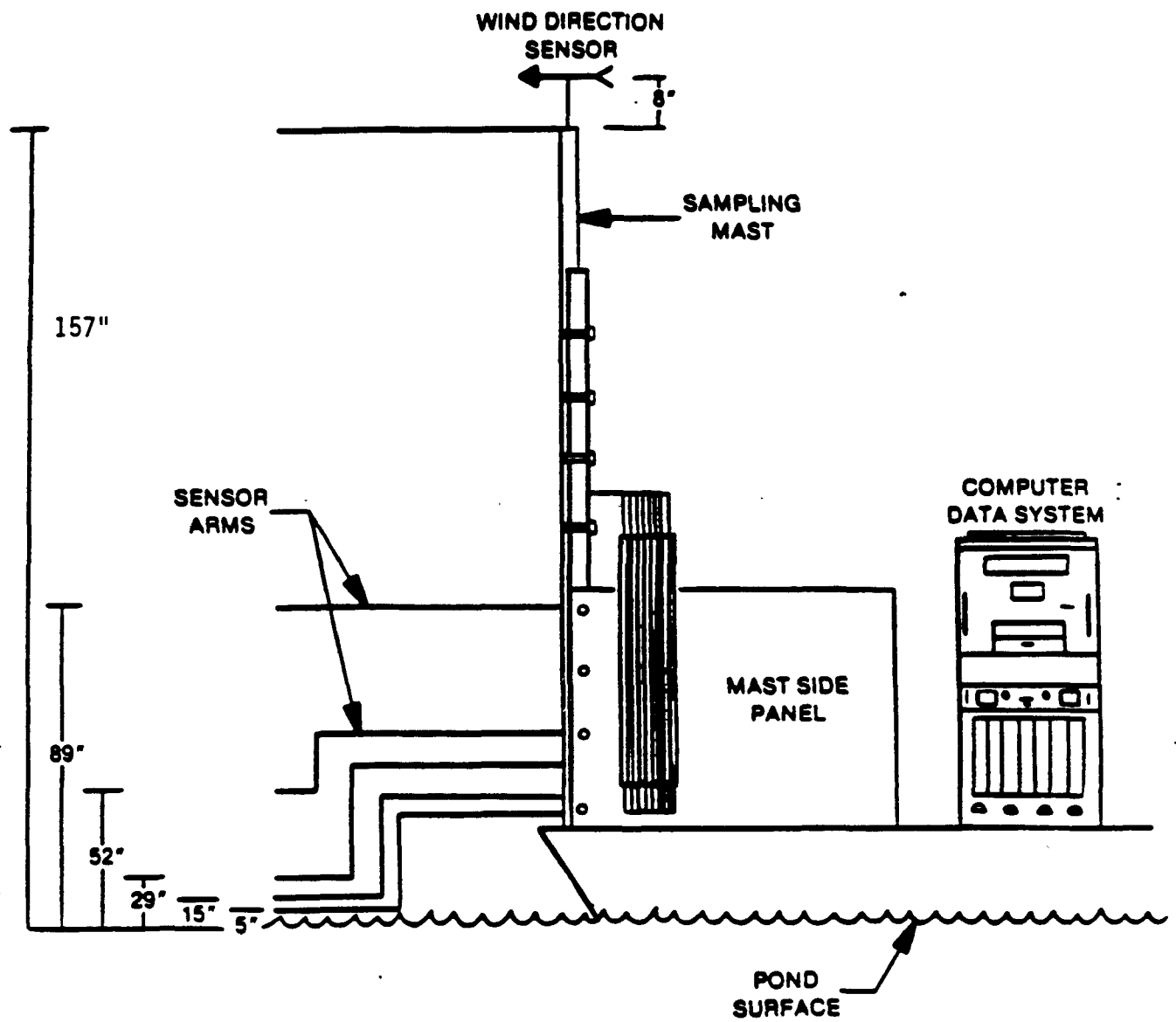
Figure 19. Mast sample collection system for C-P sampling.

K = von Karman's constant;

ϕm = Businger wind shear parameter; and

S_c = turbulent Schmidt number.

The term $(\phi m_2 S_c)^{-1}$ represents an atmospheric stability correction factor and is expressed as a function of the Richardson number. The function is an empirical correlation which corrects the estimated emission rate for water vapor to measured values under various atmospheric stabilities. For this reason, the correction factor is valid only under specific meteorological conditions.

The sampling equipment consists of a 4-meter mast with a wind direction indicator, wind speed sensors, temperature sensors, and air collection probes at six logarithmically spaced heights above the area source; a continuous real-time data collection system; and a thermocouple for measuring water temperature. Prior to sample collection, meteorological conditions must be monitored to determine if sampling conditions meet the necessary meteorological criteria. Once acceptable meteorological conditions are documented, the sample collection period is initiated. During the sample collection period, wind speed, air temperature, and relative humidity are measured.

Applicability--

The C-P technology is applicable to emission rate measurement from many types of large area sources including landfills, lagoons, and areas of contaminated soils. The technology is applicable for both volatile and particulate emission rate measurement. It is applicable both for undisturbed and disturbed site conditions, and for testing emission control technologies.

Limitations--

The technology requires that meteorological conditions during sampling, particularly wind speed and direction, match the predetermined conditions used to select the sampling location. The sampling location must be on the approximate plume centerline.

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The technology also assumes that the site is fairly homogeneous; therefore, the technology may not be applicable to heterogeneous sites. The technology is not applicable to sites where there is insufficient distance downwind to set up the sampling equipment. The technology also may not adequately collect emissions from point sources within an area source, such as cracks in landfill covers or vents.

The technology requires upwind sampling to account for other potential sources. Finally, the technology is not applicable during quiescent or unstable wind conditions, and may produce false negative results during these conditions.

4.2.5 Transect (In-Depth Technology)

The transect technology, also referred to as plume mapping, measures the concentration of the emitted species at several downwind locations aligned perpendicular to the anticipated plume centerline (21,35). The in-depth transect technology is an indirect emission measurement approach that has been used to measure fugitive particulate and gaseous emissions from area and line sources. This technology has been successfully tested at a variety of waste sites, including landfills. Figure 20 illustrates the transect sampling array.

The transect technology 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 (21):

$$E_i = \frac{u}{A_s} \iint_{A_p} C_i(h,w) \, dh \, dw \qquad \text{(Eq. 15)}$$
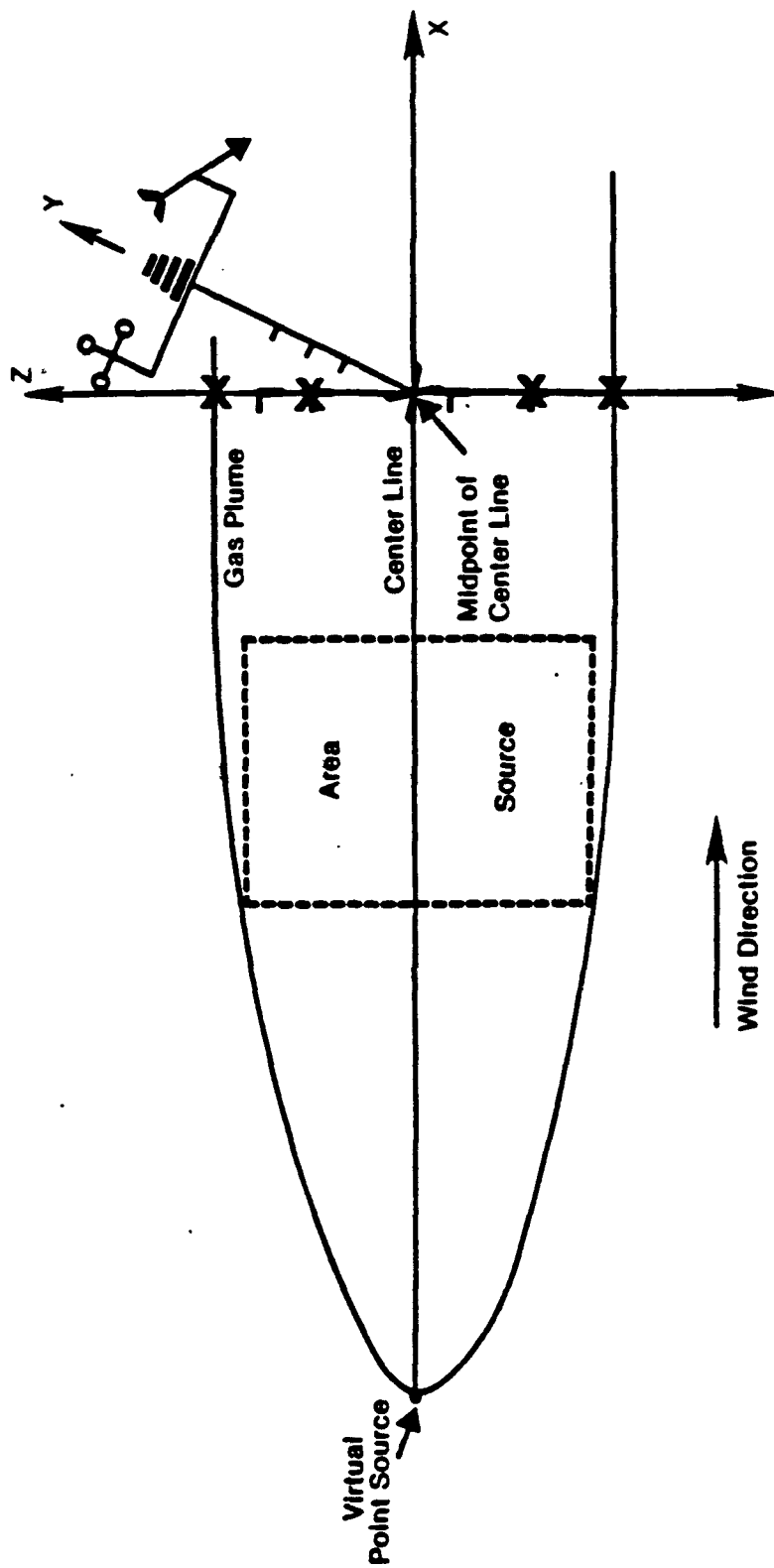
Figure 20.   Example of transect technique sampling.

where E_i = emission flux of component i (ug/m^2-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 (ug/m^3);

h = vertical distance coordinate (m); and

w = horizontal distance coordinate (m).

For particulates, the emission flux is calculated as (36):

$$E = \frac{1}{t\ A_s} \iint_{A_p} \frac{m(h,w)}{a}\ dh\ dw \qquad \text{(Eq. 16)}$$

where   E = emission flux (ug/m^2-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 (ug);

h = vertical distance coordinate (m);

w = horizontal distance coordinate (m); and

a = intake area of sampler (m^2).

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 (33):

$$\text{E.R.}_i = \sum_1^n \pi\ X_i K_i\ \sigma_y\ \sigma_z\ C\ \overline{U} \qquad \text{(Eq. 17)}$$

where E.R._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 reponse 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).

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 technology is somewhat less susceptible to changing meteorological conditions than the concentration profile technology, 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 technology because the technology 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 technology is applicable to emission rate measurement
from all forms of area sources, including lagoons, landfills, open dumps, and
waste piles.

The technology can be used for both volatile and particulate matter
emission rate assessment. The technology is applicable both for undisturbed
and disturbed site conditions, and for testing of emission control
technologies. The technology 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
technology 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 technology 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 technology 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 technology provides only limited vertical profiling of the
plume. The technology is not applicable during quiescent or unstable wind
conditions; it may produce false negative results during these conditions.

Preferred Technology--

The transect technology is a preferred indirect emission assessment
technology. The technology 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 man-power needs suggest this technology as a preferred technology relative to other indirect approaches.

4.2.6 Boundary Layer Emission Monitoring

Boundary layer emission monitoring can be used to determine the emission rate of pollutants from large heterogenous area sources (37). The technique is similar to the transect technique in that samples are collected along an array that is perpendicular to the emission plume. However, rather than fixed sampling locations, the boundary layer technique involves a cart with three or more samplers traversing the plume with each sampler at a different height. During the plume traversing the sampling rate is adjusted to be proportional to the sine of the angle between the wind vector and the direction of the traverse path. Each run takes about an hour. The average concentrations are adjusted for any upwind concentration and then used to calculate an average vertical concentration profile. This profile is numerically integrated (with the wind velocity profile) over the contaminant boundary layer to derive an emission rate for the source.

The emission rate is (37):

$$\left[E = C_o WV_o \times 10^{-6} \right] \int_0^{Z_b} (z/10)^p (1-z/Z_b)^b \ dz \qquad \text{(Eq. 18)}$$

where
E = emission rate (g/sec);
C_o = ground level concentration (ug/m^3);
W = cross-wind distance (m);
V_o = average wind speed at 10m (m/sec);
Z_b = boundary layer thickness (m);
p = exponent of wind-velocity profile; and
b = exponent of concentration profile.

Applications--

The technique can be used for measuring an emission rate from any type of source with constant emissions.

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Limitations--

The method assumes that both the contaminant emission rate and the wind speed and direction are reasonably steady while sampling is conducted. The major sources of error are in the average measured wind velocity and in accounting for upwind contamination. The method should be limited to area sources that do not have significant plume buoyancy, to periods of 1-10 m/sec winds, and to sampling heights less than the depth of the mixing layer. The technique has not been validated by the EPA.

4.3 AIR MONITORING TECHNOLOGIES

Air monitoring technologies that measure the ambient air concentration resulting from area emission sources are combined with air dispersion modeling to calculate the area source emission rate. The primary difference between indirect emission measurement technologies and air monitoring technologies is the distance at which measurements are made downwind from the source. In-direct measurements are made near the source or units of a combined site (usually on site) and may be able to distinguish between multiple units within a site, depending on the spacing between units. Air monitoring is generally performed at considerable distance downwind from the source and usually cannot distinguish between multiple units within a combined site. Air monitoring typically measures lower concentrations because the contaminant plume is subject to additional air dispersion.

The first step to use the ambient air sampling data to develop emission rate estimates is to select an air dispersion model which accurately reflects the site-specific conditions, including regional and local terrain, typical wind stability, etc. Guidance for selecting an appropriate model is given in the EPA's Guideline on Air Quality Models (38). Preferred models given in the guidance document include the Climatological Dispersion Model (CDM 2.0), Gaussian Plume Multiple Source Air Quality Algorithm (RAM), Industrial Source Complex Model (ICS), and Single Source (CRSTER) Model. A number of other potentially applicable models are included in the guidance document. Models not included in EPA's manual also may be applicable at uncontrolled hazardous

waste sites, including the Point Plume Model (PTPLU), and the Gifford and Hanna Simple Box Model (39). The models are used with air monitoring and meteorological monitoring data to estimate emission rates.

Air monitoring and air dispersion models are used to determine the emission rate through an iterative process. An emission rate is first estimated for the area source. This estimated emission rate, along with meteorological data collected during air monitoring, is used to calculate a predicted downwind concentration. The predicted concentration is then compared to the measured downwind concentration. Based on this comparison, the estimated emission rate is adjusted appropriately, and the process is repeated until acceptable agreement is reached between the measured and predicted downwind air concentrations.

The air monitoring technologies that can be used to develop BEEs are listed below. These technologies were described in Section 4.2 and can be used at greater distances downwind of the emission source as air monitoring technologies.

Screening Technologies--

   4.2.1 Upwind/Downwind

In-Depth Technologies--

   4.2.4 Concentration-Profile
   4.2.5 Transect
   4.2.6 Boundary Layer Emission Monitoring

4.4 EMISSIONS (PREDICTIVE) MODELING

Emissions models have been developed to predict emission rates for a variety of waste site types including landfills without internal gas generation, landfills with internal gas generation (typically co-disposal sites), open dumps, waste piles, spills, land treatment operations, aerated

lagoons, non-aerated lagoons, and lagoons with an oil film. These models are almost exclusively theoretical, and each model is generally applicable to only one type of waste site.

The predictive models can be used as screening or in-depth technologies. Emissions models, used as screening technologies, use data that can be obtained or calculated from information available in the literature, or can be assumed with some level of confidence. Emissions models, used as in-depth technologies, require site-specific site and waste characterization data. The selection of model input sources (site-specific, literature value, or assumed) should be based on the requirements of the decision-making process and the level of resources available. Site-specific data should be used whenever possible to increase the accuracy of emission rate estimates.

Several predictive models are presented below to acquaint the reader with the types of available models for emission rate estimation. The models presented do not include all available models. Specific methods for calculating the model input variables, such as diffusion coefficients, have been presented by the authors of the models, but are not included here for sake of brevity. Each model requires estimating the emission rate of the individual components of the waste; and then summing the emission rates to determine the overall emission rate. For complex waste, application of the models is best performed on a computer to speed the calculation. An emission flux can be calculated by dividing the emission rate by the emitting area.

A wide variety of variables are associated with each of the predictive models; however, a number of key inputs are required by many of the models. These key inputs for landfills include: the vapor diffusion coefficient through the soil or mass transfer coefficient across the air/soil boundary for waste constituents; the physical size of the source expressed as area, length, and/or width, depending on the model used; physical parameters of the landfill cover, such as depth of cover, permeability, and soil porosity (total, air-filled, and/or effective porosity); physical/chemical parameters of the waste, including chemical composition, weight or mole fraction for constituents, vapor concentration of constituents at the waste surface or

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within the soil cover, and partial pressures of constituents; atmospheric conditions, such as temperature, wind speed and direction, and barometric pressure; and estimates of the soil gas velocity through the soil cover. The key inputs for lagoons include: mass transfer coefficients; physical/chemical parameters of the waste, including chemical composition, weight or mole fractions, partial pressures, and Henry's Law Constants; physical dimensions of the lagoon surface; atmospheric conditions, such as temperature, and wind speed and direction; layering of waste within the lagoon; and physical/ chemical parameters of a surface crust.

While all of these parameters can be estimated with varying levels of confidence, it is best, when possible, to collect site-specific data. Physical/chemical measurements of waste constituents can be obtained from sampling and analysis programs, although a records review is advisable to identify key constituents and ensure representative sampling. Likewise a sampling and analysis program combined with a records search is desirable to determine the physical size and shape of the source and the porosity and permeability of any soil cover. Atmospheric conditions are easily obtained from various weather services which can provide regional data; however, collecting some site-specific meteorologic data to ensure representativeness is desirable. Diffusion and mass transfer coefficients are typically calculated based on the wastes' chemical composition and their known chemical properties, such as Henry's Law Constants, although tabulated diffusion coefficients are now available. The referenced literature includes suggested methods for calculating the diffusion coefficients as well as some tabulated data. Diffusion and mass transfer coefficients can also be determined experimentally in the lab; however, disturbance of the waste and landfill cover to obtain site-specific materials would probably introduce uncertainty.

The landfill models presented here can be categorized into five types:

- Closed landfills without internal gas generation--Farmer Model, Shen Model, Thibodeaux a Model, Logarithm Gradient Model, and RTI Closed Landfill Model;

- Closed landfills with internal gas generation--(Thibodeaux) Convective "Add On" Model, Thibodeaux b Model, and (Thibodeaux) Exact Model;

- Open landfills--Arnold's Open Landfill Model, Shen Open Landfill Model, and RTI Open Landfill Model;

- Landfarming--RTI Landtreatment Model and Thibo-deaux-Hwang Model; and

- Fugitive dust -- AP-42.

The lagoon models presented here can be categorized into two types:

- Non-aerated lagoons -- Mackay-Lienonen; Thibodeaux, Parker, and Heck; Smith, Bomberger, and Haynes; Shen; and RTI.

- Aerated lagoons -- Thibodeaux, Parker, and Heck; and RTI.

The bases for most of the landfill models are Fick's First Law of steady-state diffusion, Fick's Second Law of unsteady-state diffusion, the Equation of Continuity, and Darcy's Law.

4.4.1 Emission Models for Closed Landfills without Internal Gas Generation

Farmer Model--

The Farmer Model (40-43) was one of the first models developed and generally accepted to predict emission rates from covered landfills. The rate at which a compound is lost to the atmosphere from the land surface is controlled by the compound's molecular diffusion through the soil covering the waste. Farmer et al. developed this model to determine hexachlorobenzene vapor diffusion through a soil cover. They found that the two prime factors controlling/determining vapor movement through the soil were soil depth and soil air-filled porosity. The model should be applicable to other compounds as well.

The Farmer Model combined Fick's First Laws for steady-state diffusion with the Millington and Quirk evaluation of the diffusion coefficient. The latter included a porosity term accounting for the soil's geometric effects on diffusion for a given compound.

The Farmer equation is (41):

$$J = D_i(C_1-C_2)(P_a^{10}/^3/P_T^2)/L \qquad \text{(Eq. 19)}$$

where J = volatilization vapor flux through the soil cover $(ug/cm^2\text{-day})$;

D_i = vapor diffusion coefficient in air (cm^2/day);

P_a = air-filled soil porosity (cm^3/cm^3);

P_T = total soil porosity (cm^3/cm^3);

C_2 = concentration of volatilizing material at the surface of soil layer (ug/cm^3);

C_1 = concentration of the volatilizing material at the bottom of the soil layer (ug/cm^3); and

L = depth of the soil layer (cm).

Farmer et al. simplified the equation somewhat by assuming a worst-case scenario, where the soil is completely dry $(P_a$ equals $P_T)$ and where the concentration at the surface (C_2) equals 0, meaning any increase in C_2 would effectively reduce the driving force behind the vapor flux and, thus, reduce the vapor flux from the soil surface. Farmer et al. called this equation the Assessment Application (41):

$$J = D_i P_T^{4/3} C_s/L \qquad \text{(Eq. 20)}$$

Applicability--

The Farmer Model provides an estimate of individual compound emissions. The intended applicability of the Farmer Model is quantification of steady-state volatile chemical fluxes from hazardous waste landfills. This model does not account for convective transport due to biogas generation and

is not applicable to municipal landfills or other landfills containing gas generating wastes. Use of the Farmer Model assumes the transport of a volatile compound through the soil cover layer is controlled by a molecular diffusion process.

Limitations--

The Farmer Model assumes that the soil/waste below the soil cover layer is saturated with constituent i. This assumption tends to overestimate the emissions by not accounting for the true concentration gradient below the soil cover. Additionally, the Farmer Model does not account for the emissions associated with atmospheric/meteorological effects such as barometric pressure fluctuations. Also, at high concentrations (greater than 5 percent by volume), the diffusion process creates its own convective sweep or apparent velocity within the landfill. This convective mechanism is not accounted for by the Farmer Model (44). These latter two limitations are likely to result in underestimates of landfill emission rates.

Shen Model--

Shen modified the Farmer Model (45,46,47) to determine a vapor emission rate, as opposed to the vapor flux rate, and to enable calculation of the volatilization of specific components of the complete waste mixture. This modification assumes Raoult's Law applies. Shen multiplied the Farmer equation by the exposed contaminated surface area and by the weight fraction of the component in the mixture. The modified equation is (45):

$$E_i = D_i C_i A(P_t^{4/3}) \frac{1}{L} \frac{W_i}{W} \qquad \text{(Eq. 21)}$$

where
E_i = emission rate of the component i (g/sec);
D_i = diffusion coefficient of component in air (cm^2/sec);
C_i = saturation vapor concentration of component i (ug/cm^3);
A = exposed area (cm^2);
P_t = total soil porosity (dimensionless);
L = effective depth of the soil cover (cm); and
W_i/W = weight faction of component i in the waste (g/g).

The model assumes completely dry soil and zero concentration of volatilizing material at the soil surface, a worst-case scenario considered appropriate for cap design and most analyses for volatilization release from landfill wastes. This assumption should be used in all cases except where cover soils can be shown to have significant soil moisture. In these instances, the soil air-filled porosity should be substituted into the equation for the total porosity by replacing $P_t^{4/3}$ with $P_a^{10/3}/P_T^2$.

Applicability--

The Shen Model differs from the Farmer Model in that it relates emissions to the waste composition with a weight factor (wi) and multiplication of the flux by the landfill area. Like the Farmer Model, the intended applicability is quantification of steady-state volatile chemical emission rates from hazardous waste landfills. This model does not account for convective transport due to biogas generation and is not applicable to municipal landfills or other landfills containing gas generating wastes. In the use of the Shen Model, it is assumed that the relatively toxic properties of organic waste placed in hazardous and industrial waste landfills minimize gas production due to biodegradation.

Limitations--

The Shen Model does not account for the landfill gas losses in leachate systems, run off, or soils. But here again, due to the inert properties of the volatile constituents, this accountability is considered by Dr. Shen to be minute. The Shen Model also assumes that the soil is completely dry with no internal gas generation. However, the Shen Model can be modified to account for biogas generation with a multiplicative factor of 6. This assumption would tend to overestimate emissions by not accounting for actual wet soil conditions below the soil cover layer. As with the Farmer Model, the Shen Model does not account for emissions due to meteorological fluctuations (e.g., barometric pressure pumping).

Another limitation of the Shen Model is the incorporation of Raoult's Law to relate the waste composition to emission rate. Raoult's Law is applicable only to waste saturated with constituent i and ideal solutions. Application

of the Shen Model to wastes containing dilute concentrations of the
constituent i is likely to result in an overestimate of emission rate.

Thibodeaux a Model--

The Thibodeaux a Model (43,48) was developed by Thibodeaux to estimate
the emissions of volatile constituents due to interphase vapor transport from
landfills with no internal gas generation. The model is derived from Fick's
Law of steady state diffusion. Molecular diffusion is the controlling and
only transport mechanism addressed by the Thibodeaux a Model for the movement
of volatile constituents toward the soil/air interface and then to the
overlying air. To describe this mechanism, the two-resistance theory is used
to describe the two-film resistance in which the movement of chemical
constituents is limited by their ability to diffuse through the soil and after
migration from the surface, through the air.

The model assumes that a pure component i exerts its pure component vapor
pressure under the earth, subject to normal geophysical and meteorological
factors. Thibodeaux defines an overall mass transfer coefficient to describe
vapor movement which is hindered by both the resistance due to soil
characteristics and diffusion resistances at the air interface.

$$E_i = {}^1K_i \ (C_i - C_{i1}) \ A \qquad \text{(Eq. 22)}$$

$$E_i = E_{soil} + E_{air/soil} \qquad \text{(Eq. 23)}$$

where ${}^1K_i$ = overall soil phase mass-transfer coefficient (cm/sec);
        C_{i1} = concentration of i above the soil/air interface (g/cm^3);
        C_i = concentration of i in the sand-filled chamber pore spaces
            (g/cm^3);
        Ei = rate of vapor movement within the soil phase (g/sec); and
        A = landfill surface area (cm^2).

$$E_{soil} = \frac{{}^1D_i}{L} \ (C_i - C_s) A \qquad \text{(Eq. 24)}$$

where ^1D_E = effective diffusivity of constituent i within the pore spaces (cm/sec);

L = depth of the soil fill cover (cm); and

C_s = concentration of i at the air/soil interface (g/cm^3).

$$E_{air/soil} = {}^3D_i\ (C_s-C_{i1})\ A \qquad (Eq.\ 25)$$

where ^3D_i = gas phase mass-transfer coefficient using the equation developed by MacKay and Matsugu (m/hr).

$$^3D_i = 0.0292\ V_x^{0.78}\ L_x^{-0.11}\ S_c^{-0.67} \qquad (Eq.\ 26)$$

where V_x = wind speed measured at 10 m (m/hr);

L_x = length of the ground emission source in the direction of the wind (m); and

S_c = Schmidt number for the gas.

Overall mass-transfer coefficient:

$$\frac{1}{^1K_i} = \frac{1}{^1D_i} + \frac{1}{^3D_i} \qquad (Eq.\ 27)$$

where $^1D_i = D_i\xi/T_h$

T_h = tortuosity, taken to be 3

ξ = porosity of the cover material

Applicability--

Like the Farmer and Shen models, the intended application of the Thibodeaux a Model is a hazardous waste landfill. This model does not account for convective transport due to internal gas generation typically present in municipal landfills.

Limitations--

The Thibodeaux a Model does not account for the possible emissions due to barometric pressure fluctuations or internal gas generation. In addition, the

Thibodeaux a Model does not account for the convective sweep of a volatile constituent caused by high concentrations greater than 5 percent by volume. A number of factors, such as waste composition, multicomponent systems, and biological or chemical reactions, greatly increase the uncertainty in the use of the two-resistance theory.

Logarithm Gradient Model--

The Logarithm Gradient Model (43) is the modern day interpretation of the Farmer Model developed to address volatile constituent emission rates for landfill concentrations greater than 5 percent by volume. In general, this model takes into account both the diffusive mechanism as described by Fick's Law and the convective mechanism due to the sweep or apparent velocity which diffusion can create with high concentrations.

The Logarithm Gradient Model is (43):

$$E_i' = D_E \, P_T \, \frac{M}{RTL} \, Ln \left(\frac{P_T - P_i}{P_T - P_i{}^*} \right) A \qquad \text{(Eq. 28)}$$

where

E_i = emission rate (g/sec);

D_E = effective diffusion coefficient (cm^2/sec);

P_T = total pressure below the cover layer (mm Hg);

M = mole weight of constituent (g/mol);

R = molar gas constant (cm^3 mm Hg/mol °K);

T = absolute temperature (°K);

L = length of soil cover (cm);

P_i = partial pressure at the air-soil surface (mm Hg);

$P_i{}^*$ = partial pressure of the volatilizing material in soil gas at the bottom of the soil depth (mm Hg); and

A = landfill surface area (cm^2).

Applicability--

This model can generally be applied to landfill situations where molecular diffusion is the controlling vapor transport mechanism. The model accounts for the apparent velocities associated with high volatile

concentrations, but does not account for the convective sweep movement associated with co-disposal (biogenic gas production) practices.

Limitations--

The limitations indicated for both the Farmer Model and the Shen model apply to this model. However, the Logarithm Gradient Model accounts for convective transport resulting from the diffusion of highly volatile constituents (greater than 5 percent by volume).

RTI Closed Landfill Model--

The Research Triangle Institute (RTI) closed landfill model (43,47) accounts for emissions via two mechanisms: diffusion through the soil cap and convective loss from barometric pumping through passive landfill vents. The model is based on the Farmer Model (above) which was modified to account for convective losses due to barometric pumping and the decline in emission rate over time.

The total instantaneous emission rate is a function of the total initial emission rate at the time of landfill closure which is the sum of the instantaneous emissions associated with diffusion through the cap and barometric pumping.

$$E_i^* = E_{1i} + E_{2i} \qquad \text{(Eq. 29)}$$

where
E_i^* = total initial emission rate at the time of closure (g/sec);

E_{1i} = emissions associated with diffusion through the cap (g/sec); and

E_{2i} = emissions associated with barometric pumping (g/sec).

The equations for estimating E_{1i} and E_{2i} are present below.

$$E_{1i} = \frac{AD_i}{L} \left(P_A^{10/3} / P_T^2 \right) (C_i - C_s) \qquad \text{(Eq. 30)}$$

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where A = landfill surface area (cm^2);

D_i = vapor diffusion coefficient in air (cm^2/sec);

P_A = soil cap air-filled porosity (cm^3/cm^3);

P_T = total porosity of the soil cap (cm^3/cm^3);

C_i = concentration of constituent in the vapor space beneath the cap (g/cm^3);

C_s = concentration of constituent in the air above the cap (g/cm^3) assumed to be 0; and

L = cap thickness (cm).

$$E_{2i} = Q \, C_i \, A \qquad \text{(Eq. 31)}$$

where Q = flow rate of gas through the vent ($cm^3/cm^2 \cdot sec$);

C_i = concentration of constituent in the gas within the landfill (g/cm^3); and

A = landfill surface area (cm^2).

$$Q = \left[hA \, E_{fw} \quad \left(\frac{P_r}{P_1}\right) \left(\frac{T_1 + 273}{T_r + 273}\right) \; -1 \right] \Big/ (\Delta t \, A) \qquad \text{(Eq. 32)}$$

where h = thickness of waste bed within landfill (cm);

E_{fw} = air porosity fraction of fixed wastes;

P_r = reference barometric pressure (mm Hg);

P_1 = final barometric pressure (mm ug);

T_r = reference landfill temperature (°C);

T_1 = final landfill temperature (°C); and

Δt = time interval over which change in pressure and/or temperature occurred (sec).

The total instantaneous emission rate at any time is then computed via an exponential decay function:

$$E_i(t) = 31.56 \; \overset{\displaystyle *}{E_i} \; \exp(-\lambda t) \qquad \text{(Eq. 33)}$$

where $E_i(t)$ = total time-dependent emission rate (mg/yr);

$\overset{*}{E_i}$ = initial emission rate, at time of landfill closure (g/sec);

t = time since landfill closure (mo); and

λ = decay constant (mo^{-1}) = 2.63 x 106 E_i^*/M_{oi}; and

M_{oi} = total mass of the constituent in the landfill (g).

The average emission rate from a closed, vented landfill over the time since landfill closure is given by the following expression:

$$E_{A_i}(t) = \frac{2.63 \ E}{\lambda} i \ [1\text{-exp} \ (-\lambda t)] \qquad \text{(Eq. 34)}$$

where $E_{Ai}(t)$ = average emission rate over the time since landfill closure (mg/yr);

t = time since landfill closure (mo);

λ = decay constant (mo^{-1}); and

$\overset{*}{E_i}$ = initial emission rate at time of landfill closure (g/sec).

The RTI closed landfill model assumes that no biodegradation occurs and that the landfill is passively vented to the atmosphere. Transport of the constituent in moving water is assumed not to occur.

Applicability--

The RTI Model estimates the time-dependent behavior of emissions from landfills. RTI modified the Farmer Model to account for the convective loses from barometric pumping through vents. In addition, the RTI Model was designed to account for the decline in the emission rate from closed landfills over an extended period of time. The time dependency was incorporated simply by adding an exponential decay function. The decay constant was taken as the ratio of the emission rate at the time of landfill closure to the total mass of the constituent in the landfill.

Limitations--

The RTI Model does not include convective or purging action associated with biogas production commonly found at municipal solid waste landfills. It assumes, as did the Shen and Farmer models, that the toxic properties of the waste will inhibit biological processes and, thus, prevent biogas generation. Furthermore, the liquid waste which contains the volatile constituent i is assumed to be bound in the fixed waste within the landfill cell. No experimental or field verification has taken place.

4.4.2 Emission Models for Closed Landfills with Internal Gas Generation

(Thibodeaux) Convective "Add On" Model--

The Convective "Add On" Model was developed by Thibodeaux to account for both the diffusion and convective mechanisms present in landfills at which co-disposal of municipal solid waste and hazardous organic waste has been practiced. The model describes the migration of a chemical constituent i due to the convective gas sweep of biological gas production within the soil cover layer. As the apparent velocity, Vy, of the constituent, approaches zero, the model reduces to the diffusion controlled Farmer Model described above.

The Convective "Add On" Model is (43):

$$E_i = \frac{V_y (C_i - C_s)}{[\exp (LV_y/D_E) - 1]} + V_y C_i A \qquad (Eq. 35)$$

where

E_i = rate of vapor movement within the soil phase (g/sec);

V_y = mean gas velocity in pore spaces (cm/sec);

C_i = concentration of i in sand chamber filled pore spaces (g/cm^3);

C_s = concentration of i at the air-soil interface (g/cm^3);

L = depth of fill cover (cm);

D_E = effective diffusivity of i within the soil pore space (cm^2/sec); and

A = landfill surface area (cm^2).

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Applicability--

The Convective "Add On" Model can be used to estimate volatile emissions from landfills with internal gas generation. This model accounts for both diffusion and convective transfer. However, the transfer due to net upward gas flow greatly overshadows the diffusion transfer mechanism (44). This deduction is based, in part, on laboratory experiments of simulated gas flow through a soil cover.

Limitations--

A major limitation of this model is the required input of mean gas velocity through the soil cover. The limitations applied to the Farmer and Shen Models apply to this model as well. However, the "Add On" Model does account for biogas convection.

Thibodeaux b Model--

The Thibodeaux b Model (43,48) includes emissions due to barometric pressure pumping. The model accounts for the air emissions resulting from concentration gradients (diffusion), biogas generation sweeps (convection), and barometric pressure pumping (convection) (49). The barometric pressure fluctuations create a pressure gradient within the landfill cell, pumping vapors to the atmosphere.

The Thibodeaux b Model incorporates Darcy's Law to characterize the laminar flow of gases flowing through porous media due to pressure gradients. The gas flow velocity within the landfill cell can be estimated as:

$$V = (k\rho g/uL)(P-p) = (Kg/L)(P-\pi)$$ (Eq. 36)

where
V = velocity;

k = specific permeability of covering material in Darcys or cm2;

u = viscosity of gas;

ρ = density of gas;

L = soil cover thickness;

P = landfill cell pressure;

π = barometric pressure;

g = acceleration of gravity; and

K = permeability (cm/sec).

The Thibodeaux b Model is (43):

$$E_i = \frac{D_E}{L} \, C_i \, \frac{R \exp R}{\exp R - 1} \, A \qquad \text{(Eq. 37)}$$

where $R = \frac{LV}{D_E}$ (Eq. 38)

$$V = \frac{k}{uL} (P-\pi) \qquad \text{(Eq. 39)}$$

E_i = emission rate (g/sec);

C_i = concentration of i in the sand chamber filled pore spaces (g/cm^3);

V = superficial velocity through the soil cover layer (cm/sec);

k = permeability of soil cover layer material (cm^2 cp/sec atm);

P = landfill cell pressure (atm);

u = landfill cell gas viscosity (cp);

π = atmospheric pressure (atm);

L = depth of soil cover layer (cm);

D_E = effective diffusivity of i within the air-filled soil pore space (cm^2/sec); and

A = landfill surface area (cm^2).

Applicability--

The Thibodeaux b Model can be applied to situations where molecular diffusion, convection, and barometric pressure fluctuations are to be expected. Efforts by Springer indicate that the annual barometric pressure

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fluctuation does not average out to one and, therefore, should be considered. Furthermore, Springer observed through computer simulations of flux with benzene that barometric pressure fluctuation only slightly influenced the flux rate at co-disposal facilities, and greatly influenced the flux rate at hazardous waste landfills where no internal gas generation is expected.

Limitations--

The limitations observed in Thibodeaux's Convective "Add On" Model applied to this model with the exception of barometric pressure fluctuations. Springer's observations indicate that the Thibodeaux b Model is applicable to landfills with no internal gas generation (49).

Exact Model--

The Exact Model, (43) developed by Thibodeaux, is a steady state model which accounts for diffusion due to concentration gradients, the convective velocity created by highly volatile compounds, and convection due to biogas generation (50). Application of the model requires an iterative procedure, since the flux term, Ji, appears on both sides of the equation. The Logarithm Gradient Model discussed above is used to calculate the initial estimation of the flux to start the iterative calculation. Since it is a steady-state model, the flux is not given as a function of time and the concentration of constituent i is assumed to be constant within the landfill cell.

The Exact Model is (43):

$$ J = \frac{VP_A M_A}{RT} \left[1 - \frac{P_A}{P_T} - \exp\left(- \left(\frac{Ji}{M_A} + \frac{VP_T}{R_T}\right) LR_T/P_T D \right) \right] \quad \text{(Eq. 40)} $$

where

J_i = volatile chemical flux (g/cm^2-sec);

V = apparent biogas velocity (cm^3/cm^2-sec);

P_A = vapor pressure of chemical A (atm);

M_A = molecular weight of chemical A (g/mole);

P_T = atmospheric pressure (atm);

L = soil layer thickness (cm);

D = effective diffusion coefficient (cm^2/sec);

$$(EN)D_{A1} = ea^{10/3}/e^2;$$

EN = enhancement factor from experimental data;

D_{A1} = diffusion coefficient of chemical A in air;

e = porosity of soil layer;

e_a = air-filled porosity of soil layer;

R = molar gas constant; and

T = absolute temperature (°K).

Applicability--

The intended applicability of this model is municipal landfills with internal gas generation. This model can be used to estimate the flux of a volatile constituent i from closed landfills due to both diffusion and convective transport mechanisms. However, this model can only be used for landfills with an internal gas velocity greater than zero.

Limitations--

When the model predictions were compared to the experimental data developed by Thibodeaux, large discrepancies were observed. The experimental emission rates were higher than the model predictions, and Thibodeaux attributes this deviation to surface diffusion which occurs in parallel with pore diffusion and, in general, enhances the total diffusion rate.

Thibodeaux incorporates the enhancement factor, EN, in the Exact Model to account for the discrepancies observed between the effective diffusivity (obtained by laboratory experiments) and the Millington-Quirk diffusivity. Therefore, one major limitation of Thibodeaux's Exact Model is the availability and accuracy of the enhancement factor. Another limitation of Thibodeaux's Exact Model is that the value of the apparent gas velocity, V, needs to be known. In order to apply Thibodeaux's Exact Model, the enhancement factor needs to be experimentally obtained for the specific constituent, soil type, soil cover depth, gas type, gas velocity, and gas humidity.

Thibodeaux's Exact Model may be useful in estimating the order of magnitude value of the emission flux if the soil cover depth is less than 10 cm. The enhancement factor for a shallow soil cover (i.e., 7.62 cm) ranges from 1.58 to 4.93 compared to the range of 5.54 to 17.2 for a deep soil cover layer (i.e., 38.1 cm).

4.4.3 Emission Models for Open Landfills

Arnold's Open Landfill Model--

The Arnold Open Landfill Model (43) provides an estimate of the cumulative vapor release from the surface of open landfills as a function of time. Arnold's Open Landfill Model applies Fick's Second Law of unsteady-state diffusion to describe the diffusion process from a liquid surface at which the concentration of volatilizing liquid remains constant. The model assumes that the air space above the liquid surface is at a constant pressure and convective forces are absent.

In applying Fick's Second Law, Arnold incorporated a correction factor for Fick's Second Law to account for the displacement of the air (or inert gas medium) by the volatilizing constituent. This correction factor is a function of the equilibrium vapor pressure of the constituent. Values of Fick's correction factor, Fv, are plotted against equivalent vapor pressure in Figure 21.

The Arnold Open Landfill Model is (43):

$$V^o = 2y^* A \sqrt{\frac{D_i t}{\pi F_v}}$$
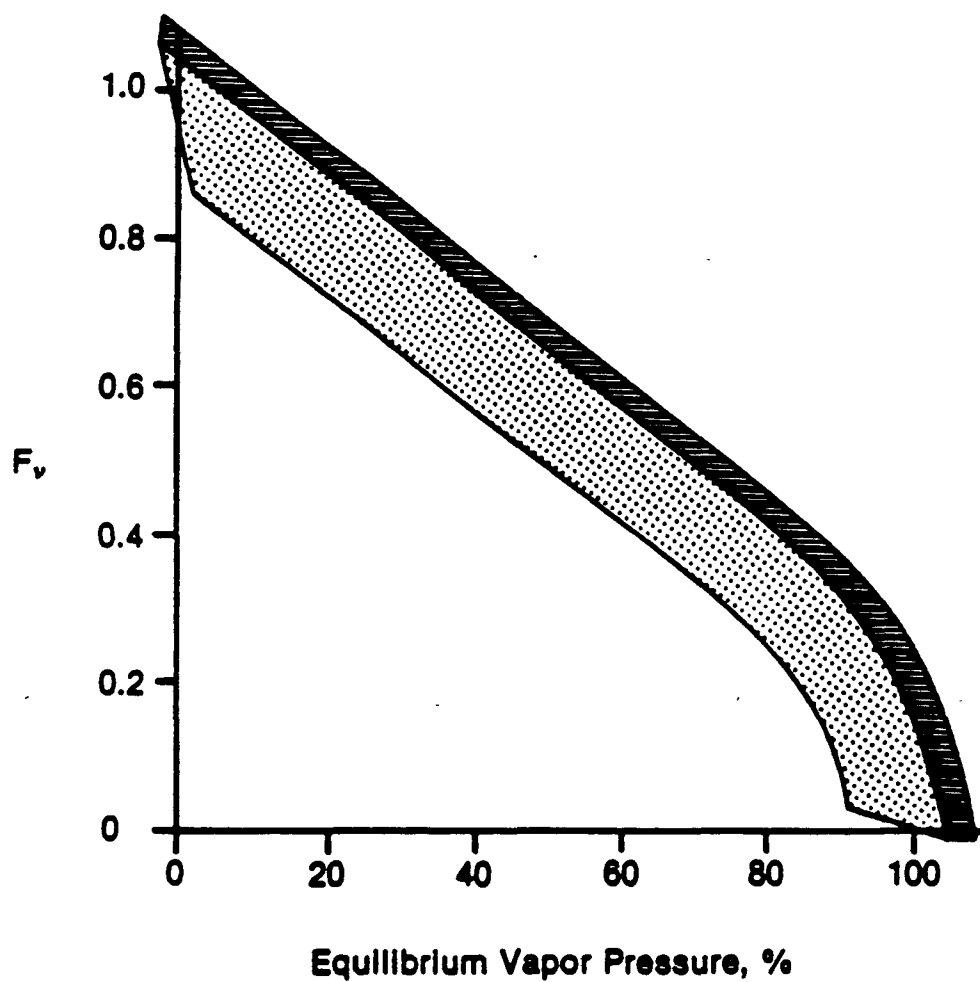
(Eq. 41)

Figure 21. Fick's correction factor, Fv, plotted against equivalent vapor pressure, Ce.

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where V^o = volume of vapor released at ambient pressure and temperature (cm^3);

y^* = equilibrium mole fraction of the volatilizing component in the gas phase at the liquid-gas interface;

A = area of the liquid surface (cm);

D_i = diffusivity of volatilizing component in air (cm2/sec);

t = time (sec);

F_V = Fick's Law correction factor; and

π = 3.1416

Applicability--

The Arnold Open Landfill Model is applicable to open landfills and dumps where emissions are due to volatilization at the landfill surface.

Limitations--

The model assumes that emissions do not occur due to biogas production or barometric pumping. The model also does not account for the effects of wind speed which would tend to increase the emission rate. Finally, the model assumes a constant waste source, whereas, a surface crust may form as volatile constituents are lost from the surface soil. This crust may then act similar to a landfill cover.

Shen's Open Landfill Model--

Shen's Open Landfill Model (43) provides the average volumetric emission rate of the volatile constituent from open landfill surfaces. Shen modified the Arnold Open Landfill Model to account for the convection due to wind speed. Shen took the time derivative of the Arnold Model and changed the time function, t, in the model to a position function. This position function is related to the length of the open dump and the wind speed.

The Shen Open Landfill Model is (43):

$$\frac{dV_i}{dt}\bigg|_{avg} = 2y^* W_L \sqrt{\frac{D_i L_L U}{\pi F_V}} \qquad \text{(Eq. 42)}$$

$$\frac{dV_i}{dt_{avg}} = \text{average emission rate } (cm^3/sec);$$

where y_i^* = equilibrium mole fraction;

W_L = width of open landfill (cm);

D_i = diffusion coefficient (cm2/sec);

U = wind speed (cm/sec);

F_v = Fick's law correction factor;

L_L = length of open landfill (cm); and

π = 3.1416

The model has also been presented as Ziegler's modification of Arnold as (45,50):

$$\frac{dV}{dt} = 2 \, CeW \, (DLv/\pi FY)^{1/2} Wi \qquad \text{(Eq. 43)}$$

where $\frac{dV}{dt}$ = emission rate;

W = width of landfill;

L = longest dimension of the landfill;

v = wind speed;

Wi = weight fraction of a specific compound in the waste;

Ce = equilibrium vapor concentration;

D = diffusion coefficient; and

FY = correction factor.

The emission rate can increase with increasing wind speed; however, the dilution fraction also increases. The net effect of wind speed on ambient concentration, therefore, becomes compensative and depends on receptor location.

Applicability--

The Shen Open Landfill Model is applicable to open landfills where emissions are due to volatilization at the landfill surface. It appears that this model is useful as a screening process to examine whether volatilization will be significant for a given contaminant (46).

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Limitations--

The model does not provide for biogas generation or barometric pumping. The model also does not provide for the formation of a weathered surface which would tend to reduce emissions similar to a closed landfill cover.

RTI Open Landfill Model--

Research Triangle Institute (RTI) modified the Shen Open Landfill Model by introducing the mole fraction of the constituent to account for more than one volatile constituent in the liquid. The RTI Open Landfill Model, shown below, uses the ideal gas law to convert the volumetric emission of the Shen Open Landfill Model and provide an average mass emission rate.(40,41)

The RTI Open Landfill Model is (43):

$$E_i = \frac{2PM_i Y_i^* W_L}{RT} \sqrt{\frac{D_i L_L}{\pi F_V} U} \qquad (Eq. \ 44)$$

where
E_i = average mass emission rate of component i (g/sec);

P = ambient pressure (mm Hg);

M_i = molecular weight of component i;

Y_i^* = equilibrium mole fraction of component i;

W_L = width of open landfill;

D_i = diffusivity of component i in air (cm^2/sec);

L_L = length of open landfill (cm);

U = wind speed (cm/sec); and

F_V = Fick's Law correction factor.

Applicability--

The RTI Open Landfill Model is applicable to open landfills where emissions are due to volatilization at the landfill surface.

Limitations-- The model does not account for biogas production, barometric pumping, or formation of a surface crust.

4.4.4 Emission Models for Landtreatment

RTI Land Treatment Model--

Research Triangle Institute (RTI) has developed a model (42,43) for estimating emissions from land treatment areas. The model is comprised of two equations; one for short time (immediately after application or tilling) and one for longer times. The RTI land treatment equations are based on the premise that emissions are limited by vapor diffusion through the soil. The model accounts for the removal of organic material from the land treatment area by both biological degradation and air emissions.

The expression for the instantaneous emission rate for short time periods immediately following initial waste deposition is given by:

$$E = \left[\frac{M_o}{1} \frac{e_a}{\frac{e_a}{K_q K_g} + \frac{\pi t}{K_q D_e}^{1/2}} \right] e^{-t/t_b} \qquad \text{(Eq. 45)}$$

where

E = emission rate of constituent $(g/cm^2\text{-sec})$;

M_o = area loading of constituent (g/cm^2);

1 = depth of waste in open landfill (cm);

e_a = volume fraction of air-filled voids in the soil (dimensionless);

K_q = ratio of gas-phase constituent to total constituent in solid waste (dimensionless);

K_g = gas-phase mass transfer coefficient (cm/s);

t = time after waste application to the landfill site (sec);

D_e = effective diffusion coefficient of constituent in the solid waste (cm^2/sec); and

t_b = time constant for biological decay (i.e., time required for 63.2% of constituent to be degraded.

For longer times after application or tilling, when most of the constituent is not present in the soil, the short-term equation will over estimate air emissions. Under these conditions, the following equation is applicable:

$$E = \frac{2 M_o \, Keq \, D_e}{l^2} \quad exp \left[\frac{-D_e \, Keq \, _D^2 t}{4 \, l^2} \right] \quad e^{-t/t_b} \qquad (Eq. \ 46)$$

where   E =   emission rate a long time after application or tilling
              (g/cm^2-sec); (all other parameters are the same as
              presented above).

Applicability--

The RTI Land Treatment Model is applicable to sites where liquid or semi-liquid waste is applied to the soil surface. The model assumes that emissions from the surface are limited by diffusion of vapors through the pore space of the soil/waste mixture. The model accounts for removal of organic material from the soil/waste mixture by both biological degradation and air emission.

Limitations--

The model is not applicable to wastes which are easily biodegraded, or to sites with highly porous soils which allow easy vertical migration of the liquid waste. The model does not account for losses to these or other pathways.

Thibodeaux-Hwang Model--

Thibodeaux and Hwang developed a model for determining volatile emissions from land treatment operations (49,51,52). The liquid being land-treated is assumed to soak into the soil, coating the pore walls. The liquid then evaporates from the pore walls and diffuses through the soil pores to the soil/air interface. After a short period of time, a dry zone develops at the soil surface, with a wet zone below. Over time, the thickness of the dry zone increases while the thickness of the wet zone decreases.

The rate of emission can be determined by:(51)

$$E_i = \cfrac{D_{ei} \; C_{ig}}{\left[h_s^2 + \cfrac{2 \; D_{ei} \; t \; A \; (h_p - h_s) C_{ig}}{M_{io}} \; 1/2\right]}$$ (Eq. 47)

$$C_{ig} = \left[\cfrac{H_c \; C_{io}}{1 + \cfrac{H_c \; D_{ie} \; Z_o}{D_{wi} \; A_s \; f(y)}}\right] C_{io}$$ (Eq. 48)

where A = surface area over which waste is applied (cm^2);

A_s = interfacial area per unit volume of soil for the oily waste, (cm^2/cm^3);

C_{ig} = effective wet zone pore space concentration of component i (g/cm^3);

C_{io} = concentration of component i in oil (g/cm^3);

D_{ei} = effective diffusivity of component i in the air-filled soil pore spaces (cm^2/s);

D_{wi} = effective diffusivity of compound i in the oil (cm^2/s);

E_i = flux of component i from the soil surface (g/cm^2-sec);

$f(y)$= $(h_p^2 + h_p h_s - 2h_s^2)/6$ accounts for the lengthening dry zone;

H_c = Henry's Law constant in concentration form (cm^3 oil/cm^3 air);

h_p = depth of soil contaminated or wetted with landtreated waste (cm);

h_s = depth of subsurface injection, if applicable (cm);

M_{io}= initial mass of component i incorporated into the zone $(h_p - h_s)$, (g);

t = time after application (sec);

y = height of wetted soil remaining after partial drying (cm); and

Z_o = oil layer diffusion length (cm).

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Applicability--

The Thibodeaux-Hwang land treatment Model is applicable to determining volatile emissions from landfarming of liquid wastes, including oily wastes.

The model assumes that the soil column is isothermal, liquid movement does not occur by capillary action, adsorption to soil particles does not occur, and biochemical oxidation does not occur (49). All of these factors would tend to reduce the emission rate.

Limitations--

The model is not applicable to wastes which are easily biodegraded, or to sites with highly porous soils which allow easy vertical migration of the liquid waste. The model does not account for losses to these or other pathways.

4.4.5 Fugitive Dust

Fugitive dust at hazardous waste sites (airborne wastes or contaminated soils) most commonly results from wind erosion of the wastes or vehicular travel over unpaved contaminated roads. The U.S. EPA has developed equations to estimate fugitive dust emissions arising from vehicle travel on unpaved roads (AP-42). The U.S. Soil Conservation Service (SCS) has developed a model for predicting fugitive dust emissions resulting from wind erosion.

The SCS model takes into account such factors as surface soil moisture content, roughness, and cloddiness, type and amount of vegetative cover, wind velocity and the amount of soil surface exposed to the eroding wind force. The SCS equation can be expressed as:

$$E = f(I',C',K',L',V) \qquad \text{(Eq. 49)}$$

.where   E = potential annual average wind erosion soil loss;
          I' = soil erodibility index;
          C' = climatic factor;
          K' = soil ridge roughness factor;

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L' = field length along the prevailing wind direction; and

V = vegetative cover factor.

The SCS wind equation computes total fugitive dust emissions due to wind erosion which result from the combination of surface creep, saltation, and suspension. If only the fraction of soil loss that is suspendable and trans-portable over significant distances by wind is desired, the wind equation must be adjusted (reduced) to reflect emissions from only this phenomenon. The SCS wind erosion equation is not reliable when altered to estimate short-term emissions. The model is designed to estimate annual erosion losses only.

The U.S. EPA has developed the following equations which can be used to estimate fugitive dust emissions resulting from vehicular travel on contaminated unpaved roads (53):

$$E_{VT} = k(5.9) \left(\frac{s}{12}\right) \left(\frac{S_p}{30}\right) \left(\frac{W}{3}\right)^{0.7} \left(\frac{w}{4}\right)^{0.5} \left(\frac{365-D_p}{365}\right) \qquad \text{(Eq. 50)}$$

or in metric form:

$$E_{VT} = k(1.7) \left(\frac{s}{12}\right) \left(\frac{S_p}{48}\right) \left(\frac{W}{2.7}\right)^{0.7} \left(\frac{w}{4}\right)^{0.5} \left(\frac{365-D_p}{365}\right) \qquad \text{(Eq. 51)}$$

where

E_{VT} = emission factor for vehicular traffic;

k = 0.45 = particle size multiplier for particles <10um (i.e., particles that may remain suspended once they become airborne and which can be inhaled into the respiratory system);

s = silt content of road surface material;

S_p = mean vehicle speed;

W = mean vehicle weight;

w = mean number of wheels; and

D_p = number of days with at least 0.254mm (0.01 inch) of precipitation per year.

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To estimate fugitive emissions due to vehicle travel for a given time period, the emission factor, EVT defined above, is multiplied by the vehicle miles traveled during that time period. Maximum release conditions may be estimated by using a small value of D_p in the model to reflect assumed drought conditions. Average emissions can be estimated by using annual average value for D_p.

Applicability--

The AP-42 dust model is only applicable to dust resulting from vehicular traffic. The SCS model is applicable for wind-blown dust.

Limitations--

The SCS model, as presented, does not provide sufficient detail for application.

4.4.6 Additional Models

Additional models identified but not included here are: Hwang's modification of Farmer, (51,54) RTI Open Dump Model, (42) Hartley Method, (36,55) Hamaker Method, (55) and Dow Method (55). The latter three equations were developed for volatilization of pesticides applied soil.

4.4.7 Non-Aerated Lagoons

Mackay and Leinonen Dynamic Two-Film Model--

This dynamic model (56,57) best serves those instances involving isolated disposal of a given quantity of waste, as opposed to the steady-state scenario offered by the other models. Laboratory validation of this model was reported (57).

This model assumes that nearly stagnant films of well mixed bulk air and water systems occur on both sides of the liquid/air interface.

$$N_i = K_{iL} (C_i - P_i/H_i) \qquad \text{(Eq. 52)}$$

where N_i = mass flux rate (mol/m2-hr)

K_{iL} = overall mass transfer coefficient (m/hr)

C_i = concentration of i (mol/m³)

P_i = equilibrium partial pressure of i in the vapor (atm)

H_i = Henry's Law constant for i (atm-m³/mol)

Applicability--

The model offers an alternative to the steady-state scenario. However, Wetherold (36) reports that despite its theoretical validity, the model is difficult to apply to the "real world." The input parameters are difficult to determine or find in available literature. And, this model best applies to the emissions of single compounds.

Limitations--

The model fails to provide for white caps, thermoclines, eddy diffusion and other similar phenomena, tending to under-predict emissions when these conditions occur at the lagoon.

Thibodeaux, Parker and Heck Model--

This model (52), which can be applied to both non-aerated and aerated lagoons, evolved from basic accepted theories of mass transport. It is used to determine emission rates of individual compounds, assuming that the concentration of each compound remains constant in the aqueous phase (it does not interact with the other compounds present). It also assumes that the influx of the compound is steady, that its biodegradation rate is steady, and that the lagoon surface can be clearly separated into either quiescent (non-aerated) or turbulent (aerated) zones.

To use the equation, four mass transfer coefficients must be determined from impartial relationships.

$$q_i = M_i K_{1i} (X_i - X_i^*)$$ (Eq. 53)

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For each volatile component i:

$$K_i = (\overset{t}{\mathring{K}_i}A_t + \overset{n}{\mathring{K}_i}A_n)/(A_t + A_n) \tag{Eq. 54}$$

$$\frac{1}{K^t} = \frac{1}{k^t} + \frac{1}{Hk_g^t} \tag{Eq. 55}$$

$$\frac{1}{K_i^n} = \frac{1}{k_i^n} + \frac{1}{Hk_g^n} \tag{Eq. 56}$$

where q_i = flux of component i from the lagoon surface (g/cm2-sec);

M_i = molecular weight of component i (g/g-mol);

K_{1i} = overall liquid-phase mass transfer coefficient for component i (mol/cm^2-s);

X_i = mole fraction of component i in the aqueous phase (this must be measured); and

$X_i{}^*$ = mole fraction of component i in equilibrium with the mole fraction of i in air, (Y_i, where if Y_i is assumed to be negligible, $X_i{}^*$ can equal 0);

K_i^t , k_i^n = overall liquid-phase mass transfer coefficient for aerated non-aerated zones of a lagoon, respectively (mol/cm^2-s); and

A_t, A_n = surface areas of aerated and unaerated zones, respectively (cm);

K_i^t, k_i^n = individual liquid phase mass transfer coefficients for the aerated and unaerated zones, respectively (mol/cm-s);

K_g^t , K_g^n = individual gas phase mass transfer coefficients for the aerated and unaerated zones, respectively (mol/cm-s); and

H = Henry's Law constant in mole fraction form ($y = H_x$).

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Applicability--

The Thibodeaux, Parker, and Heck model is applicable to aerated, non-aerated, and combined lagoons. The model assumes steady-state conditions and, therefore, is applicable to undisturbed lagoons. The model is probably not applicable to disturbed (disturbed sludge) conditions.

Limitations--

The accuracy of this model has not been verified as of 1982. Wetherold (36) expressed some skepticism regarding the accuracy or availability of some parameters necessary for the calculation of the mass transfer coefficients. Also, the model requires additional development to satisfy the need for a predictive model capable of predicting total VOC emissions from a lagoon containing a complex mixture of compounds (36).

One way to deal with this, as suggested by DeWolf (52), is to sum up the emissions estimated for several classes of compounds by selecting a representative compound from each class. Acknowledging this selection as "arbitrary", DeWolf provides some suggestions, noting that some compounds are more likely to be encountered and those in mid-molecular weight range of 4 to 8 carbons are "likely to dominate in frequency of occurrence". He suggests:

Class	Compound
Paraffins	Hexane
Olefins	Butene
Aromatics	Toluene
Halogenated hydrocarbons	Methylene chloride
Oxygenated hydrocarbons	Acetone

Smith, Bomberger, and Haynes Model--

The Smith et al. model (36) is applicable to emissions prediction for highly volatile compounds in a lagoon setting. The model is not applicable to low and intermediate volatility compounds. Also, liquid phase resistance should be the controlling resistance.

The volatilization rate is expressed as a first-order kinetic equation.

$$E = (K^a)_{env} (c) \qquad \text{(Eq. 57)}$$

$$(K^a)_{env} = \left(\frac{K^a}{K^o_{Lab}}\right) (K^o)_{env} \qquad \text{(Eq. 58)}$$

where E = mass emission rate per unit volume (lbs/gal-day);

$(K^a)_{env}$ = volatilization rate constant for compound a in the environment (day^{-1});

c = concentration of compound a (lbs/gal);

$\dfrac{K^a}{K^o_{Lab}}$ = ratio of volatilization constants of compounds a and oxygen as K lab measured in laboratory (dimensionless); and

$(K^o)env$ = oxygen reaeration rate in the environment (day^{-1}).

Applicability--

The model is applicable to volatilization of high volatility compounds from non-aerated waste disposal lagoons.

Limitations--

The model is limited in that it is designed to predict emission rates of highly volatile individual compounds and it may be difficult to apply to complex multicomponent wastes. The model is not appropriate for estimating emissions of low or intermediate volatility compounds. Also, Wetherold (1982) notes that determining the ratio of volatilization constants of a compound (K^a/K^o) is expensive in the laboratory; attempts to estimate this ratio simply using diffusion coefficient valves increase the model's overall uncertainty.

Shen Model--

The Shen Model (47,58) presents an empirical equation for determining volatile emissions from lagoons. The Shen Model is (47):

$$ER_{p_i} = 18 \times 10^{-6} \ K_{L_i} \ A \ C_i \qquad\qquad \text{(Eq. 59)}$$

where ER_{p_i} = emission rate potential of compound i (g/sec);

         A = lagoon surface area (cm^2);

         C_i = concentration of compound i in lagoon (mg/l); and

         K_{L_i} = liquid-phase mass transfer coefficient of compound i (g-mol/cm^2-sec).

and,

$$K_{L_i} = 4.45 \times 10^{-3} \ (M_i)^{-0.5} \ (1.024)^{t-20} \ (U)^{\ 0.67} \ (H)^{-0.85} \qquad \text{(Eq. 60)}$$

where M_i = molecular weight of compound i (g/mole);

         t = lagoon surface temperature (o_C);

         U = surface velocity = 0.035 wind speed (cm/sec); and

         H = average liquid depth of the lagoon (meter).

Applicability--

The Shen Model is applicable as a screening technology to estimate volatile emission rates from lagoons. It appears, from Shen's discussion, that the model assumes the lagoon is a dilute water solution, although this is not explicitly stated. Shen indicates that the model should only be used when "emission rates and risks are clearly acceptable or unacceptable."[47]

Limitations--

The model should be limited to use as a screening technology.

RTI Model--

The RTI Model is a simple volatile constituent mass transfer model [42]:

$$E_i = K_i A \ C_i \qquad\qquad \text{(Eq. 61)}$$

where E_i = air emissions for component i from the liquid surface (g/sec);

K_i = overall mass transfer coefficient for component i (m/sec);

A = liquid surface area (m^2); and

C_i = concentration of component i in the liquid phase (g/m^3).

The calculation of the mass transfer coefficient (K_i) will depend on whether the lagoon is quiescent, turbulent, a combination of quiescent and turbulent, or has an oil film. In addition, the equation can be adjusted to account for losses due to biodegradation. Several methods for calculation of K_L are given in the listed reference as well as examples for applying the model to specific site types.

Applicability--

The RTI Model is applicable to assessing volatile emissions from aerated and non-aerated lagoons. The model is applicable to quiescent and turbulent lagoons and can be adjusted to include biodegradation, although the toxic nature of most waste lagoons will limit biological activity. The model is applicable to both undisturbed and disturbed site conditions.

Limitations--

The model is not applicable to lagoons with a surface crust. While the calculation of the mass transfer coefficient includes wind speed for quiescent lagoons, the turbulent lagoon calculations appear to consider wind speed to have negligible affect on the emission rate.

4.4.8 Aerated Lagoons

Thibodeaux, Parker, and Heck Model--

This model is described in 4.4.7.

RTI Model--

This model is described in 4.4.7, and can be adjusted for aeration.

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SECTION 5
CASE STUDIES

Section 5 is a collection of five case studies that demonstrate the protocol described in this manual for developing BEEs. The purpose of this section is to document different experiences regarding site investigation and characterization and to demonstrate the protocol for developing BEEs as applied to these case studies. The sites selected represent different regions of the country, different types and distributions of waste, varying levels of air emissions potential, and varying levels of historical air pathway analyses (APA) performed in support of the Remedial Investigation/Feasibility Study (RI/FS) process.

Only the first case study demonstrates application of the complete protocol. The protocol was implemented only partially at the other sites. The assessment technologies used (or not used) in these case studies do not necessarily represent the best or most technically suitable assessment technologies. Many factors influenced the decision-making process concerning the development of BEEs leading to air pathway evaluations. Also, the work at these sites was conducted without the benefit of a formalized protocol for designing APA programs and developing BEEs.

5.1 CASE STUDY 1: PETROLEUM WASTE LANDFILL/LAGOON

Case Study 1 is a disposal area for wastes from a defunct refinery.

5.1.1 Site History

The petroleum waste site resulted from years of dumping bottom sludge from refinery vessels and tanks at a disposal area located adjacent to the refinery. The on-site disposal activity was performed as general refinery upkeep and was typical of the oil industry at that time.

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This small refinery was located in Southern California between the foothills of a mountain range and a small community. The refinery dumped its wastes on site from about 1930 to 1950. In 1952, the refinery was dismantled except for an old garage and several tanks. Since 1953, the site has been a crude oil pumping station. No known dumping has resulted from the pumping station operation; therefore, all waste dates back over 35 years. At present, the property is separated from an elementary school and a number of residences by a fence and a drainage channel. The site is shown in Figure 22.

The refinery dumped most of its sludge in a landfill on the western edge of the property. The landfill covered approximately one acre of surface area and was bermed at the middle at some unknown time, thereby separating the landfill at the north end from a lagoon at the south end. The landfill is believed to have resulted from dumping soil into the landfill to solidify the liquid waste. Investigations of the site disclosed that the entire landfill/lagoon contained roughly 11,100 cubic yards of waste to a depth of about 6 feet. The waste was an oily sludge, with an odor and appearance typical of refinery wastes.

The site is subject to hot summers and mild winters. Precipitation is approximately 20 inches per year, occurring p. .dominantly during the winter months. During site work, winds generally were light and easterly or northeasterly during cooler periods. During warmer periods, onshore sea breezes yielded moderate breezes from the west and southwest. The residential neighborhood was downwind of the lagoon and landfill most of the time.

5.1.2   Objectives

The objectives of the site work, from an air pathway perspective, were several-fold: provide estimates of the undisturbed and disturbed site emissions; to use BEEs to develop a mitigation plan; and to conduct ambient monitoring during the remedial investigation and mitigation to ensure worker and community protection through the setting of appropriate action levels.

Figure 22. Location of suspected disposal areas.

N

Third St.

Second St.

Property Line

Road

1

8

2

101

103

1050

Main
Waste Pit

Office

2

1

Pole Creek

Sespe Ave.

Flood Control Channel

8

5028

5

6

7

7404, 7403

3

4

Road

Old
Garage
Building

Southern Pacific Railroad

Santa Clara St.

◆   30-foot Meteorological Tower

▲   10-foot Meteorological Tower

▨   Suspected Disposal Areas, 1-8

0 100 200 300 400 500
FEET
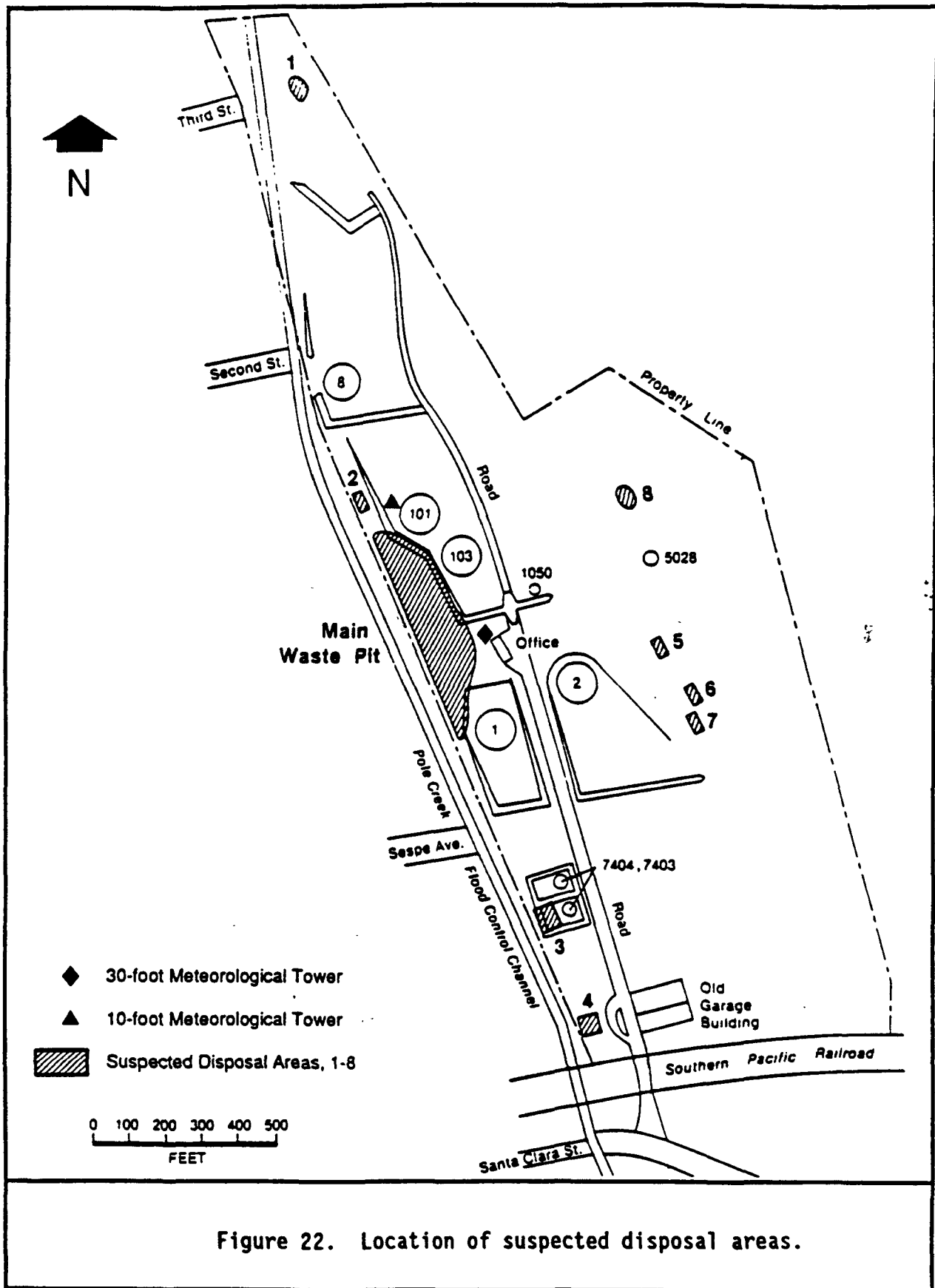
Table 14 summarizes the activities conducted at the site to address the air pathway. These activities are described below.

5.1.3   Scoping

In late 1980, the owner sought regulatory agency approval to remove the waste and apply it to site roads. California's Regional Water Quality Control Board denied the request after two sets of samples, sent to two independent laboratories, disclosed high lead concentrations in the waste. The owner then sought a more thorough environmental evaluation of the site and recommendations for remediation.

The initial task in completing the scoping phase of the site characterization was a review of existing data. Information was collected from the owner's site files, from files at a similarly operated refinery, from public agencies, and from available references. The collected data were reviewed to provide a working knowledge of the site history, conditions, and environmental setting. Essentially no activities had been conducted to determine waste volume, environmental impacts, emissions characteristics, or waste existence and type in other suspected disposal areas.

The site investigation was initiated by a site inspection. The inspection served to familiarize the crew with the site, to locate special features, and to assist in the development of appropriate sampling methods. This undertaking identified two types of wastes: a tar-like waste and a granular waste that gave off fumes and white vapors when it came in contact with water. The granular waste caused eye irritation and hindered breathing. Based on this site scoping, the potential for volatile air emissions during site mitigation was deemed to be high and further site characterization activities were initiated.

TABLE 14. APA ACTIVITIES CONDUCTED AT THE SITE

APA Objectives

Determine the baseline and disturbed emissions for the site using direct
emission measurement technologies. Protect on-site workers and the public
from air emissions during the investigation by using air monitoring and action
levels to stop site work.

Scoping

The lagoon and landfill were determined to contain petroleum waste that had a
moderately high volatile organic air emissions potential. Particulate
emission potential from the sludge/tar-like solid waste was considered to be
low.

Screening Measurements

The site was surveyed using real-time instruments (indirect technology) for
indicator compounds on a grid system. Soil samples were collected for head
space analyses to assess air emissions potential (direct technology). These
data were used to design the in-depth measurement strategy.

In-Depth Measurements

The in-depth emission measurements included:

- Undisturbed baseline emission measurements using the surface
  emission isolation flux chamber;

- Disturbed baseline emission measurements using the downhole emission
  chamber; and

- Air monitoring for worker and public protection.

These data were used to develop undisturbed and disturbed site BEEs.

Mitigation

Undisturbed and disturbed BEEs were used to develop a remedial alternative
that included excavation and removal of the waste and air emissions control
technologies.

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5.1.4 Overview of Fieldwork for Site Characterization

An undisturbed emission survey (see 5.1.5) was completed to assess the atmospheric impacts of volatilized compounds under prevailing site conditions. The emission survey used indirect real-time instrument measurement techniques. Knowledge of the type of waste indicated that total hydrocarbons and benzene, as representative of aromatic species, were good indicator compounds for volatile emissions from the petroleum waste. It was also possible that sulfur dioxide (SO_2) could be an air contaminant from the waste. Thus, total hydrocarbons, benzene, and SO_2 were selected as the indicator compounds. Other compounds may have been equally well suited for use as indicators, but the compounds selected proved to be adequate. Testing for these compounds showed low emissions (less than three times background levels) of total hydrocarbons, benzene, and SO_2. This result was obtained by comparing on-site emission rate data to background or off-site data. It was concluded that no significant atmospheric impacts existed on or off site for undisturbed site conditions.

To assess the potential impacts of air emissions of the combined site during remediation and to provide adequate monitoring for on-site personnel and nearby residences, a monitoring program was conducted that included: constant meteorological monitoring at two stations; monitoring for emissions from waste disturbance activities at the property boundary between the waste and the nearby residences; and surveying of corehole borings.

Two meteorological towers (see Figure 22) were used to collect continuous data. A 33-foot tower equipped with meteorological instrumentation collected the primary meteorological site data during the field activity. In addition, a 10-foot tower provided micro-meteorological wind speed and wind direction data. The towers were positioned upwind and downwind of the landfill and lagoon. Meteorological data were used in receptor modeling, in conjunction with the measured emission rate data, for planning remedial options.

Additional waste characterization efforts were performed. Five core holes were drilled through the waste and into the soils below the waste to

permit sampling of the waste and soils and examination of waste and soil stratification and physical properties. They also provided a means for measuring volatile species emissions as a function of depth in the waste. Wastes were found to be only 5 or 6 feet deep over the 50,000 square-foot pit area, for a total of approximately 11,100 cubic yards of wastes in the landfill and lagoon. Wastes were generally soft and semi-fluid in the lagoon and hard or soil/waste mixtures in the landfill. The waste had a pH below 2.0, contained varying levels of trace metals (including high concentrations of lead in some samples), and had a very high percentage of organic material. Soils below the wastes were predominantly alluvial gravels mixed with sand and silt. The soils rapidly buffered acidic waste leachate. Trace metals were found in varying concentrations and no apparent trend existed with depth. The underlying soils had been impacted by low levels of hydrocarbons originating in the waste pit.

In addition to the air-related work described above, extensive work was undertaken to assess the impact of the site on local ground water. Also, eight small areas suspected of being former waste disposal areas were investigated.

The site inspection data were reviewed and a subsequent site investigation plan was developed. This included an undisturbed emission survey, air monitoring on-site and at the fenceline during drilling and sampling of wastes in the landfill and lagoon, and an emissions survey under disturbed conditions to estimate the potential for emissions during possible future disturbance of the wastes during an excavation activity.

5.1.5 Undisturbed Emissions Survey

Both screening and in-depth measurements were performed.

Screening Measurements--

A survey of the undisturbed surface emissions was conducted. First, the main waste pit disposal area was surveyed and a map was prepared with a grid

system overlying the waste area to provide location reference. An emissions survey was performed which consisted of a real-time instrument survey (an indirect measurement screening technology) for indicator species at randomly selected grid points mapped over the landfill and lagoon. This survey provided general data on the level of gas concentrations from the landfill and lagoon, identified potential areas of higher concentrations, documented background conditions (i.e., gas species concentration background levels), and provided input into the safety program, ensuring adequate worker/operator protection. This screening technology was selected because it was a quick and inexpensive way to survey the site for areas of high air emissions potential. These data could then be used to design the in-depth measurement approach.

During the emission screening, portable, real-time monitors were used to determine sulfur dioxide (SO2), total hydrocarbon compounds (THC), and aromatic compounds (benzene). THC measurements were made with an organic vapor analyzer (OVA). SO_2 measurements were made with an electrochemical cell instrument. The HNU analyzer was used to detect aromatic species reported as benzene. SO_2, THC, and benzene, as well as surface and air temperature, were measured at 27 grid node points under quiescent conditions. The portable analyzers provided rapid feedback, but could not differentiate between various hydrocarbon or sulfur species.

For this site, benzene, SO_2, and THC were used as indicators of air emissions. Benzene is a carcinogenic contaminant representative of aromatic compounds. Sulfur dioxide was a possible inorganic air contaminant on site. Total hydrocarbons were monitored for an indication of total organic air emissions.

In-Depth Measurements--

After completion of the screening measurements, in-depth measurements were conducted to quantitate the gas emissions from the undisturbed site for risk assessment purposes and to aid in siting drilling locations. The need for this type of sampling was determined before any screening measurements were performed, based on the waste type and the proximity of receptors (i.e., the suspected large volume of highly volatile wastes was considered likely to

cause significant air impacts during any remedial waste removal or disturbance activities). Direct emission measurements were performed using an emission isolation flux chamber. This in-depth technology was selected because it is ideally suited to obtain emission rates from homogenous area sources. The flux chamber is relatively easy to use and multiple measurements (i.e., 8 to 10) can be obtained in one day. Gas samples collected from the flux chamber outlet line were analyzed using real-time analyzers. Samples also were collected in gas canisters for detailed hydrocarbon speciation in an off-site laboratory.

The site was divided into zones of high and low emissions potential based on plotted results from the real-time instrument survey. Locations for in-depth measurements were randomly selected from grid cells in these different zones. Based on the results of the real-time instrument survey, nine flux chamber measurements were performed to assess the undisturbed emission from the main landfill/lagoon. The flux chamber was constructed and operated as described in Section 4. Measurements at a given grid point were typically made over a 40-minute time period.

Chemical measurements performed on the air leaving the emission chamber included:

- Continuous determination of SO_2 (Interscan);
- Continuous determination of THC (OVA);
- Continuous determination of benzene (HNU); and
- Grab sampling for organic speciation (Photovac 1010).

Undisturbed Emission Survey Results--
A total of 27 grid nodes were sampled, including sampling at five background locations (upwind of each block), five duplicate sample points, and sampling at one control point location at three different times of the day (morning, noon, and afternoon). The control point was one of the grid points that was regularly sampled to establish an estimate of the temporal variability in emissions at the site.

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Very low gas concentrations were observed over the exposed waste. Most of the screening measurements showed background levels at the locations sampled for SO_2, THC, and benzene as shown in Table 15. Moderately low levels of undisturbed emissions were observed over exposed waste in the lagoon and the landfill. Table 16 provides undisturbed site emissions data.

The results of the screening and in-depth emissions testing showed that:

- The emissions were highest in the landfill and lagoon where wastes were exposed (especially where natural disturbances occurred; i.e., cracking of surface, waste seeps, etc.);

- Control point sampling at various times of the day (same location) indicated a large temporal variation in emissions due primarily to solar surface heating;

- Areas surrounding the combined site or in overburden on top of the waste material showed background levels of emission; and

- Volatile emission rates from the combined site (landfill and lagoon) were low for SO_2 and benzene under undisturbed conditions. For steady-state conditions: SO_2 emission rates ranged from background to 5.6 ug/m^2 minute^{-1}; THC emission rates ranged from background to 120 ug/m^2, minute^{-1}; and benzene from background to 470 ug/m^2, minute^{-1}. Emissions did show a high dependence on diurnal temperature fluctuations with more emissions observed during the hottest periods, as expected. The field photovac analytical capability provided limited hydrocarbon speciation data that helped direct more detailed hydrocarbon sampling and analysis. The photovac data were not used to determine emission estimates.

5.1.6 Disturbed Emissions Survey

Both screening and in-depth measurements were performed.

TABLE 15. SUMMARY OF SCREENING MEASUREMENTS OF UNDISTURBED WASTE

Number of Measurements	SO$_2$ (ppm)		THC (ppm)		Benzene (ppm)	
	Peak	Average	Peak	Average	Peak	Average
41	0.005	0.005	2-4[a]	2-4[a]	0.01-0.80[b]	0.01-0.70[b]

[a] Differences probably due to instrument drift.

[b] Background levels only detected at 30 of 41 points.

TABLE 16. CASE STUDY 1: SUMMARY OF UNDISTURBED SITE EMISSIONS DATA

Lagoon Location (Surface)	SO_2 (mg/m², min⁻¹)	THC[a] (ug/m², min⁻¹)	Benzene[b] (ug/m², min⁻¹)
#1	0.14	1.8	4.7
#2	0.14	120	470
#3	0.14	7.3	43
#4	0.14	44	1.8
#5	5.6	7.3	11
Average	1.2	36	98
Landfill Location			
#1	0.14	7.3	3.6
#2	1.4	29	3.6
Average	0.77	18	3.6

[a] As determined by portable FID (OVA).

[b] As determined by portable PID (HNu).

Screening Measurements--

Samples of soil/waste were collected during drilling at each sampling point as part of the screening survey. Screening for volatile organic compounds (VOCs) in these samples was performed at the field site with a Photovac 1010 portable photoionization gas chromatograph (GC). This GC has part-per-billion (ppb) level sensitivity for milliliter volumes of air. Soil and waste samples were collected (2 to 3 grams) and stored in 40 mL VOA vials with Teflon\ SEPA. The vials were equilibrated in a 30°C water bath for 30 minutes prior to the head space analysis for VOCs. This sampling procedure is considered a direct measurement screening-technology.

During disturbance activities, fenceline monitoring for SO_2 and benzene was conducted using portable real-time instruments. Also meteorological conditions were monitored during all work disturbing the site. Action levels were established to require cessation of site activities if exceedances were noted (none occurred) to protect the local community.

Downwind and border monitoring consisted of three activities:

- SO_2 and THC were monitored immediately downwind of the disturbance activity;

- SO_2 and THC were monitored at a mobile unit approximately 40 feet downwind of the initial disturbance activities; and

- SO_2 and benzene were monitored at a mobile unit at the downwind fenceline between the drilling operation and the nearby residences.

Standard monitoring procedures (see Volume IV of this series of manuals) were used in operating the border and downwind stations. Air analyzers were operated according to written quality control protocols and continuous data printouts were collected using strip chart recorders. The monitoring stations were positioned each day based on wind direction data from the meteorological stations.

In-Depth Measurements--

Downhole emission measurements at various depths in the waste were conducted during drilling activities to determine an emissions "profile" in the waste. These data were used to characterize the waste properties and to predict potential gas emission from the wastes if they were excavated.

Downhole emissions measurements were performed using the direct emissions measurement technique (i.e. downhole flux chamber). This technique is considered an in-depth measurement technology and was applicable for the landfill and the lagoon. The plexiglas chamber had an exposed surface area of 0.00318 m^2. The chamber input and output lines were 40 feet long, facilitating flux measurement to 30 feet below land surface.

Five locations for drilling were selected as part of the solid waste investigation. They are shown in Figure 23. They were representative of waste bodies and were equally spaced across the waste areas. Hydrocarbon samples were collected in 2.8-liter stainless steel canisters. After collection, the canisters were shipped to an off-site laboratory for analysis.

A total of 18 downhole emission measurements were performed and realtime data for SO_2, THC, and benzene were collected at each point using the real-time analyzers. Canister samples were collected at six locations (at various depths within the five core holes) for speciation analyses. Canister samples were not collected at all sampling locations in an effort to conserve project resources. The indicator compounds were used to represent air emissions potential in the absence of the canister samples.
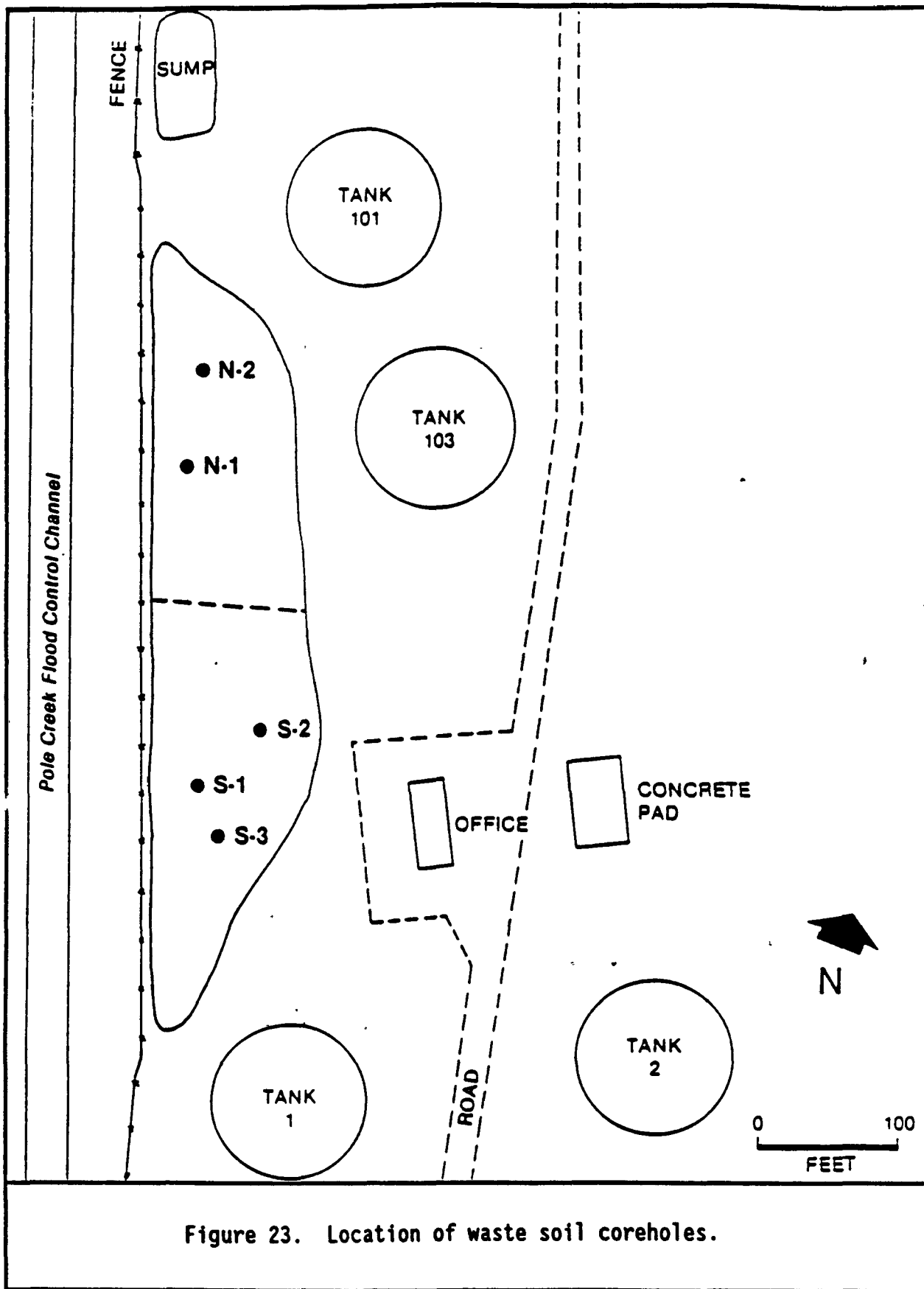
Figure 23. Location of waste soil coreholes.

Disturbed Emission Survey Results--

The results of air monitoring conducted during drilling are summarized in Table 17. The results of border and immediate downwind monitoring for disturbed site activities indicated no significant impact from fugitive emissions downwind from the site (northeast) boring activities. Even though the disturbed waste had a high emissions potential, small amounts of waste were exposed in the drilling operations following the conservative operating procedure. The border station was positioned on the west border to ensure neighborhood safety. This location also provided valuable onsite safety information for site operations personnel.

The results of the downhole emissions survey included peak and steady-state emissions for SO_2 and THC at the given depth. Benzene data were not collected due to the lack of an extractive pump in that analyzer that could pull the sample through the long sampling lines. The steady-state values are more representative of the level of emissions expected involving a disturbance of the waste (i.e., removal). Data results are presented in Table 18 to illustrate the SO_2 and THC emissions observed as a function of the type of waste/soil. This format illustrates the relative emissions characteristics of SO_2 and THC per depth in the cores as well as the emission tendencies of the waste/soil. A comparison of peak to steady-state emission values is used to identify emission sources in the waste pit (i.e., limit of vertical contamination).

Volatile emission rates from the site under disturbed conditions were higher than the undisturbed site and demonstrated potential for volatile emissions during waste disturbance activities. The SO_2 emission rates under disturbed conditions ranged from background (1.6 EE4 ug/m^2, minute^{-1}) to 1.1. EE6 ug/m_2, minute^{-1}, and the THC emission rates ranged from 3.8 EE3 ug/m^2, minute^{-1} to 3.8 EE6 ug/m^2, minute^{-1}. The results of the hydrocarbon speciation analyses indicated the following hydrocarbon composition:

TABLE 17. DOWNWIND/BORDER MONITORING RESULTS

Location	Date	Species	High Level[d] (ppmv)	Duration
West Border (Fence) Core S-1	08/02/83 08/02/83 08/02/83	Benzene[a]	0.12^c Background Background	Elevated Background
Downwind 40 m Core S-2	08/03/83	SO_2[b]	Background	
West Border (Fence) Core S-2	08/03/83 08/03/83	Benzene SO_2	Background Background	
West Border (Fence) Core S-3	08/05/83 08/05/83	Benzene SO_2	0.35 0.12	<5 minutes
West Border (Fence) Core N-1	08/08/83 08/08/83	Benzene SO_2	0.12^c Background	
West Border (Fence) Core N-2	08/09/83 08/09/83	Benzene SO_2	0.16^c Background	

[a] Benzene instrument (HNU) background typically 0.1 ppmv.

[b] SO_2 instrument (Interscan Analyzer) background typically 0.05 ppmv.

[c] Reading attributed to instrument drift.

[d] Background refers to instrument reading in "clean" air.

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TABLE 18. SUMMARY OF DOWNHOLE EMISSIONS DATA

Core	Depth (ft)	SO_2 (ug/m^2 min^{-1}) Peak	SO_2 Steady[b] State	THC (ug/m^{2}min^{-1}) Peak	THC Steady[b] State
S-1	5	$<1.9E^4$	$7.2E^3$	$1.6E^2$	$3.8E^1$
	7-1/2	$>1.1E^4$	$3.8E^3$	$1.3E^4$	$6.8E^3$
	15	$2.2E^3$	$\leq 8.3E^2$	$>3.8E^4$	$6.8E^1$
Average			$3.9E^3$		$2.3E^3$
S-2	2-1/2	$1.1E^4$	$5.4E^3$	$1.9E^3$	3.83^1
	4-1/2	$6.0E^3$	$1.9E^3$	$8.3E^3$	$3.8E^1$
	15	$2.5E^3$	$1.7E^3$	$>3.8E^4$	$9.5E^1$
	20[a]	$>1.1E^4$	$>1.1E^4$	$>3.8E^4$	$>3.8E^4$
	20	$4.0E^3$	$2.9E^3$	$>3.8E^4$	$3.8E^2$
Average			$4.6E^3$		$9.3E^5$
S-3	5	$1.6E^2$	$1.6E^2$	$4.6E^2$	$7.6E^1$
	10	$4.6E^2$	$4.6E^2$	$>3.8E^4$	$>3.8E^4$
	15	$7.6E^2$	$4.6E^2$	$1.6E^4$	$7.6E^3$
	20	$3.0E^2$	$1.6E^2$	$>3.8E^4$	$2.3E^2$
	30	$6.0E^2$	$1.6E^2$	$>3.8E^4$	$6.0E^2$
Average			$2.3E^2$		$9.3E^5$
N-1	5	$1.1E^3$	$1.6E^2$	$>3.8E^4$	$3.8E^2$
	10	$1.7E^3$	$1.7E^3$	$1.1E^4$	$8.8E^2$
	15	$9.7E^2$	$7.6E^2$	$2.3E^4$	$2.0E^2$
	25	$1.1E^3$	$7.6E^2$	$>3.8E^4$	$2.9E^2$
Average			$8.5E^2$		$4.4E^2$
N-2	10	$1.6E^3$	$1.3E^3$	$>3.8E^4$	$5.6E^3$
	20	$6.7E^2$	$6.8E^2$	$>3.8E^4$	$2.6E^2$
Average			$9.9E^2$		$2.9E^2$

[a]Range of emissions, two measurements were conducted.

[b]Steady-state values were averaged by core by operable unit to determine BEEs.

E = Exponential Notation ($7.2E^3$ = 7.2×10^3 = 7200).

Hydrocarbon Class	Average %	Range %[a]
Alkanes	79.0	68 - 87
Alkenes	15.0	0.87 - 21
Aromatics	4.2	2.4 - 8.1
Oxygenates	0.62	0.15 - 1.5
Halogenated	1.2	0.091- 3.3
Sulfonated	ND	ND
Unidentified	2.0	0.42 - 6.6

[a] 5 cores, 6 canister samples

These data show that most of the air emissions were alkane species and of no significant concern regarding toxicity. The aromatic fraction was, as expected, around 5 percent, and was composed of numerous compounds.

5.1.7 Development of BEEs

Calculation of baseline emission estimates (BEEs) can be developed from either ambient concentration data (indirect techniques) or from emission rate measurement data (direct techniques). BEEs can be calculated for each contaminant species detected or for a group Table 18 of contaminant species. BEEs obtained from direct measurement techniques which provide rate data (i.e., mass per unit time per given surface area) are preferable. The BEE is normalized for the area of the source and has units of mass of contaminant or group of contaminants per time.

BEEs can be calculated from individual emission sources and summed for sites containing multiple emission sources (operable units), such as a lagoon and a landfill with each source characterized by different air emission rates and contaminant species.

The calculation of an undisturbed emission estimate for this site included the following considerations. The site consisted of a waste area containing a landfill in the northern portion and a lagoon in the southern portion, separated by a berm. Each portion of the site was evaluated separately. Undisturbed emission factors for each of the two operable units were calculated separately and then averaged to provide an overall site

emission estimate. The undisturbed emission rates for the lagoon and the
landfill, and the combined site emission estimate calculations are presented
below.

The undisturbed BEE for the lagoon (average) was calculated for SO_2 and
THC. The surface emission isolation flux chamber survey results from five
single measurements were averaged by species and multiplied by the lagoon
surface area to determine the unit BEE.

$$\text{Lagoon BEE}_{SO_2} = (1.2 \text{ug/m}^2\text{-min})(6860 \text{ m}^2) = 8.2 \times 10^3 \text{ ug/min of } SO_2$$

$$\text{Lagoon BEE}_{THC} = (36 \text{ ug/m}^2\text{-min})(6860 \text{ m}^2) = 2.5 \times 10^5 \text{ ug/min of THC}$$

Similarly, the BEE for the landfill operable unit (average) was calculated for
SO_2 and THC. The emission isolation flux chamber survey results were averaged
for each species and multiplied by the surface area of the landfill to
determine the unit's BEE.

$$\text{Landfill BEE}_{SO_2} = (0.77 \text{ ug/m}^2\text{-min})(7240 \text{ m}^2) = 5.6 \times 10^3 \text{ ug/min of SO}$$

$$\text{Landfill BEE}_{THC} = (18 \text{ ug/m}^2\text{-min})(7240 \text{ m}^2) = 1.3 \times 10^5 \text{ ug/min of THC}$$

The overall site BEE (for SO_2 and THC) can be obtained by summing the
respective unit BEEs by species.

Calculation of emission estimates for disturbed site conditions can be
performed from either air monitoring data (concentration measurements) during
waste disturbances or from direct emission rate measurement data.
Concentration values can be expressed as a concentration (ppm-v) for each
species, as a ratio of the species concentration to the total concentration
from all species, or as a percentage value for the species of interest over
the total concentration contributed from all other species. The disturbed
site emission flux data has the units of mass per time per unit area.

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The emission estimate is calculated by multiplying the average measured emission rate by the total surface area of disturbed material. This results in a single value of mass per unit time which provides a relative estimate of the rate of air emissions from the source. Emission estimates can be calculated for a site with either individual sources or with multiple sources. These operable units often are investigated and remediated independently. Emission estimates for a combined site can be calculated by using the highest disturbed emission estimates for each source and summing the emission per time for each source.

Summaries of the average disturbed emissions flux for both units of the Case Study 1 site are presented below:

Landfill

SO_2 = 9.2 x 10^2 (ug/m^2-min)

THC = 1.7 x 10^3 (ug/m^2-min)

Lagoon

SO_2 = 2.9 x 103 (ug/m^2-min)

THC = 6.4 x 103 (ug/m^2-min)

These data can be used in conjunction with estimates of exposed disturbed waste to predict air impacts from various waste disturbance and treatment technologies.

Example

Excavation of the landfill would typically expose 50 m^2 of waste at a time. The estimate of THC air emissions from the site activity would be:

THC (landfill) = 1.7 x 10^3 (ug/m^2, minute^{-1}) x 50m^2
= 8.5 x 10^5 (ug/min)

Depth-specific information could be used to provide area and depth-specific emission estimates as needed.

5.1.8 Summary

The Case Study 1 investigation was generally a thorough, well documented study that fully addressed the air pathway for volatile contaminants. The study followed closely the steps outlined in this manual's protocol and all objectives were met. Furthermore, site personnel report that the knowledge of the potential for emissions, ultimately resulted in a safer and more cost-effective remediation of the site. BEEs were used in risk assessment and in designing removal plans. Air emission control technologies were selected based on the BEEs.

5.2 CASE STUDY 2: BRUIN LAGOON

Case Study 2 is a disposal lagoon that received various wastes from a mineral oil refinery. This site was under remediation in 1984 when subsurface gases were unexpectedly released during cleanup. Work was halted and the remedial design was reassessed. A second Remedial Investigation/Feasibility Study (RI/FS) was then performed. This case study focuses on the APA conducted during this second RI/FS (see Table 19).

5.2.1 Site History

Bruin Lagoon is located about 45 miles north of Pittsburgh, in Bruin Borough of Butler County, Pennsylvania. The 4-acre site is situated along the western bank of Bear Creek's South Branch, approximately 7 miles upstream of the creek's confluence with the Allegheny River. Part of the site lies within the creek's 100-year floodplain. To the west, the site is bordered by private homes and State Route 268. Bruin Borough's main residential and commercial areas are within five blocks of the site and more than 30 residences are within 500 feet of the lagoon. To the south is an abandoned refinery, which is the source of the wastes deposited in the lagoon. Also, adjacent to the site are two ponds and a small stream that drain into Bear Creek.

TABLE 19. APA ACTIVITIES CONDUCTED AT THE CASE STUDY #2 SITE

APA Objectives

Assess the extent and composition of subsurface gas pockets. Monitor the ambient air for health and safety reasons.

Scoping

Initially, the lagoon was determined to contain wastes that had minimal potential for volatile or particulate matter emissions (first RI/FS). The second RI/FS did assume that volatile emissions from subsurface gas pockets were likely.

Screening Measurements

A variety of portable, real-time analyzers and detector tubes were used to monitor the ambient air during drilling activities. Monitoring took place at the site perimeter and in the ambient breathing zone near the drill rig. Soil samples were collected and the emissions from the samples were scanned. The screening data were used to design the in-depth measurement strategy.

In-Depth Measurements

The in-depth emission measurements involved collecting and analyzing grab samples of gas from boring/wells whenever the ambient breathing zone monitoring showed elevated concentrations significantly over background levels. However, these data were not used to develop undisturbed and disturbed site BEEs.

Mitigation

The disturbed waste emissions data were used in the development of the remedial action plan. Although disturbed emission rates were not calculated, knowledge of areas considered to be "hot spots" were used to conduct site operations in a way that prevented major releases of air toxics to the air. The remedial alternative included gas monitoring during on-site stabilization and neutralization of the unstabilized sludge and collecting, venting, and treating as necessary.

Currently in remediation, Bruin Lagoon is an unlined earthen diked lagoon that has been partially covered with 9300 cubic yards of stabilized soil/ sludge mixture treated during the first attempt at remediation. Beneath this material is approximately 17,200 cubic yards of unstabilized sludge/tar, with up-welling of the waste in a number of areas. The sludge/tar contains sulfuric acid and heavy metals, along with other contaminants. The lagoon area of the site is generally level and lacks vegetation. A cross-sectional view of the site is shown in Figure 24.

Bruin Oil Company, producer of white (mineral) oil, began disposing of its wastes at the lagoon in the 1930s. This continued for more than 40 years. Materials discarded there included:

- Residues scraped from crude oil storage tanks;
- Used bauxite, charcoal filtering agents, and bone powder;
- Oils not meeting specification;
- Coal fines;
- Lime;
- Spent alkali; and
- Boiler house coal and ashes.

The lagoon attracted national attention in 1968 when about 3,000 gallons of acidic sludge spilled into the South Branch of Bear Creek through a breach in the dike. In the Allegheny River, roughly 4 million fish died and many downstream communities temporarily lost their water supplies. The spill was addressed, but the remedial investigation of the site didn't begin until 1981.

The abandoned refinery and the lagoon were owned by AH & RS Coal Company, which underwent bankruptcy proceeding in 1986.
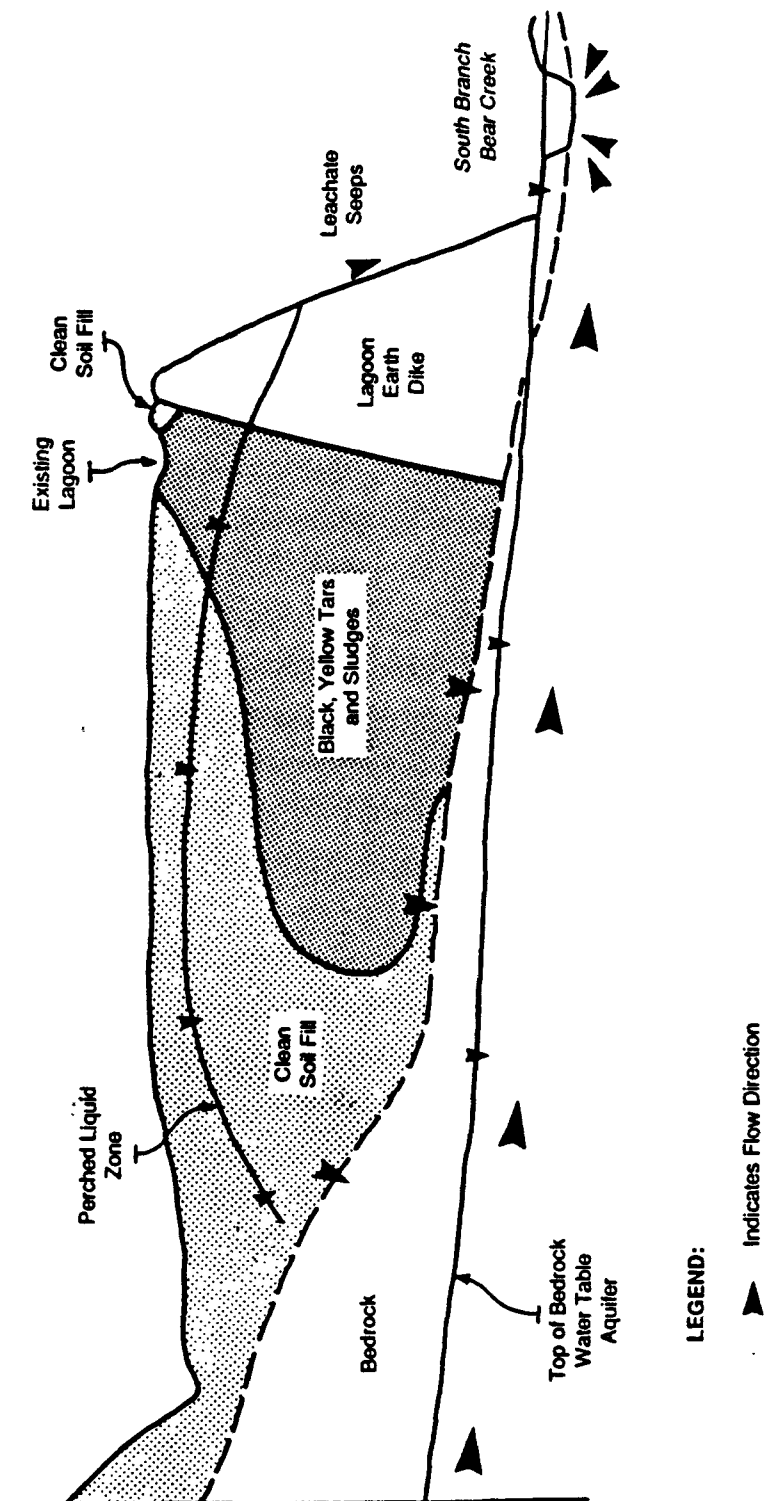
Figure 24. Generalized flow regime of perched zone and bedrock aquifer.

5.2.2 Objectives

The objectives of the site work, from an air pathway perspective, were two-fold: to monitor the ambient air for health and safety reasons; and to assess the extent and composition of subsurface gas pockets. To meet the latter objective, sampling and analysis of vapors contained in the shallow wells were performed to: identify the composition and extent of gases trapped under the site; determine their regeneration rates; and assess the potential for their release into the atmosphere during remedial construction work.

5.2.3 Scoping

The existing data were reviewed to provide a working knowledge of the site history, conditions, and environmental setting. Based on this review, no specific potential emission characterization was called for in the first RI/FS. After unexpected emissions were encountered when drilling through the bottom of the lagoon during remediation, the second RI/FS did address the air pathway to a greater extent.

5.2.4 Overview of Fieldwork For Site Characterization

EPA contractors began what would become the first RI/FS at Bruin Lagoon in July 1981. Air monitoring during this remedial investigation failed to find detectable levels of organics, sulfur dioxide (SO_2), hydrogen sulfide (H_2S), hydrogen chloride (HCl), or hydrogen cyanide (HCN) in ambient air at the site. Although one well boring showed organic vapors during drilling operations, the levels were not detectable at the ambient breathing zone. Significantly, no borings through the open lagoon were performed in this initial effort.

With the RI/FS completion in January 1982, EPA and the Pennsylvania Department of Environmental Resources (PADER) selected a remedial alternative that included sludge stabilization, dike reinforcement, debris removal, and construction of a multi-layer cap to cover the lagoon. Design kicked off in September 1982 and cleanup actually started in August 1983.

The project proceeded until May 4, 1984, when hazardous gas and acid mist escaped from an unanticipated crust, thought to be the bottom of the lagoon, that was broken during mitigation. These organic vapors and sulfur dioxide or hydrogen sulfide reached the ambient breathing zone but were not detectable at the site perimeter. Gas sampling was performed for worker and public protection. Gas samples from beneath the crust revealed high concentrations of carbon dioxide, hydrogen sulfide, and sulfuric acid mist. Consequently, EPA suspended cleanup activities and immediately launched in emergency response, which included some removal, covering the lagoon with stabilized sludge, installing 13 shallow gas monitoring wells, and collecting and analyzing additional sludge and soil samples.

The site remained in the emergency mode until September 1984. The second RI/FS was initiated the following January. Air monitoring conducted throughout this RI included:

- Health and safety;
- Site perimeter;
- Ambient breathing zone;
- Downhole concentration sampling and analysis; and
- Sample screening.

Conclusions drawn from a review of all of these activities (the two RI/FS endeavors and the emergency action) included identification of a "hot spot" in the unstabilized portion of the lagoon that contained carbon dioxide, hydrogen sulfide, sulfur dioxide and methane at levels deserving attention during remediation. The RI/FS concluded, however, that subsurface gases were not present throughout the site. To address the "hot spot" the remedial alternative selected in September 1986 included gas monitoring, venting, and treating during excavation, followed by post-closure monitoring.

5.2.5 Undisturbed Emissions Survey

Based on the available documentation, no screening or in-depth measurements were made to assess the undisturbed emission at the site. Since the site contains heavy metals and is unvegetated, an evaluation of the entrained particulate matter from the site would have been advisable, and some screening measurements for particulates and inorganic gases may have been warranted. Some air monitoring was performed immediately prior to site disturbances. These limited data do address undisturbed emissions.

5.2.6 Disturbed Emissions Survey

Both screening (air monitoring and sample headspace) and in-depth (soil vapor well) measurement techniques were used to assess the emissions during site disturbances such as drilling. The following discussions are largely taken from the second RI/FS prepared for the Bruin Lagoon site (59).

Screening Measurements--

The following air monitoring equipment was available on site during all drilling activities:

- HNU photoionization detector (PID) with 11.7 and 10.2 eV probes;
- OVA (organic vapor analyzer) flame ionization detector (FID);
- H2S portable gas monitor;
- SO_2 portable gas monitor;
- H_2S monitor alarms;
- Explosimeter/oxygen monitor; and
- Detector tubes SO_2, H_2S, H_2SO_4, O_2, CO_2, natural gas.

Based on gases detected in past site work, portable direct reading real-time instrumentation was primarily used for gas characterization and health and safety purposes. Detector tubes were used for screening of possible instrumentation interferences, confirmation of direct reading concentrations, and analysis of gases not detected on available instrumentation.

The direct reading monitoring instruments determined to be most effective for monitoring drilling operations were the HNU PID (11.7 eV), H_2S portable gas monitor, H_2S monitor alarms, and SO_2 portable gas monitor. The HNU PID was selected over the OVA FID due to the sensitivity of this instrument to hydrogen sulfide gas. The HNU PID could detect both hydrogen sulfide gas and organic vapors. This selection was made because of past historical data demonstrating possible H_2S gas release.

Periodic monitoring of ambient air at the site perimeter was routinely performed during drilling operations. Also, if ambient breathing zone concentrations indicated possible gas releases, perimeter monitoring was immediately initiated. Seventeen monitoring locations were established along the site fence line at intervals of approximately 150 feet and marked with stakes. Figure 25 shows the perimeter monitoring locations. Perimeter monitoring was conducted with the H_2S and SO_2 portable gas monitors and the HNU PID.

During all drilling operations, the H_2S and SO_2 portable gas monitor, H_2S monitor alarms, explosimeter/oxygen monitors, and HNU PID were used for characterization of the ambient breathing zone. Background levels were determined prior to starting the drilling.

Portable instrument readings provided continuous, real-time monitoring of each split spoon and drilling depth to determine at what depth, if any, gas releases occurred. Each split spoon and core sample was scanned with Figure 25 all direct reading instrumentation immediately after collection. Samples showing positive readings were usually selected for chemical analysis.

In-Depth Measurements--

If ambient breathing zone monitoring showed elevated concentrations significantly above background levels, a grab sample of the gas present in the boring/well was collected for analysis. These grab samples were analyzed to characterize the emitted gases. Grab samples were collected from a point approximately 3 feet below the ground surface by inserting tubing into the
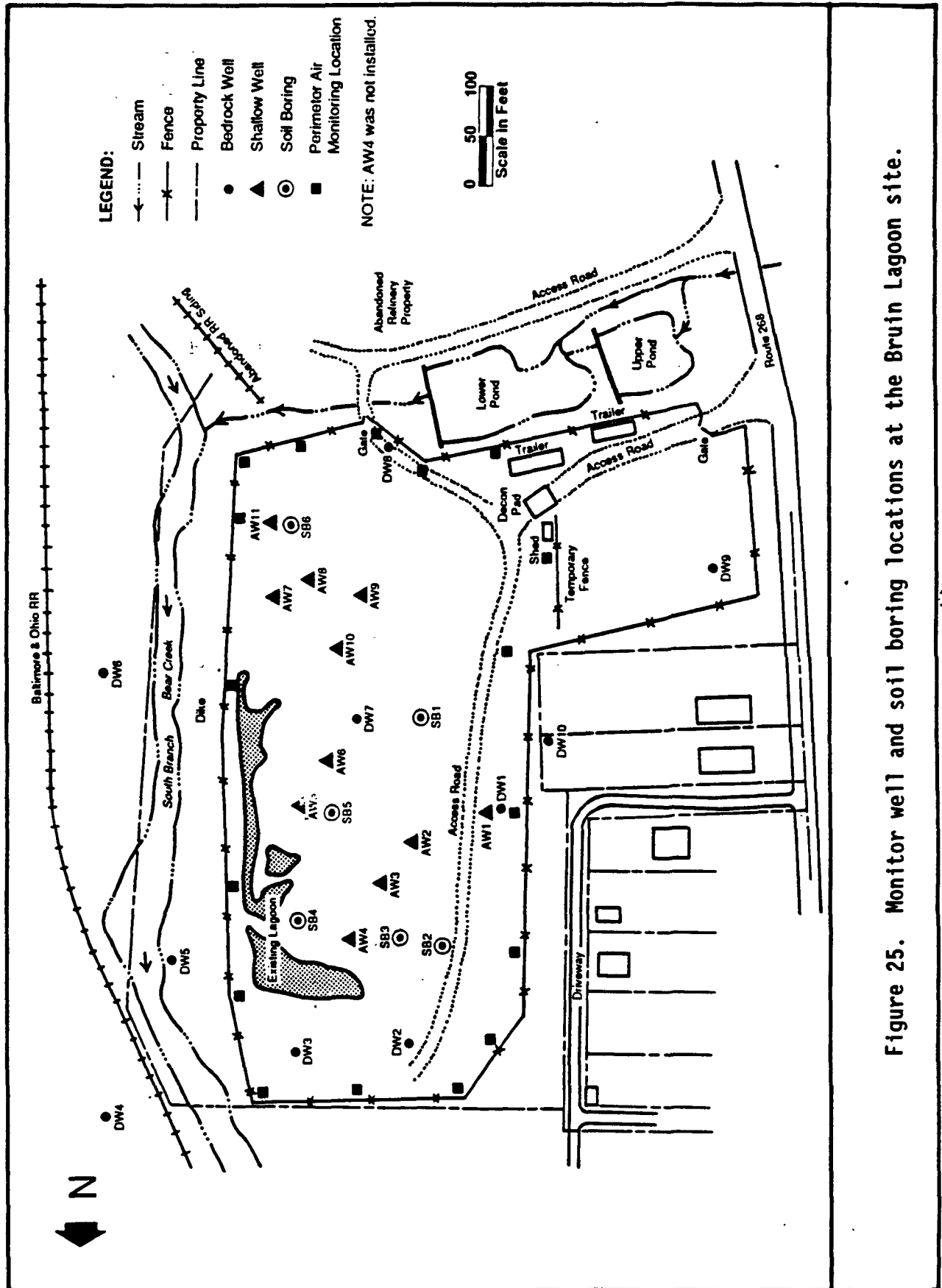
Figure 25. Monitor well and soil boring locations at the Bruin Lagoon site.

boring/well and pumping the gas into an air bag collector. The bag sample was then sealed and analyzed on-site using available instrumentation and detector tubes.

Disturbed Emission Survey Results--

The following results are taken from the second RI/FS prepared for the Bruin Lagoon site (59).

Air monitoring conducted during the 1981 remedial investigation of Bruin Lagoon revealed no detectable levels of organics, SO_2, H_2S, HCl, or HCN in the ambient air at the site. Organic vapors were detected within one well boring during drilling operations; however, no detectable levels were found in the ambient breathing zone at this location. It should be noted that no borings were constructed through the open lagoon during the initial RI and, as a result, the gases trapped below the crust were not encountered.

Background air monitoring performed during field work in June 1984 showed no detectable levels of H_2S or methane. Air samples collected from the soil boring indicated the presence of H_2S, CO_2, methane, and aromatic hydrocarbons. SO_2 was not detected in the downhole samples. H_2S was present in the soil gas on the average at about 300 to 400 ppm; initial concentrations were greater by an order of magnitude or more.

Low levels of organic vapors, sulfur dioxide and hydrogen sulfide were released into the ambient breathing zone when the subsurface of the site was disturbed by drilling operations. SO_2 concentrations were observed as high as 50 ppmv but typically were found at 0.5 to 18 ppmv in the breathing zone during drilling operations. H_2S concentrations were lower with high concentrations observed at 14 ppmv with typical concentrations of 1 to 10 ppmv. However, concentrations of these gases were not detectable at the site perimeter.

The analytical results for the subsurface gas samples collected from the 13 shallow wells installed during the 1984 emergency action showed various concentrations of volatile organics, SO_2, H_2SO_4, and methane in the wells.

Methane was observed in all the wells ranging from 2.6 to 4,400 ppm. These concentrations showed good correlation with the organic CH_4 levels measured in the field by the OVA. Analysis of carbon tube samples collected for each well showed no detectable volatile organic compounds. Sulfur dioxide was found to be present in 11 of the 13 wells, with four wells having SO_2 concentrations greater than 100 ppm.

The results of the 1984 sampling of subsurface gases at the Bruin Lagoon site showed elevated levels of SO_2. The presence of H_2SO_4 mist was limited to three wells (A-8, A-10, and A-13). Additionally, reactions and gas releases occurred during the installation of each of these wells. Elevated levels of SO_2 also were detected in well A-2. These wells are all located within 50 feet of one another, and, as a result, the data suggest that this area of the site is a "hot spot" with respect to potentially harmful trapped subsurface gases. Additional sampling one year later confirmed the presence of a "hot spot" area located in the central part of the site.

5.2.7 **Development of BEEs**

No baseline emission estimates or disturbed emission estimates were generated. It was noted, however, that remediation may result in the release of pockets of hazardous gases trapped below a crust at the bottom of the lagoon. BEEs would allow performance of risk assessments for various release and meteorological scenarios at receptor points of interest.

Given the available data, the best method for determining BEEs for this site would be to take the existing ambient air monitoring data and back-calculate an emission rate using an air dispersion model. This is done by setting up the model's run conditions to match those at the site as closely as possible, and then varying the source term to find an emission rate that produces downwind concentrations equal to those actually measured. Using the respective air monitoring data sets, this procedure could be used for both undisturbed and disturbed conditions. However, the accuracy of this procedure is limited by the amount and representativeness of the available air monitoring data.

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5.2.8 Summary

The Case Study 2 investigation points up the need to consider potential emissions from the disturbed site before any remedial actions are undertaken. Here, no soil borings through the open lagoon were performed during the first RI/FS. The initial failure to do so, or to even consider potential air emissions at this site, resulted in the need for a second RI/FS and associated schedule delays and extra expenses. The study did not closely conform to the steps outlined in the protocol of this manual. No undisturbed emission measurements were performed (beyond some background air monitoring) and no emission rate data were collected.

The best technology for screening particulate matter (PM) emissions at this site would have been to collect upwind/downwind samples on filters using high-volume sampling pumps (hi-vols). The total particulate matter present in the air would be determined by dividing the filter weight gain by the volume of air sampled. Analysis of the filter catch for selected metal species would assist in assessing the health impacts from undisturbed emissions. A less acceptable alternative would have been to measure the ambient particulate matter loadings using a portable particulate matter analyzer. The activities conducted, however, provided valuable data that were very useful in the design, selection, and implementation of the remedial alternative.

5.3 CASE STUDY 3: LOWRY LANDFILL

Case Study 3 is an active municipal landfill that formerly also accepted liquid and solid industrial wastes and domestic sewage sludge. This case study focuses on APA activities conducted at the site (see Table 20).

5.3.1 Site History

The Lowry Landfill is co-owned by the City and County of Denver, Colorado. It opened for business as a municipal landfill in 1965. The site is located about 20 miles southeast of Denver and two miles east of the City

TABLE 20.   APA ACTIVITIES CONDUCTED AT THE CASE STUDY #3 SITE

APA Objectives

A soil gas study was conducted to locate waste pits, determine the extent of off-site subsurface gas migration, and determine the waste pit contribution to such migration.   An air monitoring program was conducted to measure ambient air pollutants during installation of monitoring wells in the waste pits.

Scoping

The landfill was determined to contain both hazardous and municipal wastes. The generation of off-gases from the wastes was considered to be a hgih probability.

Screening Measurements

The ambient air was monitored upwind and downwind of the site during monitoring well installation.   Samples were collected using a variety of adsorption media.   Soil samples were collected and the emissions from the samples were scanned.

In-Depth Measurements

The in-depth emission measurements involved collection of soil gas samples at a large number of points using vapor monitoring wells for deep samplign and ground probes for shallow sampling.   However, these data were not used to develop undisturbed and disturbed site BEEs.

Mitigation

Migration plans have not yet been prepared.   The site is currently under study to further understand the air emissions potential from the site.   These study activites include air monitoring at nearby receptors of concern (e.g., community school).

of Aurora, in Arapahoe County. The site covers approximately 480 acres. The surrounding area was mostly undeveloped when the landfill was established, but is growing rapidly today. (Proximity of the closest residence was not given in the Remedial Investigation (RI) report.

From 1965 until the advent of the Resource Conservation and Recovery Act (RCRA) in 1980, the facility accepted municipal refuse, liquid and solid industrial waste (some of which was hazardous), and domestic sewage sludge. The landfill handled these wastes by excavating pits, filling them three-quarters with liquids and then covering the waste with refuse until a mound several feet above the land surface was created. Landfills were dug repeatedly, sometimes into old, filled landfills. The landfills at the south end of the facility were covered with as much as 30 to 60 feet of refuse.

In 1975, Continental Oil Company contracted with site owners to set up and run an oil sludge disposal operation in the southeastern portion of the site. This operation and the acceptance of industrial waste stopped with RCRA in 1980. At that time, the City and County of Denver hired a private firm to manage the site as a municipal waste facility only. This contractor, Waste Management, Inc., formed a subsidiary which opened a hazardous waste disposal facility just north of Lowry. This facility was closed in 1982.

In the early 1980s, Lowry Landfill began to be closely scrutinized by a number of public agencies due to odor problems and other concerns. These first cursory looks focused primarily on the groundwater contamination pathway, studying only shallow groundwater. Not all landfills were located or confirmed. Initial investigations disclosed that records of types and locations of waste were incomplete and inaccurate. Also, no measures had been taken to prevent leachate or seepage from these pits.

Among the 60 pits identified through aerial photographs, it was estimated that roughly 100 million gallons of liquid wastes were disposed on-site over 15 years. Wastes identified include: acid and alkaline sludges; caustics and solids; brines, including plating wastes and other water-based sludges; organics, both natural and synthetic, such as petroleum-based oils, grease,

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and chlorinated solvents and sludges; watersoluble oils; municipal sewage
sludge; low-level radioactive wastes; pesticide wastes; asbestos; and metallic
wastes.

EPA did not become intimately involved at the site until about 1981 when
Lowry was first considered as a candidate for the NPL. In 1984, Lowry was
placed on the NPL and formal investigations were initiated.

5.3.2 Objectives

At the Lowry site, a soil gas study and an air quality investigation were
performed as part of the RI. The soil gas study was conducted to help locate
the waste pits, to determine the extent of any off-site subsurface migration,
and to determine the waste pit contribution to such migration. The air
quality investigation was conducted to measure contaminants in the ambient air
during installation of monitoring wells in the waste pits.

5.3.3 Scoping

Existing data were collected and reviewed to provide a working knowledge
of the site history, conditions, and environmental setting. A topographic map
of the site and its environs was developed from aerial photos. Surveying was
performed to map sampling locations and determine the relative coordinates and
elevation of each location.

5.3.4 Overview of Fieldwork For Site Characterization

The purpose of the first phase, of a two-phase remedial investigation,
was to characterize the site geology and climate; identify the location and
contents of all landfills; characterize the extent of contamination, including
air and soil gas; and identify data gaps to be filled in during rememdial
investigation Phase II.

Investigatory work into some of the landfills was thwarted by three piles
of vehicle tires, two piles of roughly 2 million tires each and one pile of up

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to 8 million tires. Findings disclosed that soil gas, air, groundwater, surface water, and soil all were contaminated and that some migration was occurring. To detect air contamination, contractors sampled upwind and downwind of the site, and 50 feet downwind from the five waste pit wells shortly after installation (to demonstrate a worst-case emissions scenario). The results showed that air quality was degraded as it crossed the site from south to north (the direction of the prevailing wind). Volatile organic compounds (VOCs) were detected at 0.020 to 16 parts per billion (ppb) higher in the downwind samples relative to the upwind samples.

Separately, samples for soil gas emissions were taken from the landfills, from gas well points and probes, and from 10 gas sampling wells installed around the site perimeter by the contracted facility operator in 1981. The results disclosed 19 VOCs, found in ranges of 37 to 160,000 ppb, and verified that contaminated soil gas was migrating off-site in the vicinity of one of the perimeter wells.

A complete meteorological monitoring station has been operating at Lowry since April 21, 1985. It measures wind speed and direction, temperature, relative humidity, barometric pressure, and precipitation on a 10-meter tower. Measurements are taken by a Climatronics Electronic Weather Station (EWS) connected to a Campbell Scientific CR21 data logger. The data are read periodically into a mainframe DEC-10 computer.

5.3.5 Undisturbed Emissions Survey

No screening or in-depth measurements were made to assess the undisturbed emissions at the site. However, the Phase I RI report (60) does recommend that ambient air and meteorological monitoring be performed in the planned Phase II work to collect background data. Based on the types of waste present and the presence of contaminated soil gas, screening measurements (at a minimum) would have been warranted for this site during Phase I activities.

5.3.6 Disturbed Emissions Survey

Both screening (headspace sampling and upwind/downwind air monitoring) and in-depth (soil vapor wells) measurement technologies were used to assess the air pathway.

Screening Measurements--

Split spoon samples collected during drilling activities were retrieved and opened, then the air space above the samples was scanned using an HNU portable organic vapor analyzer.

The ambient air was monitored over a 12-day period during installation of monitoring wells in the waste pits. The monitoring took place in November and December of 1985 during which there was some snow cover; therefore, the results do not equal a worst-case scenario. Samples were collected upwind and downwind of the site and 50 feet downwind of the waste pit well installations. A controlled release of waste pit well gas was permitted to help predict ambient air impacts associated with remediation of the waste pits. Samples were collected by concentrating air on carbon molecular sieves (CMS), polyurethane foam, Tenax, and glass fiber filters. The sampling methods are listed in Table 21.

In-Depth Measurements--

Soil gas samples were collected from a number of locations, including 10 existing soil vapor wells around the perimeter of the facility and wells installed at four locations in suspected waste pits. The wells at the waste pits were drilled to within 2 feet of the water table. Ground probes also were driven into the waste pits at the same four locations to measure the gas emanating from the waste pits and municipal refuse and reaching the near-surface. Three more ground probes were installed at areas without underlying waste pits.

TABLE 21. SUMMARY OF AIR MONITORING AT LOWRY LANDFILL

Collection Media	Equipment Description	Number of Samples	Analytes	Duration of Sampling (Hours)	Method of Analysis
Tenax	Gillian HFS personal pumps	52	Highly Volatile Organic Compounds	8-12	GC/MS (Method TO-1)
Carbon Molecular Sieve	Gillian HFS personal pumps	52	VOCs	8-12	GC/MS (Method TO-2)
Glass Fiber Filters	Sierra Accu-Vol high-volume samplers	20	TSP[a], Metals	8-12	EPA Reference Methods
Polyurethane Foam (PUF)	GMW Model PS-1 high-volume samplers	26	Semi-volatiles and Pesticides/PCBs	8-12	GC/MS (Method 625 and Method TO-4)
N/A	Climatronics Wind Mark III	Continued	Met Data	N/A	N/A

[a] Total suspended particulate matter.

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Samples were collected from all locations using a pump to transfer gas to a tedlar bag within a rigid-wall container. Sample gas was extracted at roughly 1 L/min for 4 to 5 minutes. The perimeter soil vapor wells required purging (three well volumes) before sample collection; the other sampling points had free-flowing gas.

Samples were analyzed for priority pollutants by GC/MS using EPA Method 624 at an off-site location.

Disturbed Emission Survey Results--

A large data base was developed during this program and is summarized here.

The upwind/downwind sampling indicated that the site is a VOC emissions source. Total VOCs on-site were 54 ppb higher than upwind values, and downwind concentrations were 25 ppb higher than upwind values. Downwind concentrations of acetone, carbon disulfide, and toluene were 3 to 10 times the upwind values. During the controlled release, these compounds were found at 8 to 100 times the upwind values. Other compounds, such as 1,1,1-trichloroethane, benzene, and TCE also were found at elevated (4 to 20 times) levels downwind. These emissions could be expected to be greatly higher during non-winter weather conditions.

The upwind/downwind sampling showed particulate matter emissions to be a problem at the site. The upwind values averaged 187 ug/m^3 and the downwind samples averaged 325 ug/m^3 with a range of 112 to 643 ug/m^3. The average downwind total solid particulates (TSP) exceeded the Primary TSP National Ambient Air Quality Standard of 260 ug/m^3.

Nineteen hazardous volatile organic compounds were detected in soil gas samples emanating from waste pit liquid. These compounds were similar to those found in the liquid samples. Concentrations ranged from 460 to 291,000 ppb. Nineteen volatile organic compounds were found in the refuse gas samples, in ranges of 37 to 160,000 ppb. Compounds were nearly identical to those found in gas samples above waste pit liquids except that the

concentration of compounds above these liquids was two to five times greater than in the overlying refuse and six times greater than in refuse with no underlying pits. It is reasonable to conclude that the liquids and refuse are contributing to gas contamination.

The results of perimeter well gas sampling indicate that subsurface contaminant migration has occurred at Well GPM-3 and possibly at GPM-7. Thirteen hazardous substances were detected in gases at Well GMP-3, near waste pits and refuse disposal areas. Substances included volatile organics at ranges of 9 to 1,200 ppb.

5.3.7 Development of BEEs

No baseline emission estimates for either the undisturbed or disturbed wastes were generated, though sufficient data exist to estimate a disturbed BEE. Given the available data, the best method for determining BEEs for this site would be to take the existing ambient air monitoring data and back-calculate an emission rate using an air dispersion model. This is done by setting up the model's run conditions to match those at the site as closely as possible, and then varying the source term to find an emission rate that produces downwind concentrations equal to those actually measured. Using the respective air monitoring data sets, this procedure could be applied to both undisturbed and disturbed conditions.

5.3.8 Summary

The Case Study 3 investigation did not closely conform to the protocol steps outlined in this manual. No undisturbed emission measurements were performed and no emission rate data were collected. While substantial data were collected, scheduling the air monitoring during cold temperatures and snow cover conditions limited the data's applicability.

The best technology for screening undisturbed emissions at this site would be to: 1) perform ambient air monitoring around the perimeter of the facility to determine the magnitude of baseline emissions from the site and to

verify if any adverse health or safety risks are present; and 2) survey the
site using a portable analyzer and windscreen to delineate any localized
emission "hot spots." The results of these screening studies would need to be
interpreted to determine if any further undisturbed emission measurements were
warranted.

5.4 CASE STUDY 4: WESTERN PROCESSING LANDFILL

Case Study 4 is a former industrial waste processing and recycling
facility.

5.4.1 Site History

The 13-acre Western Processing site is situated in the Green River Valley
between Seattle and Tacoma, five miles inland from Puget Sound. The site was
used for agricultural purposes until 1951 when it was leased to the Department
of Defense. An anti-aircraft artillery base operated there until the lease
expired in 1960. The owner opted for a cash settlement and left in place the
installation's buildings and on-site drainage system that linked its
facilities to a septic tank, a tile subsurface drain field, a 500-gallon
chlorination tank and a ditch leading to Mill Creek which runs along the
site's western border.

Western Processing, a waste recycling operation, purchased the site in
1960 and claimed to have reclaimed or recycled millions of gallons of liquid
waste and thousands of tons of solid waste before it was shut down in 1982.
The wastes handled included: animal blood, brewer's yeast, chrome baths,
corrosive liquids, crank case oil, flue dust, lead, pickle liquor, plating
bath solutions, solvents and paints, and zinc skimmings. These wastes were
handled, stored, or disposed of in storage lagoons (acid/caustic/cyanide
wastes), a fertilizer plant, a solvent recovery plant, bulk storage tanks,
cooling water lagoons, a chlorine gas tank storage house, a laboratory,
naphtha storage tanks, a 55-gallon drum storage area, and piles of flue dust.
By the late 1970s, the below-ground surface impoundments had been filled and
were being used to store waste material.

The site is located in an industrial area. A barbed wire fence separates the site from a bicycle and jogging trail, which follows a railroad right-of-way. This is the nearest community exposure to the site. Trail users reported seeing hoses draped over the fence discharging into a ditch along the railroad tracks that feeds into Mill Creek, prior to the closure of the recycling plant (61). The site is shown in Figure 26.

5.4.2 Objectives

The Remedial Investigation/Feasibility Study (RI/FS) process did not address the air pathway for contaminant transport to any meaningful extent. Therefore, no objectives were set or met.

5.4.3 Overview of Fieldwork for Site Characterization

State and local inspections of Western Processing or its vicinity date back to 1977. These were initially concerned about the quality of water in Mill Creek. In 1982, EPA determined that the company's management practices were resulting in the release of priority pollutants and other contaminants to the environment.

A remedial investigation initiated in the fall of 1982 led to emergency and interim remedial site activities in April 1983. These included removal of some liquids, solids, and drums, and reorganization of concrete blocks from five surface impoundments to create a large diked area where excavated materials were then placed. The excavated materials contained solvents, paint sludge, and some heavy metals. Also, buried storage tanks and drums were encountered during this activity. Later in the fall, the state of Washington led an effort to prevent storm water infiltration and runoff, which included further excavation and berming as well as paving of the reaction pond.

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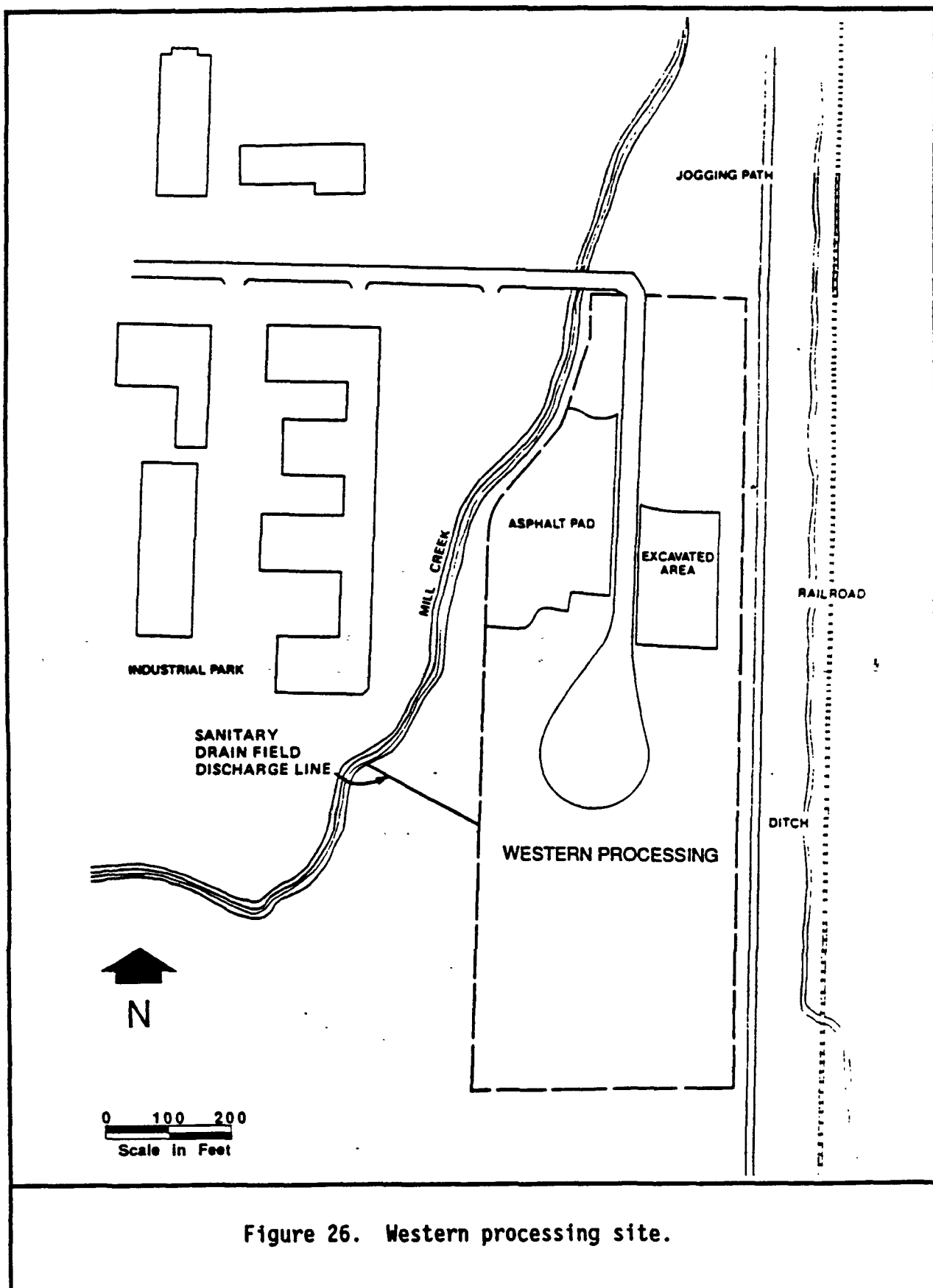
Figure 26. Western processing site.

A Phase I surface cleanup, funded by the potentially responsible parties, started with release of a remedial action plan (62) in July 1984. In that plan, it was clear that air emissions work had been limited. The report noted the northerly direction of winds would primarily deposit any contaminants stirred up or blown off waste piles in or near Puget Sound. The report cited a 1982 air analysis that showed only trace amounts of trichloroethene, toluene, xylene, and tetrachloroethene. The low levels and high volatility of these compounds, coupled with wide atmospheric dispersal, were thought to create only limited effects on receptors during past operations. "Although past releases into the atmosphere may have been greater than observed in the 1982 samples and undoubtedly included particulate matter and contaminants. Other than volatile organics, this pathway is not believed to have been significant."

That the air pathway was overlooked to some extent during the RI/FS stage is apparent. However, Phase II remediation work began in 1987 to remove shallow wastes at the site, and a comprehensive air monitoring program was initiated. This program is outlined below (as described in Lepic and Foster (63).)

An air monitoring program was implemented to ensure adequate protection of both the field team and the surrounding community. Work area monitoring was conducted to identify action levels where personnel protection levels must be upgraded. Continuous upwind and downwind perimeter monitoring was conducted.

Direct reading, real-time instruments were used to determine total gases and vapors, cyanide, gamma radiation and combustible gas; particulate concentrations also were measured. The field instrumentation used at Western Processing included:

- OVA 128: total organic vapors;
- HNU PI 101: total organic vapors;
- Hand-held aerosol monitor (HAM): total particulates;
- Gastech CGI: combustible gases;
- Ludlum 19: gamma radiation;

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- Monitox Compur 4100: cyanide;
- Draeger pump and colorimetric detector tubes: cyanide and methane;
- Hi-volume air samplers: suspended particulates; and
- Recording meteorological station: wind direction and speed.

Air was monitored regularly at 16 fixed locations around the site perimeter to detect any possible off-site migration of airborne contaminants. In addition, monitoring was conducted at each sample location to determine adequate protection levels and to ensure worker safety. These monitoring procedures are described below:

- Borehole and excavation site monitoring: an OVA, HNU and HAM were used to monitor the breathing zone at the drill rig and backhoe during the subsurface exploration and sampling activities. A cyanide detector and combustible gas indicator were used regularly; and

- Drum, tank and utility monitoring: an OVA and HNU, radiation detector, combustible gas indicator and cyanide monitor were used to test the atmosphere within containers for flammable vapors.

5.4.4 Scoping

Collection and review of the existing data were performed. Based on this data review, no need for an air pathway analysis was perceived.

5.4.5 Undisturbed Emissions Survey

No screening or in-depth measurements were made to assess the undisturbed emissions at the site. Table 22 lists some of the contamination found at the site. Based on the very high concentrations of heavy metals (e.g., lead at 31,000 ppm) found in the surface soil, an evaluation of the entrained particulate matter from the site would have been advisable, and some screening measurements were warranted.

TABLE 22. MAXIMUM AND AVERAGE CONCENTRATIONS IN SOIL FOR SELECTED CONTAMINANTS

Contaminant	Maximum Conc. (ppm)		Average[a] Conc. (ppm)
	Surface	Subsurface	
Chromium	5,300	7,600	594
Zinc	81,000	40,500	2,580
Arsenic	38	102	3.28
Antimony	98	130	8.59
Lead	31,000	141,000	5,450
Cyanide	15	179	11.2
Phenol	19.0	65.0	1.65
Aldrin	0	2.86	0.006
Dieldrin	0.145	3.34	0.007
PCB-1248	3.30	19.6	0.341
Hexachloroethane	5,090	1,80	0.0192
Phenanthrene	20,000	62.4	720
Pyrene	16,000	11.0	184
1,1,1-Trichloroethane	0	174	2.87
Methylene Chloride	0.130	49	1.49
Toluene	0	394	6.44
Trichloroethene	0.037	580	19.3

[a] Based on geometric averaging approach.

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5.4.6 Disturbed Emissions Survey

No screening or in-depth measurements were made to assess the disturbed emissions at the site. Based on the very high concentrations of organic compounds in the subsoil, an evaluation of the emission potential would have been advisable.

5.4.7 Development of BEEs

No baseline emission estimates for either the undisturbed or disturbed wastes were generated. Given the available data, the best method for determining BEEs for this site would be to take the existing ambient air monitoring data (discussed below) and back-calculate an emission rate using an air dispersion model. This is done by setting up the model's run conditions to match those at the site as closely as possible, and then varying the source term to find an emission rate that produces downwind concentrations equal to those actually measured. Using the respective air monitoring data sets, this procedure could be applied to both undisturbed and disturbed conditions.

5.4.8 Summary

The best technology for screening undisturbed particulate matter emissions at this site would have been to collect upwind/downwind samples on filters using high-volume sampling pumps (hi-vols). The total particulate matter present in the air would be determined by dividing the filter weight gain by the volume of air sampled. Analysis of the filter catch for selected metal species would assist in assessing the health impacts from undisturbed emissions. A less acceptable alternative would have been to measure the ambient particulate matter loadings using a portable particulate matter analyzer.

Screening VOC emissions also would have been advisable, based on the waste composition data. The best technology for screening undisturbed VOC emissions at this site would have been to: 1) perform ambient air monitoring around the perimeter of the facility to determine the magnitude of baseline

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emissions from the site and to verify if any adverse health or safety risks were present; and 2) survey the site using a portable analyzer and windscreen to delineate any localized emission "hot spots." The results of these screening studies would need to be interpreted to determine if further undisturbed emission measurements were warranted.

The best technology for assessing disturbed VOC emissions would have been to expose representative areas of waste using a backhoe (or drill rig), and to measure emission rates using the flux chamber technique. The best technology for assessing particulate matter emissions would have been to use hi-vol samplers arrayed downwind (i.e., transect technique) to capture emissions during site disturbances.

5.5 CASE STUDY 5: OUTBOARD MARINE CORP. LAGOON/LANDFILL

Case Study 5 is a manufacturing site where harbor sediments and nearby land are contaminated with PCBs.

5.5.1 Site History

Outboard Marine Corp. (OMC) sits on the west shore of Lake Michigan, 37 miles north of Chicago and 10 miles south of the Wisconsin border. This hazardous waste site evolved from an outboard motor manufacturer that used PCBs in die cast machines from the early 1950s to the early 1970s.

Over the years, the facility discharge created three areas of contamination (see Figure 27). The first is Waukegan Harbor, a 37-acre irregularly shaped harbor feeding into Lake Michigan. The operation also led to contamination of "North Ditch," a small tributary that drains surface water runoff into Lake Michigan. A nine-acre parking lot north of the plant was identified as another area of significant PCB contamination.
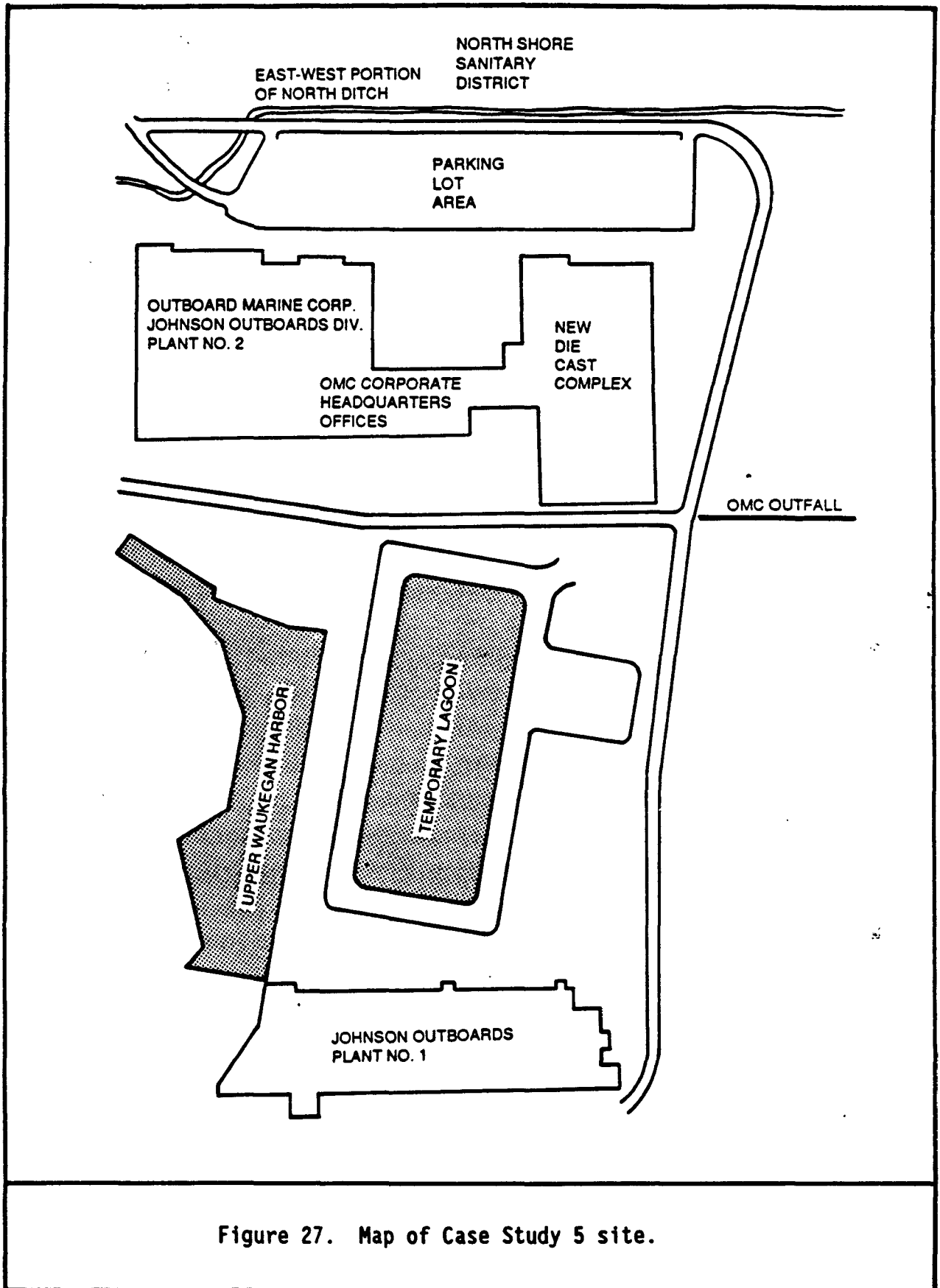
Figure 27. Map of Case Study 5 site.

Concerns about possible receptors of site contamination included the harbor's biological community and fish in Lake Michigan. The City of Waukegan, population 67,653 in 1980, is nearby, but the harbor area is zoned industrial. The 15 businesses in the immediate harbor area that employ about 3,500 people were the immediate concern. Also, the local Port Harbor received heavy recreational use and long-term plans included development of the Upper Harbor. Potentially, people in a variety of locations could be exposed to the contamination via direct contact, fish consumption or possible drinking water contamination.

OMC purchased roughly 9 million pounds of PCBs from Monsanto Co. over a 20-year period beginning in the early 1950s. OMC used the PCBs as hydraulic fluids in die casting machines and related equipment. This equipment leaked routinely and the fluids ran from the plant floor into floor drains that discharged into Waukegan Harbor and North Ditch. EPA estimated that as much as 20 percent of the PCBs purchased could have been discharged.

It was not until 1975 that the Illinois Environmental Protection Agency (IEPA) discovered the high levels of PCBs in soils and harbor sediments near OMC's plant. This discovery was triggered by a 1971 EPA study that showed PCB concentrations in Lake Michigan fish. In 1976, the EPA began to regulate PCB disposal. At that time, OMC began to sample its outfalls and then sealed two outfalls leading to North Ditch, pursuant to a joint Administrative Enforcement Order by EPA and IEPA (64). OMC later declined to immediately remove sediments contaminated with PCBs, as demanded by EPA. When clean-up negotiations among EPA, IEPA, and OMC failed, legal actions were filed. These legal actions were still pending in early 1988. Superfund money for this site became available in 1983.

5.5.2 Objectives

The objective of the APA for this site was to model the exposure of downwind receptors to PCBs during baseline conditions.

5.5.3 Scoping

Existing data were collected and reviewed to provide a working knowledge of the site history, conditions, and environmental setting. No information was uncovered that indicated a need to modify the air pathway analysis objectives.

5.5.4 Overview of Fieldwork for Site Characterization

Discovery steps through site characterization led to the conclusion that PCB concentrations were significant and that PCB release to the surrounding environment could follow a number of pathways.

Waukegan Harbor--

EPA contractors estimated that in Slip Number 3 in the harbor about 7,200 cubic yards of muck, varying in thickness from 2 to 5 feet, was contaminated by about 167,200 pounds of PCBs. Concentrations typically exceeded 500 ppm. Another 3,700 cubic yards of sand and silt (about 7 feet thick) were contaminated by about 138,000 pounds of PCBs. In one localized area near a former OMC outfall, concentrations exceeded 10,000 ppm.

In the upper harbor about 35,700 cubic yards of muck, 1 to 5 feet thick, were contaminated with approximately 5,000 pounds of PCBs. Concentrations here typically were 50 to 500 ppm.

North Ditch--

Contractors broke the North Ditch into three areas for study. In the "crescent ditch," about 28,900 cubic yards of soil, roughly 25 feet thick, were contaminated by about 403,700 pounds of PCBs, creating concentrations ranging from 5,000 to 38,000 ppm. Another 2,300 cubic yards of soil 3 feet thick north of the die storage area were contaminated by an estimated 200 pounds of PCBs. Concentrations here typically were about 200 ppm.

The "oval lagoon," about 27 feet deep, contained about 14,600 cubic yards of soil contaminated by about 85,500 pounds of PCBs in the top 5 feet. Concentrations within those 5 feet were about 26,000 ppm; no data were available for below 5 feet.

In the main part of North Ditch, about 25,000 cubic yards of soil about 25 feet thick were contaminated by at least 4,300 pounds of PCBs. Concentrations in 200 feet of the ditch's western portion were typically above 5,000 ppm PCBs and another 1,000 feet of the central/western portion of the ditch showed concentrations of 500 to 5,000 ppm.

Parking Lot--

The parking lot also showed significant contamination in contractor studies. Approximately 278,000 pounds of PCBs were found in 105,000 cubic yards of soil. Volatilization was thought to be slight because of soil cover and partial pavement. Air emission estimates were not made.

5.5.5 Undisturbed Emissions Survey

No air monitoring for the presence of PCBs was conducted at the site. Dispersion modeling was used to estimate rates of PCB volatilization. The PCB concentration expected in solution at the sediment/water interface was estimated by mixing contaminated sediment with water, decanting the mixture, and measuring the PCB concentration in the water. This concentration number was plugged into transport rate equations. Contractors assumed a volatilization rate of 3.8 mg/m^2/hour from a saturated solution, based on data provided by General Electric Corporation. Assuming volatilization to be proportional to the PCB concentration in the solution, calculations showed that roughly 3.3 pounds of PCB were leaving the harbor portion of the OMC site through the atmosphere per month. The rate would vary positively with temperature. EPA estimated that 12 to 40 pounds of PCBs were volatilizing from the harbor each year. In addition, the North Ditch was estimated to be contributing another 15 pounds of PCBs to the atmosphere per year.

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5.5.6 Disturbed Emissions Survey

No field measurements or modeling estimates were made to assess the emissions during site disturbances. It would be advisable to conduct a laboratory or field study to determine the degree to which volatilization will increase during dredging or other site remediation work. The emission estimates could then be used as inputs to dispersion models to assess the impact on downwind receptors.

5.5.7 Development of BEEs

As discussed above, undisturbed (baseline) emission estimates were developed for two of the three operable units at the site. These estimates were 12 to 40 lb. PCB/year and 15 lb. PCB/year. No disturbed emission estimates were developed. If emission rate data were available for waste in the disturbed state (e.g., flux chamber test data), then disturbed emission estimates should have been developed using the same modeling approach used to develop the BEEs.

5.5.8 Summary

The air pathway for contaminant transport was assessed at this site for undisturbed conditions using modeling techniques. This was a valid, cost-effective option, given the logistical problems of making direct field measurements at this site and the low probability of detecting PCBs in the ambient air downwind of the site.

The best technology for assessing the disturbed PCB emissions would have been to dredge up representative contaminated material and directly measure emissions with a flux chamber. As an alternative, this approach could be modified to perform the work in a laboratory setting.

SECTION 6
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APPENDIX A

ANNOTATED BILIOGRAPHY

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ANNOTATED BIBLIOGRAPHY

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II.   Alm, R.R., C.P. Hanauska, K.A. Olson, and M.T. Pike. The Use of
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          data on the effectiveness of vapor suppression foam from
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V.   Asoian, M.F., and M.J. Barboza. A Practical Methodology for Designing and Conducting Ambient Air Monitoring at Hazardous Waste Facilities. For Presentation at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, 1986. 16 pp.

> This paper presents an approach for designing ambient air monitoring programs, including a decision tree. The emphasis is placed on establishing program objectives, including why sampling is performed, for who, and what is to be sampled. The approach is intended for use for project planning rather than project execution.

VI.   Astle, A.D., R.A. Duffee, and A.R. Stankunas. Estimating Vapor and Odor Emission Rates from Hazardous Waste Sites. In: National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, et al., Washington, D.C., 1982. pp. 326-330.

> This article discusses sampling and evaluation of emissions for odor. The sampling tunnel may have some usefulness for investigating volatile emission rates versus wind speed; however, the technique would require development and testing.

*VII.   Baker, L.W., and K.P. Mackay. Screening Models for Estimating Toxic Air Pollution Near a Hazardous Waste Landfill. Journal of the Air Pollution Control Association, 35(11):1190-1195, 1985.

> Baker and Mackay evaluate performance of four air dispersion models to calculate the ambient air concentration of vinyl chloride versus measured concentration downwind of a landfill. The vinyl chloride emission rate was calculated using Shen's modification of Farmer's gas migration equation. The air dispersion models used are a ground level point source model, two virtual point source mdoels, and a simple box model.

VIII.   Balfour, W.D., R.G. Wetherold, and D.L. Lewis. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA 600/2-85/057, U.S. Environmental Protection Agency, Cincinnati, OH, 1984. 2 vol.

> Emission rates based on direct and indirect emission measurements were compared to emission rates calculated from predictive models. Emission rate measurement techniques were also compared against each other. Emission measurement techniques include surface isolation flux chamber, vent sampling, concentration profile, transect, and mass balance. Predictive models include the Thibodeaux, Parker, and Heck Models (non-aerated surface impound), the Thibodeaux-Hwang Model (land treatment), and an API model (tanks). Details for each measurement technique and model are provided.

IX.   Balfour, W.D., C.E. Schmidt, and B.M. Eklund. Sampling Approaches
       for the Measurement of Volatile Compounds at Hazardous Waste Sites.
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           Sampling techniques for measuring volatile emission rates and
           for measuring soil gas concentrations are discussed. Emission
           rate techniques included are emission isolation flux chamber,
           vent sampling, concentration profile, transect, and mass
           balance. Soil gas concentration techniques are headspace
           analysis of soil cores, soil gas probes (ground probe), and
           passive samplers.

           Each approach is described, and the applicable equations are
           presented.

X.   Balfour, W.D., and C.E. Schmidt. Sampling Approaches for Measuring
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       Corporation, Austin, TX, 1984. 13 pp.

           Balfour and Schmidt present five sampling approaches for
           measuring volatile emissions: surface emission isolation flux
           chamber, vent sampling, concentration-profile, transect
           technique, and mass balance. A comparison of the applicability
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XI.   Balfour, W.D., B.M. Eklund, and S.J. Williamson. Measurement of
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XII.   Banerjee, P., and D.H. Homer. The Impacts of Using Assumed Versus
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XIII. Berrafato, L.R., and R.A. Wadden. Predicted vs. Measured Air
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Evaporation of toluene and chlorobenzene from a simulated lagoon was measured based on the liquid concentration of these chemicals in the lagoon. The evaporation rate was compared to a predictive model similar to the Mackay-Leinonen Model. The results showed the model may be useful for order of magnitude estimates.

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This article examines the Texas administrative review process for proposed hazardous waste disposal facilities. A case study of a waste disposal facility application is reviewed.

XV.   Blasko, M.J., B.F. Cockroft, W.C. Smith, and P.F. O'Hara. Design of Remedial Measures and Waste Removal Program, Lackawanna Refuse Superfund Site. In: Superfund '87: Proceedings of the 8th National Conference, The Hazardous Control Research Institute, Washington, D.C., November 16-18, 1987. pp. 367-370.

This article discusses the development of the design and construction bid package for the remedial measures and removal program. No information on emissions data is given. The RI report would have to be reviewed directly to see if a case study exists.

XVI.   Breton, M., T. Nunno, P. Spawn, W. Farino, and R. McInnes. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-450/8-34-020, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, NC, 1984. 157 pp.

Mathematical models describing the release rate of volatile air emissions from hazardous waste treatment, storage, and disposal facilities were compiled and reviewed. Mathematical modeling techniques which predict volatile air emission release rates from landfills, landfarms, surface impoundments, storage tanks, wastewater treatment processes, and drum handling and storage facilities were assessed. Existing field test validation efforts were also reviewed. Models reviewed include: landfill -- Farmer Model, Shen modification of Farmer Model, Thibodeaux a Model, Thibodeaux Convective "Add On" Model, Thibodeaux b Model, and Shen's Open Dump Model; land treatment -- Thibodeaux-Hwang Model and Hartley Model; lagoons -- Mackay and Leinonen Model, Mackay and Wolkoff Model, Thibodeaux, Parker and Heck model, Shen Model, Smith Model, and McCord Model.

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              the general details of an emergency cleanup at an industrial
              site.

XVIII.   Caravanos, J., and T.T. Shen. The Effect of Wind Speed on the
          Emission Rates of Volatile Chemicals from Open Hazardous Waste Dump
          Sites. Source unknown.

              This article presents a modified diffusion equation (Shen
              Model), which includes wind speed as a variable. Experimental
              data are presented for benzene, carbon tetrachloride, and
              trichloroethylene applied to soil, which approximate a spill.
              The equation also could be applied to waste exposed at surface.

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XXI.   Countess, R.J., R. Brewer, and R.J. Gordon. Sampling Airborne Toxic
          Organics by Remote Control. Presented at the 78th Annual Meeting of
          the Air Pollution Control Association, Detroit, MI, 1985. 16 pp.

              This paper describes a radio-controlled air sampler, which
              would be useful as a sampling method.

XXII.   Cowherd, C. Measurement of Particulate Emissions from Hazardous
          Waste Disposal Sites. For presentation at: 78th Annual Meeting, Air
          Pollution Control Association, Detroit, MI, June 16-21, 1985.

          Article describes the MRI wind tunnel and exposure profiling
          techniques for particulate emissions rate measurement. The MRI
          wind tunnel is a portable wind tunnel which can be used for
          direct emissions measurement. The exposure profiling technique
          is used for indirect emissions measurement and is similar to
          the transect technique.

XXIII.   Cox, R.D., K.J. Baughman, and R.F. Earp. A Generalized Screening
          and Analysis Procedure for Organic Emissions from Hazardous Waste
          Disposal Sites. In: Proceedings of the 3rd National Conference and
          Exhibition on Management of Uncontrolled Waste Sites, Washington,
          D.C., 1982.

          The authors describe a technique developed by Radian
          Corporation for analysis of gas, liquid, and solid
          environmental samples. The technique uses gas chromatography
          with flame ionization, photoionization and Hall electrolytic
          conductivity detectors, as well as mass spectrometry.

XXIV.   DeWolf, G.B., and R.G. Wetherold. Protocols for Calculating VOC
          Emissions from Surface Impoundments Using Emission Models:
          Technical Note. Radian Corporation, Austin, TX, EPA Contract No.
          68-02-3850, U.S. Environmental Protection Agency, Research Triangle
          Park, NC, 1984. 34 pp.

          DeWolf and Wetherold present the Thibodeaux models for aerated
          and nonaerated steady-state impounds and the Mackay and
          Leinonen Model for unsteady-state impounds. Input variables
          are defined, sources of these variables are suggested, and
          approximate precision levels for the variables are given.
          Physical property inputs are discussed and methods for their
          estimation are given, along with selected values for some
          materials.

XXV.   DeWolf, G.B., and R.G. Wetherold. Protocols for Calculating VOC
          Emissions from Land Applications Using Emission Models. Radian
          Corporation, Austin, TX, EPA Contract No. 68-02-3850, U.S.
          Environmental Protection Agency, Research Triangle Park, NC, 1984.
          28 pp.

          The authors present the Thibodeaux-Hwang Model for land
          treatment and the Farmer Model for landfills. Input variables
          are defined, sources of the variables are suggested, and
          approximate precision levels for the variables are given.
          Physical property inputs are discussed and methods for their
          estimation are given, along with selected values for some
          materials.

XXVI.   Dupont, R.R. A Flux Chamber/Solid Sorbent Monitoring System for Use
         in Hazardous Organic Emission Measurements from Land Treatment
         Facilities. Presented at the 79th Annual Meeting of the Air
         Pollution Control Association, Minneapolis, MN, 1986. 15 pp.

         This paper reports on testing of the emission isolation flux
         chamber with Tenax\ tubes as the sampling media.

XXVII.   Dupont, R.R. A Flux Chamber/Sorbent Tube Monitoring System for
         Hazardous Organic Emission Measurements from Land Treatment
         Facilities. In: 192nd National Meeting, American Chemical Society,
         Division of Environmental Chemistry, 26(2):394-397, 1986.

         This is not useful for a case study; the technology is already
         known. The article reports that testing of the emission isola-
         tion flux chamber with Tenax\ tubes for sample collection was
         effective for measuring specific volatile species under both
         laboratory and field conditions.

XXVIII. Dupont, R.R. Measurement of Volatile Hazardous Organic Emissions.
         Journal of the Air Pollution Control Association, 37(3):168-176,
         1987.

         An emissions isolation flux chamber was laboratory tested in
         combination with Tenax\ and charcoal tube sampling to determine
         the recovery efficiencies for selected organics. The testing
         validates the use of a "Radian-style" flux chamber. Testing
         included the use of flow rates significantly below the standard
         protocol.

XXIX.   Eklund, B.M., W.D. Balfour, and C.E. Schmidt. Measurement of
         Fugitive Volatile Organic Emission Rates. Environmental Progress,
         4(3):199202, 1985.

         This article describes the design and operation of a "Radian-
         style" emission isolation flux chamber. It also provides
         limited data from several projects, which can be used as
         emission measurement case studies.

XXX.   Eklund, B. Detection of Hydrocarbons in Groundwater by Analysis of
         Shallow Soil Gas/Vapor. Radian Corporation, Austin, TX, 1985. 78
         pp.

         This report describes five methods of measuring soil vapor
         concentrations: surface flux chamber, soil probe, downhole
         flux chamber, accumulator, and soil coring. All five methods
         would be useful for data collection for direct measurement
         ·and/or predictive modeling.

XXXI.   Eklund, B.M., W.D. Balfour, and C.E. Schmidt. Measurement of
Fugitive Volatile Organic Compound Emission Rates with an Emission
Isolation Flux Chamber. For presentation at: AIChE Summer National
Meeting, Philadelphia, PA, 1984. 8 pp.

> The authors present the procedures for using the surface
> emission isolation flux chamber for direct emission rate
> measurement. Also presented are the results of measurements at
> two spill sites, three landfills, several surface impounds, a
> landfarm, and a remedial action.

XXXII.   Eklund, B.M., M.R. Kienbusch, D. Ranum, and T. Harrison.
Development of a Sampling Method for Measuring VOC Emissions from
Surface Impoundments. Radian Corporation, Austin, TX, no date. 7
pp.

> This paper describes the development program for evaluating and
> modifying the design and operation of the surface isolation
> flux chamber for use on surface impounds.   •

XXXIII. Enfield, C.G., R.F. Carsel, S.Z. Cohen, T. Phan, and D.M. Walters.
Approximating Pollutant Transport to Ground Water. Ground Water,
20(6): 711-722, 1982.

> This article does not provide information on emission rate
> determination. It present three transport models for
> evaluating the movement of organic chemicals through the soil
> to the groundwater. The models include losses due to
> degradation and sorption. Field data are compared to the
> models.

XXXIV. Engineering Science, Inc. Determination of Air Toxic Emissions from
Non-Traditional Sources in the Puget Sound Region. EPA 910/9-86-
148, U.S. Environmental Protection Agency, Region X and Puget Sound
Air Pollution Control Agency, Seattle, WA, 1986. 108 pp.

> This report develops emission estimates for several selected
> sources in the Puget Sound Region including POTWs, industrial
> wastewater treatment plants, Superfund sites, municipal land-
> fills, and TSDFs. Emissions are based on theoretical
> equations. The report contains some useful examples of
> theoretical equation applications. The report may also provide
> case study site information.

XXXV.   Farino, W., P. Spawn, M. Jasinski, and B. Murphy. Review of
Landfill AERR Models. In: Evaluation and Selection of Models for
Estimating Air Emissions from Hazardous Waste Treatment, Storage,
and Disposal Facilities. Revised Draft Final Report. Contract No.
68-02-3168, U.S. Environmental Agency, Office of Solid Waste, Land
Disposal Branch, 1983. pp. 5-1 - 5-13.

This section describes six predictive models that estimate
volatile emissions: Farmer, Shen's modification of Farmer,
Thibodeaux (three variations), and Shen's Open Dump. The first
five models are based primarily on gas diffusion through the
landfill cover.

XXXVI.   Farmer, W.J., M.S. Yang, J. Letey, W.F. Spencer, and M.H. Roulier.
Land Disposal of Hexachlorobenzene Wastes: Controlling Vapor
Movement in Soils. In: Land Disposal of Hazardous Wastes.
Proceedings of the Fourth Annual Research Symposium, U.S.
Environmental Protection Agency, Municipal Environmental Research
Laboratory, San Antonio, TX, March 6, 7, and 8, 1978. pp. 182-190.

Farmer presents a predictive equation for determining
hexachlorobenzene vapor diffusion through a soil cover.
Volatilization through soil, water, and polyethylene film was
studied in laboratory simulations. The predictive equation
should be applicable to other waste types.   •

XXXVII. Farmer, W.J., M.S. Yang, J. Letey, and W.F. Spencer. Land Disposal
of Hexachlorobenzene Wastes: Controlling Vapor Movement in Soil.
EPA-600/280-119, U.S. Environmental Protection Agency, Office of
Research and Development, Municipal Environmental Research
Laboratory, Cincinnati, OH, 1980. 69 pp.

The volatilization fluxes of hexachlorobenzene through a
covering of soil, water, and polyethylene film were simulated
in the laboratory. Volatilization through soil was directly
related to soil porosity. Farmer develops a diffusion equation
for determining flux rates through the soil covering.

XXXVIII. Gillespie, D.P., F.J. Schauf, and J.J. Walsh. Remedial Actions at
Uncontrolled Hazardous Waste Sites, Survey and Case Study Investiga-
tion. In: Proceedings of the Second National Symposium on Aquifer
Restoration and Ground Water Monitoring, National Water Well
Association, Worthington, OH, 1982. pp. 369-374.

This paper is not useful. It discusses how nearly half of all
remedial actions completed by 1980 were ineffective at cleaning
up the sites.

XXXIX.   Gravitz, N. Derivation and Implementation of Air Criteria During
Hazardous Waste Site Cleanups. Journal of the Air Pollution Control
Association, 35(7):753-758, 1985.

This article presents an approach for developing fenceline air
monitoring criteria to protect community health. The approach
is dependent on developing acceptable community exposure
levels, and back calculating the fenceline concentration by
assuming Gaussian wind dispersion. The method does not require
emissions measurement.

XL. Greenberg, M. A Review of: 1) A Technical Approach for Sampling and Analysis of VOCs at Hazardous Waste Sites and 2) Some Case Studies in New Hampshire. Presented before the Fall Meeting, Air Pollution Control Association New England Section, Conference on Air Toxics, Worcester, MA, October 6-7, 1986. 30 pp.

This document contains overhead slides for a conference presentation on sampling VOCs in ambient air at landfills. Case studies are not worked up as emission estimates.

XLI. Hanisch, R.C., and M.A. McDevitt. Protocols for Sampling and Analysis of Surface Impoundments and Land Treatment/Disposal Sites for VOCs. EPA Contract No. 68-02-3850, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1984. 88 pp.

The report gives detailed description for analysis of volatile organics by Radian gas chromatography with multiple detectors (GC/MD) system and gas chromatography with mass spectrometry (GS/MS) system. The report gives a brief discussion of predictive emission models and lists inputs to models, but does not present models. A description of a statistical approach to collecting sufficient samples for representativeness is included.

XLII. Helsing, L.D., M.P. Morningstar, J.B. Berkowitz, and T.T. Shen. Risk. Analysis of Pollutants at Hazardous Waste Sites: Integration Across Media is the Key. In: Superfund '87: Proceedings of the 8th National Conference, The Hazardous Control Research Institute, Washington, D.C., November 16-18, 1987. pp. 471-475.

This paper describes the types of pollutants frequently found at hazardous waste sites and how they can be transferred from one media to another. This paper describes how all media need to be taken into account when performing risk analysis. No information on emission rate determination is provided.

XLIII. Hwang, S.T. Measuring Rates of Volatile Emissions from Non-Point Source Hazardous Waste Facilities. Presented at the 75th Annual Meeting of the Air Pollution Control Association, New Orleans, LA, 1982. 22 pp.

This paper presents Concentration Profile, Plume Mapping (transect), and Upwind/Downwind models for indirectly measuring emission rates.

XLIV. Hwang, S.T. Toxic Emissions from Land Disposal Facilities. Environmental Progress, 1(1):46-52, 1982.

Hwang gives theoretical equations for emission rate estimates
from surface impoundments (natural surface and aerated), land-
fills (based on soil diffusion), and land treatment (oily
wastes). The equations require knowledge of waste and site
characteristics to determine variables and coefficients. All
equations would be difficult to apply for a complex waste,
requiring computer calculation. The equations can be applied
more easily to a single component waste, or its primary compo-
nents.

XLV.   Hwang, S.T. Comparison of Model Predicted Volatile Emission Rates
         Versus Results of Field Measurements at Hazardous Waste Sites.
         Presented at: American Institute of Chemical Engineers, National
         Meeting, Summer 1984. American Institute of Chemical Engineers, New
         York, NY. 18 pp.

         Paper presents a comparison of measured and estimated emission
         rates based on field sampling results and theoretical models.
         Measurements were performed at landfills, surface impounds, and
         land treatment facilities. Field sampling techniques used were
         concentration profile, transect, and surface emission isolation
         flux chamber. The predicted emission rates were generally
         within the confidence intervals of the measured emission rates,
         although the author indicates that more study is required to
         validate the models. The specific models used are referenced
         but not discussed.

XLVI.   Hwang, S.T. Estimating and Field-Validating Hazardous Air Emissions
         from Land Disposal Facilities. In: Third Pacific Chemical
         Engineering Conference, Seoul, Korea, 1983. pp. 338-343.

         Models for estimating volatile emissions are reviewed,
         including Shen's modification of Farmer's equation (landfill),
         the Thibodeaux-Hwang equation (land treatment) and surface
         impound equation. Predicted versus measured emissions
         (concentration profile and upwind/downwind techniques) are
         compared, but limited data are given.

XLVII.   Hwang, S.T. Model Prediction of Volatile Emissions. Environmental
         Progress 4(2):141-144, 1985.

         Hwang presents a comparison of measured and predicted emission
         rates. Measurement techniques include transect and
         concentration profile techniques. Isolation flux chambers and
         upwind/downwind are also discussed. The article contains
         limited data from potential case studies.

XLVIII. ICF, Incorporated. The RCRA Risk-Cost Analysis Model Phase III
         Report Appendices. Submitted to the Office of Solid Waste, Economic
         Analysis Branch, U.S. Environmental Protection Agency, 1982.
         Appendix E, 31 pp.

Appendix E describes natural chemical, physical, and biological processes that reduce the concentration of chemicals in the environment. These processes are the basis for deriving surface and groundwater decay rates for the chemicals included in the RCRA Risk-Cost Analysis Model. Important for baseline emission rate estimates is the discussion on volatilization from water.

XLIX. Jubach, R.W., R.R. Stoner, T.F. Iaccarino, and D.R. Smiley. An Atmospheric Field Program Conducted at a Hazardous Waste Site. Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI, 1985. 14 pp.

This study characterizes the atmospheric dispersion at a hazardous waste site from ground level release. The study consists of releasing a tracer gas and measuring the concentration with two sampling arrays (i.e., transect techniques). Measuring the of actual waste releases are not included. Downwind data could be useful as a theoretical case study.

L. Kaplin, E.J., A.J. Kurtz, and M. Rahimi. VOC Sampling for Emission Rate Determination and Ambient Air Quality on an Inactive Landfill. Presented at New England Section, Air Pollution Control Association, Fall 1986 Conference, Worcester, MA, October 6-7, 1986. 27 pp.

This paper describes sampling performed at an inactive landfill in New York (a municipal waste landfill containing industrial waste). Sampling included ambient air, emission flux chamber (crude), crevices, and vent, sampled with Tenax, PUF/GFF, mylar bags, impingers, and high volume samplers with GFF. Flux measurements included both covered and uncovered areas. Data are somewhat limited, but this study may be useful as a case study.

LI. Karably, L.S., and K.B. Babcock. Effects of Environmental Variables on Soil Gas Surveys. In: Superfund '87: Proceedings of the 8th National Conference, The Hazardous Control Research Institute, Washington, D.C., November 16-18, 1987. pp. 97-100.

This may be useful as a case study if sufficient soil data are available. Soil gas was measured at 40 locations and over time at a fire fighting training area. This paper reports how environmental conditions (principally weather) affected results. Limited analytical data are presented.

LII. Karimi, A.A., W.J. Farmer, and M.M. Cliath. Vapor-phase Diffusion of Benzene in Soil. Journal of Environmental Quality, 16(1):38-43, 1987.

The authors use Farmer's diffusion model and laboratory testing method to determine benzene emission rates through soil (i.e., landfill emissions). The effects of soil bulk density and moisture content are investigated.

LIII.   Keinbusch, M.R. Measurement of Gaseous Emission Rates from Land Surfaces using an Emission Flux Chamber: Users Guide, EPA Contract 68-02-3889, Radian Corporation, Austin, TX, 1986.

This document includes a detailed description for using the emission isolation flux chamber, including design of sampling program, QA/QC, data reduction, and examples.

LIV.   Kerfoot, H.B. Soil-Gas Measurement for Detection of Groundwater Contamination by Volatile Organic Compounds. Environmental Science and Technology, 21(10):1022-1024, 1987.

This article describes sampling using a ground probe system for soil gas. Soil gas data are correlated with groundwater data showing good correlation. Soil gas data are correlated with soil probe depth below ground surface, also showing good correlation. Ground water was at shallow depth in this study (3-4m). Data could be used as a case study if additional soil characteristics data are available.

LV.   Kerfoot, H.B., and P.B. Durgin. Soil-Gas Surveying for Subsurface Organic Contamination: Active and Passive Techniques. In: Superfund '87: Proceedings of the 8th National Conference, The Hazardous Control Research Institute, Washington, D.C., November 16-18, 1987. pp. 523-524.

This article provides an overview of considerations in designing a soil-gas survey. It does not provide information on sampling techniques for air pathway assessment.

LVI.   Lepic, K.A., and A.R. Foster. Remediation at a Major Superfund Site: Western Processing -- Kent, Washington. In: Superfund '87: Proceedings of the 8th National Conference, The Hazardous Control Research Institute, Washington, D.C., November 16-18, 1987. pp. 78-84.

This article summarizes a remedial investigation conducted at a Western Processing site. Continuous upwind and downwind air monitoring was conducted, as well as some location-specific sampling. It may be useful as a case study. No data on air monitoring are presented; the author would have to be contacted.

LVII.   Lewis, R.G., B.E. Martin, D.L. Sgontz, and J.E. Howes. Measurement
         of Fugitive Atmospheric Emissions of Polychlorinated Biphenyls from
         Hazardous Waste Landfills. Environmental Science and Technology,
         19(10):986-991, 1985.

         This article describes air sampling for PCBs at three
         uncontrolled landfills and one controlled landfill. Emission
         rates were not calculated. The data set may be usable for
         calculating emission rates. Sampling was performed using low-
         volume and high-volume samplers and PUF cartridges.

LVIII.   Mackay, D.M., P.V. Roberts, and J.A. Cherry. Transport of Organic
         Contaminants in Groundwater. Environmental Science and Technology,
         19(5): 384-392, 1986.

         This article describes the mechanisms involved in the transport
         of organic chemical contaminants in ground water, including
         advection, dispersion, sorption and transformation.

LIX.   Mackay, D., and P.J. Leinonen. Rate of Evaporation of Low-
         Solubility Contaminants from Water Bodies to Atmosphere.
         Environmental Science and Technology, 9(13): 1178-1180, 1975.

         The authors present predict models (Mackay and Leinonen) for
         emission rates from aqueous systems. Equations are presented
         for both steady and unsteady state systems.

LX.   Mackay, D., and A.T.K. Yeun. Mass Transfer Coefficient Correlations
         for Volatilization of Organic Solutes from Water. Environmental
         Science and Technology, 17(4):211-217, 1983.

         Volatilization rates of organic compounds in water were
         measured in a wind-wave tank for compounds of varying Henry's
         Law Constants. The data yielded correlations for liquid and
         vapro-phase transfer coefficients as a function of windspeed,
         and showed that interactions did not occur when mixtures of
         compounds volatilized simultaneously.

LXI.   Marquardt, G.D. Toxic Air Quality Investigation at a Hazardous
         Waste Site. In: Superfund '87: Proceedings of the 8th National
         Conference, The Hazardous Control Research Institute, Washington,
         D.C., November 16-18, 1987. pp. 284-295.

         This article does not provide data for baseline conditions.
         However, it may be useful as a case study. Sampling was per-
         formed upwind, on site, and downwind during field investigation
         (drilling) and during a controlled release from a gas well.
         Sampling techniques could be used for indirect measurement of
         baseline emissions; techniques include Tenax\, carbon molecular
         sieve, high-volume particulate sampler, and PUF.

LXII.   Meegoda, N.J., and P. Ratnaweera. A New Method to Characterize
         Contaminated Soils. In: Superfund '87: Proceedings of the 8th
         National Conference, The Hazardous Control Research Institute,
         Washington, D.C., November 16-18, 1987. pp. 385-389.

         This paper is not related to emission rate determination; it
         presents an electrical method to determine engineering
         characteristics of soil.

LXIII.   Miller, G.C., V.R. Herbert, and R.G. Zepp. Chemistry and
         Photochemistry of Low-Volatility Organic Chemicals on Environmental
         Surfaces. Environmental Science and Technology, 21(12):1164-1167,
         1987.

         This article discusses factors affecting the transformation,
         mobility, and fate of xenobiotic chemicals (specifically
         dioxins and PAHs). Emphasis is placed on discussing effects on
         and near the soil surface and factors that affect the rate of
         photolysis.

LXIV.   Panaro, J.M. Air Monitoring and Data Interpretation During Remedial
         Action at a Hazardous Waste Site. In: Hazardous Wastes and
         Environmental Emergencies: Management, Prevention, Cleanup, Control,
         Hazardous Materials Control Research Institute, Houston, TX, 1984.
         pp.160-164.

         Panaro describes the air monitoring program employed during
         initial remedial measures at a chemical recycling plant. He
         does not address emission estimates.

LXV.   Polcyn, A.J., and H.E. Hesketh. A Review of Current Sampling and
         Analytical Methods for Assessing Toxic and Hazardous Organic
         Emissions from Stationary Sources. Journal of the Air Pollution
         Control Association, 35(1):54-60, 1985.

         This article is a brief review of sampling methods (i.e.,
         sample collection media) and analytical methods. The methods
         are summarized in tables, and give references for detailed
         descriptions. The article does not discuss measurement
         techniques (i.e., sampling design) or modeling.

LXVI.   Quimby, J.M., R.W. Cibulskis, and M. Gruenfeld. Evaluation and Use
         of a Portable Gas Chromatograph for Monitoring Hazardous Waste
         Sites. Source unknown.

This paper evaluates the use of the Century Systems Organic Vapor Analyzer Model OVA-128 which is a portable gas chromatograph with a fume ionization detector (GC-FID). The paper addresses instrument operating performance, QA/QC consideration, operational difficulties and recommended field uses. Instruments can be used to perform field screening of ambient air, as well as other uses.

LXVII.   Radian Corporation. Review of Soil Gas Sampling Techniques. Austin, TX, 1983. 26 pp.

Report presents the results of a literature review to identify techniques applicable to soil gas sampling and measurement.

LXVIII.   Radian Corporation. 3M Foam Evaluation for Vapor Mitigation: Technical Memorandum. Sacramento, CA, 1986. 95 pp.

The effectiveness of temporary and stabilized foam for controlling VOC emissions from petroleum refinery waste was tested. Testing was performed using the surface emission isolation flux chamber.

LXIX.   Radian Corporation. Air Quality Engineering Manual for Hazardous Waste Site Mitigation Activities, Revision No. 2. Sacramento, CA, 1987. 291 pp.

This guidance document provides general information for designing and reviewing air monitoring programs for hazardous waste site remedial programs. An overview of New Jersey's agency involvement in the remedial process is given. Sampling and analysis methods are discussed in detail.

LXX.   Radian Corporation. Ambient Air Monitoring at Hazardous Waste and Superfund Sites, Revision No. 2. Sacramento, CA, 1987. 389 pp.

This guidance document provides information for reviewing air quality engineering activities for hazardous waste site remediation programs. It also provides an overview of the phases of the hazardous site remediation process and the role of New Jersey's agencies in the process. Descriptions are given for types of waste sites, potential air contaminants, and basic remedial processes.

LXXI.   Radian Corporation. Survey and Assessment of Air Emission Modeling Techniques for Landfills. Draft Final Report. EPA Contract 68-01-7287, U.S. Environmental Protection Agency, Washington, D.C., 1988. 115 pp.

Article reviews theoretical models for landfill air emissions including: Farmer Model, Shen Model, Thibodeaux a Model, Thibodeaux Logrithmic Gradient Model, RTI Closed Landfill Model, Thibodeaux Convective "Add On" Model, Thibodeaux b Model, Thibodeaux Exact Model, Arnold's Open Landfill Model, Shen's Open Landfill Model, and RTI Open Landfill Model.

LXXII.   Saeger, M.L., and E.E. Rickman, Jr. Final Report: Ambient Air Monitoring at Hazardous Waste Treatment, Storage, and Disposal Facilities, Phase I. EPA Project Number 68-02-4326, U.S. Environmental Protection Agency, Emissions Standards and Engineering Division, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1968.

The authors contacted several state and federal regulatory agencies and treatment, storage and disposal facilities (TSDFs) to determine the air monitoring requirements for TSDFs. Few of the states contacted had established requirements, and there was no consistency among states. The program was of a limited scope and was intended to determine if a study should be conducted to assess the feasibility of conducting air monitoring programs at TSDFs.

LXXIII.   Schmidt, C.E., and D.L. Gordy. Designing Air Monitoring Programs for Remediation at Hazardous Waste Sites. Presented at the Annual Conference of the Air Pollution Control Association, San Francisco, CA, 1985. 14 pp.

This paper presents a methodology for developing site-specific air monitoring programs for hazardous waste site remediation. The information presented focuses on fugitive gas phase air contaminants.

LXXIV.   Schmidt, C.E., and J.K. Meyer-Schmidt. Assessment, Monitoring, and Modeling From a Superfund Site Remedial Action. Presented at the Air Pollution Control Association Annual Conference, San Francisco, CA, 1985. 20 pp.

This paper gives a brief overview of RI/FS activities performed at the McColl waste site in Fullerton, California. Measurements included surfaces screening survey, surface flux, ground probes, and downhole flux. Indirect measurements were performed by ambient air sampling. Modeling was used to predict downwind concentrations from direct measurement. Data can be used directly as a case study for both direct and indirect emission estimates. Data can also be used with predictive models.

LXXV.   Schmidt, C.E., R. Stephens, and G.A. Turl. Case Study: Control and Monitoring of Air Contaminants During Site Mitigation. Radian Corporation, Sacramento, CA, 1987. 8 pp.

This article presents an RI/FS/RM case study where an air pathways assessment was performed at a hazardous waste site. Both baseline and disturbed site air emissions were measured and reported.

LXXVI.   Schmidt, C.E., and M.W. Eltgroth. Off-Site Assessment of Air Emissions from Hazardous Waste Disposal Facilities. Reprinted from: Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Silver Spring, MD, 1983.14 pp.

Field data and modeling (Lugrangian model) were used to estimate downwind air concentrations of contaminants using measured disturbed site emissions data. Modeled data were compared to measured data.

LXXVII.   Schmidt, C.E., and W.D. Balfour. Direct Gas Emission·Measurement Techniques and the Utilization of Emissions Data from Hazardous Waste Sites. Reprinted from: National Conference on Environmental Engineering Proceedings, Environmental Engineering Division, ASCE, 1983. 8 pp.

This article describes direct emissions measurement techniques and discusses various applications of these techniques to waste management. Techniques included are surface and downhole isolation flux chambers, ground probes, and soil vapor monitoring wells.

LXXVIII.   Schmidt, C.E., R. Vandervort, and W.D. Balfour. Technical Approach and Sampling Techniques Used to Detect and Map Subsurface Hydrocarbon Contamination. For presentation at the 79th Annual Meeting, Air Pollution Control Association, Minneapolis, MN, 1986. 31 pp.

This paper presents a case study where several direct air emissions measurement techniques were used to detect emissions from a gasoline plume on groundwater about 90 feet below the land surface.

LXXIX.   Shen, T.T., and T. J. Tofflemire. Air Pollution Aspects of Land Disposal of Toxic Waste. In: National Conference on Hazardous Material Risk Assessment, Disposal and Management, Miami Beach, FL, April 25-27, 1979. pp. 153-159.

This paper provides a general discussion of the air pollution dangers inherent in landfilling industrial waste, especially co-disposal with municipal waste. Volatilization processes are discussed. Also discussed are methods for reducing the rate of volatile loss.

LXXX.   Shen, T.T.   Estimating Hazardous Air Emissions from Disposal Sites.
           Pollution Engineering, 13(8):31-34, 1981.

           This article presents Shen's modification of Farmer's equation
           for the diffusion of volatiles from a landfill, and Ziegler's
           modification of Arnold's equation for open dumps (also referred
           to as Shen's open dump equation). A table of diffusion
           coefficients for selected compounds is given. Two example
           calculations for PCB emission are also given.

LXXXI.   Shen, T.T., and G.H. Sewell. Air Pollution Problems of Uncontrolled
           Hazardous Waste Sites. Civil Engineering for Practicing and Design
           Engineers, 3(3):241-252, 1984.

           Shen and Sewell provide three theoretical equations for
           predicting emission rates (Shen landfill model, Shen landfarm
           model, Shen lagoon model) for volatiles and one for dust. The
           equations require some field data about soil, waste
           characteristics, site size, etc., but no direct or indirect
           measurement of emissions. The equations should be used with
           caution, and some speciesspecific coefficients may be difficult
           to determine or infer.

LXXXII.   Shen, T.T.   Air Pollution Assessment of Toxic Emissions from
           Hazardous Waste Lagoons and Landfills. Environment International,
           11(1):71-76, 1985.

           Shen briefly discusses the available methods for determining
           emission rates and their drawbacks. He does not provide
           technical detail for the use of methods, but includes isolation
           flux chamber, transect, concentration profile, and predictive
           models.

LXXXIII.   Shen, T.T.   Air Quality Assessment for Land Disposal of Industrial
           Wastes. Environmental Management, 6(4):297-305, 1982.

           Shen presents a models for predicting emission rates from land-
           fills (Shen modification of Farmer), dumps (Arnold Model) and
           lagoons based on the diffusion theory. Shen also presents data
           on the comparison of predicted versus measured ambient concen-
           tration of PCBs at a New York landfill. This article may be
           useful as a case study.

LXXXIV.   Shen, T.T. Hazardous Air Emissions from Industrial Waste Treatment
           Facilities. In: Industrial Waste: Proceedings of the Fourteenth
           Mid-Atlantic Conference, June 27-29, 1982, J.E. Alleman and J.T.
           Kavanagh, eds., Ann Arbor Science, Ann Arbor, MI, 1982. pp. 361-
           372.

           Shen presents predictive models for dust and volatile organics
           emissions from lagoons (Shen Model), and discusses the fate of
           volatile emissions in the environment in general terms.

LXXXV.   Sherman, S., W. Dickens, and H. Cole. Analysis Methods and Quality
           Assurance Documentation of Certain Volatile Organic Compounds at
           Lower Detection Limits. In: Superfund '87: Proceedings of the 8th
           National Conference, The Hazardous Control Research Institute,
           Washington, D.C., November 16-18, 1987. pp. 280-283.

           This paper is not useful. It discusses modification of EPA
           Method 624 to allow lower detection limits for groundwater
           analysis.

LXXXVI.   Skipa, K.J., D.F. Elias, and J.D. Gram. Monitoring and Evaluating
           Multiple Source Emissions at Hazardous Waste Sites. Presented at
           the 78th Annual Meeting of the Air Pollution Control Association,
           Detroit, MI, 1985. 11 pp.

           This paper discusses, in a generic form, the issues to be con-
           sidered in selecting monitoring and modeling approaches to
           assess the air impacts from a hazardous waste site.

LXXXVII.   Smith, P.G., and S.L. Jensen. Assessing the Validity of Field
           Screening of Soil Samples for Preliminary Determination of
           Hydrocarbon Contamination. In: Superfund '87: Proceedings of the
           8th National Conference, The Hazardous Control Research Institute,
           Washington, D.C., November 16-18, 1987. pp. 101-103.

           This paper compares results from vapor screening of samples in
           the field using portable analyzers (FID and PID) to results
           from laboratory TPH analyses. Comparison of the results showed
           poor correlation indicating the field screening of vapors
           should not be used as the sole criteria for selecting samples
           for analysis.

LXXXVIII. South Coast Air Quality Management District. Landfill Gas
           Emissions: Report of the Task Force, El Monte, CA, 1982.

           This report describes task force activities, including sampling
           of emissions at several landfills in the South Coast Air
           Quality Management District. Data presented are very limited;
           sampling methods were headspace over landfill, shallow ground
           probe, and vent sampling. Site-specific sampling results could
           possibly be worked up as a case study.

LXXXIX.   Springer, C., K.T. Valsaraj, and L.J. Thibodeaux. In Situ Methods
           to Control Emissions from Surface Impoundments and Landfills.
           Journal of the Air Pollution Control Association, 36(12):1371-1374,
           1986.

This article discusses various control measures to reduce air emissions from landfills and lagoons. Included are air-supported structures, floating objects, shape modification, aerodynamic redesign, oil and surfactant covers, and synthetic membrane covers. The effectiveness and other considerations for use of each method are discussed in general.

XC.   St. Clair, A.E., and K.T. Ajmera. Remedial Action at Uncontrolled Hazardous Waste Sites. Environmental Progress, 3(3):188-193, 1984.

This paper describes the feasibility study approach used to develop and select a cost-effective remedial action alternative for the McColl Superfund site in Fullerton, California. Data from the McColl remedial investigation, not presented in this paper, can be used as a case study of baseline emission rate determination.

XCI.   Thibodeaux, L.J., and S.T. Hwang. Landfarming of Petroleum Wastes - - Modeling the Air Emission Problem. Environmental Progress, 1(1):42-46, 1982.

This article reviews volatilization from land farming of petroleum wastes, discusses distribution of oil waste in the soil, and presents a gradientless diffusion model for estimating emissions (Thibodeaux-Hwang Model). The article also gives predicted versus measured emission rates for Deldrin.

XCII.   Thomas, R.G. Volatilization from Soil. In: Handbook of Chemical Property Estimation Methods, W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, eds. McGraw-Hill, New York, NY, 1982. pp. 16.1 - 16.50.

This chapter presents a discussion of the theory of volatilization of organics from soil. Thomas presents five models for calculating volatile loss from the soil. The models are: Hartley Model; Hamaker Model; Meyer, Letey, and Farmer Model; Jury, Grover, Spencer, and Farmer Model; and Dow Methods. This work is based on pesticides applied to soil. A decision tree indicating which models apply for varying conditions is included. The models could be applied to sites with known contaminants.

XCIII.   Thomas, R.G. Volatilization from Water. In: Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds, W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, eds., McGraw-Hill, New York, NY, 1982. pp. 15-1 to 15-34.

Chapter describes the volatilization process from water. Various methods for estimating volatilization rates are discussed. The Mackay and Leinonen model and others are presented.

XCIV.   Thorneloe, S. Summary of Reports Prepared for the Development of
         Air Emission Standards for Hazardous Waste Treatment, Storage, and
         Disposal Facilities. U.S. Environmental Protection Agency, Office of
         Air Quality Planning and Standards, Emission Standards and
         Engineering Division, Chemicals and Petroleum Branch, Research
         Triangle Park, NC, 1987.

              This report contains annotated bibliographies and contacts for
              several studies and reports. Most are directly applicable to
              treatment, storage, and disposal facilities, but some may
              provide sampling techniques applicable to uncontrolled sites.

XCV.   Tucker, W.A., and L.H. Nelken. Diffusion Coefficients in Air and
         Water. In: Handbook of Chemical Property Estimation Methods:
         Environmental Behavior of Organic Compounds, W.J. Lyman, W.F. Reehl,
         and D.H. Rosenblatt, eds. McGraw-Hill, NY, 1982. pp. 17-1 to 17-25.

              Chapter discusses molecular diffusion in air and water.
              Methods are not useful for estimating dispersion in air.
              Methods may be relevant to uncontrolled sites (i.e., within
              lagoon or landfill), however, factors such as wind mixing
              (lagoons) or soil gas flow (landfills) may outweigh molecular
              diffusion.

XCVI.   U.S. Environmental Protection Agency. Letter from J.R. Farmer,
         Director, Emission Standards and Engineering Division, to D. Kolar,
         Environmental Counsel, Browning Ferris Industries, dated October 30,
         1987, regarding EPA's investigation of techniques for controlling
         air emissions from municipal landfill facilities.

              The U.S. EPA sent a questionnaire to Browning Ferris Industries
              requesting information on their landfills. The results, des-
              cribed in this memorandum, do not provide information for base-
              line emissions.

XCVII.   U.S. Environmental Protection Agency. Material on RCRA Facility
         Investigation Guidance (RFI) provided by the U.S. Environmental
         Protection Agency, Office of Air Quality Planning and Standards, to
         Radian Corporation, Sacramento, CA, December 1987.

              The material provided includes a Section 12 on Air, Case Study
              14: Use of Air Monitoring Data and Dispersion Modeling to
              Determine Contaminant Concentrations Down-Wind of a Land
              Disposal Facility, and Case Study 15: Use of Meteorological
              Data to Design an Air Monitoring Network. This material
              provides a recommended strategy for characterizing releases to
              the air. Air monitoring and modeling are discussed in general
              form. The Field Methods section provides considerable
              information on available sampling media and appropriate species
              applications.

XCVIII. U.S. Environmental Protection Agency. RCRA Facility Investigation (RFI) Guidance, Volume III, Section 12, Air and Surface Water Releases. OSWER Directive 9502.00-6C, Office of Solid Waste, 1987.

Provide recommended strategy for characterizing releases to air, which includes characterizing the source and the environmental setting for removal actions at RCRA facilities.

XCIX. U.S. Environmental Protection Agency. Superfund Exposure Assessment Manual. OSWER Directive 9285.5-1, Office of Solid Waste and Emergency Response, Washington, D.C.

Section 2.3 of this manual presents eight equations for predicting short-term and long-term emission rates for landfills with and without internal gas generation, lagoons, landfarms, spills and leaks. Both particulates and volatile emissions are discussed. Equations and discussions are given for determining input variables.

C. U.S. Environmental Protection Agency. Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF) -- Air Emission Models. EPA-450/3-87-026, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1987.

Analytical models are presented for estimating air emissions from hazardous waste treatment, storage, and disposal facilities (TSDF). Air emission models have been developed for aerated and nonaerated surface impoundments, land treatment facilities, landfills, and wastepiles (RTI models). Emission model predictions are compared to available field data. This report also includes emission factors for transfer, storage, and handling operations at TSDFs. The models have been assembled into a spreadsheet that is included in this report as floppy diskette for use on a microcomputer. Appendices include a list of physical-chemical properties for approximately 700 compounds and a comprehensive source list of pertinent literature in addition to that cited in the report.

CI. Vandervort, R., C.E. Schmidt, and W.D. Balfour. Surface and Subsurface Gas/Vapor Monitoring Techniques Applied to Environmental Contamination Caused by Petroleum Products and Processing Wastes. Radian Corporation, Sacramento, CA. 12 pp.

This paper discusses the application of surface and subsurface emission rates and vapor concentration measurements for investigating petroleum leaks and hazardous waste site investigations.

CII.   Vaught, C.C. A Basic Programming Technique for the Estimation of VOC
         Emissions from Hazardous Waste Treatment, Storage, and Disposal
         Facilities. Presented at the 78th Annual Meeting of the Air
         Pollution Control Association, Detroit, MI, June 16-21, 1985. 9 p.

         This paper describes a BASIC program for use on microcomputer.
         The program uses unspecified predictive models to estimate
         emission rates for surface impounds, landfills, land treatment,
         and storage tanks. The program includes a chemical library of
         required model variables which are accessed by use of CAS num-
         bers, as well as estimation programs for filling data gaps, and
         adjustments for site- specific temperature conditions. The
         program was developed in 1985 and may have been updated.

CIII.   Vogel, G.A. Air Emission Control at Hazardous Waste Management
         Facilities. Journal of the Air Pollution Control Association, 35(5):
         558-566, 1985.

         This article is not related to emissions measurement. It
         identifies a method to control toxic air emissions from tanks,
         lagoons, landfills, land treatment facilities, and waste piles.
         Control cost information is also included.

CIV.   Walker, K.A. Air Emissions from Hazardous Waste Treatment, Storage
         and Disposal. Presented at the 77th Annual Meeting of the Air
         Pollution Control Association, San Francisco, CA, 1984. 14 pp.

         Summarizes OSW's work which is presented in detail by Balfour,
         Wetherold, and Lewis (1984) included elsewhere is this biblio-
         graphy. Volatile air emissions at TSDFs were compared for
         measured versus predictive models.

CV.   Weston, R.F. Performance of Remedial Response Activities at Uncon-
         trolled Hazardous Waste Sites (REMII): Draft Remedial
         Investigation/ Feasibility Study Report for the Bruin Lagoon Site,
         Bruin Borough, Pennsylvania. U.S. EPA Contract No. 68-01-6939, U.S.
         Environmental Protection Agency, 1986.

         This report presents the results of the remedial investigation
         performed at a refinery waste lagoon located 45 miles north of
         Pittsburg in Bruin Borough, Butler County, Pennsylvania. Air
         pathway analyses were performed for determining the health and
         safety requirements for workers and nearby residences during
         excavation of the lagoon. Also, sampling and analysis of sub-
         surface soil gas from wells located in the lagoon were
         performed to determine the soil gas composition, regeneration
         rates, extent of trapped soil gas within the lagoon and to
         assist in the assessment of the potential for the release of
         soil gas into the atmosphere during future excavation.

CVI.   Wetherold, R.G., and D.A. Dubose. A Review of Selected Theoretical
        Models for Estimating and Describing Atmospheric Emissions from
        Waste Disposal Operations. EPA Contract 68-03-3038, U.S.
        Environmental Protection Agency, Office of Research and Development,
        Industrial Environmental Research Laboratory, Cincinnati, OH, 1982.
        73 pp.

        This report presents models for determining emissions from
        landfills, land treatment, lagoons, waste piles, and tanks.
        Models include both predictive models and indirect measurement
        techniques. Estimates of model precision and accuracy, and
        potential sources for model variables are included. Models
        included are: Hartley Model; Thibodeaux-Hwang Model; Farmer
        Model; Smith, Bomberger, Haynes Model, Mackay and Leinonen
        Model; Thibodeaux Concentration Profile; and Thibodeaux,
        Parker, and Heck Model.

CVII.   Wetherold, R.G., B.M. Eklund, and T.P. Nelson. A Case Study of
        Direct Control of Emissions from a Surface Impoundment. In:
        Proceedings of the 11th Annual Research Symposium on Incineration
        and Treatment of Hazardous Waste, Annual Solid Waste Research
        Symposium, U.S. Environmental Protection Agency, Cincinnati, OH,
        1985. pp. 85-92.

        Testing was performed to determine the effectiveness of an
        inflated flexible dome enclosure in controlling VOC emissions
        from an aerated wastewater lagoon. Effectiveness was investi-
        gated by performing a mass balance of VOCs around the system.
        The article is not directly applicable to baseline emission
        estimates.

        Wood, J.A., and M.L. Porter. Hazardous Pollutants in Class II Land-
        fills. South Coast Air Quality Management District, El Monte, CA,
        1986.

        This report describes sampling for air toxics at several Class
        II landfills. Landfill gas sampling was performed at 20 sites
        from vents (when present) and headspace over the site. Ambient
        air sampling was performed at five sites. Air toxics were
        detected even though the species cannot be legally disposed of
        at Class II landfills.

APPENDIX B

CHEMICAL AND PHYSICAL PROPERTIES
AFFECTING BASELINE EMISSION ESTIMATES

CHEMICAL AND PHYSICAL PROPERTIES OF THE WASTE MATERIAL AFFECTING EMISSIONS

Property	Effect
Saturation Concentration	The waste will tend to reach equilibrium with the soil vapor. If sufficient waste is present, the equilibrium concentration within the air-filled voids of the soil matrix will reach saturation. Because the rate of emission to the atmosphere is directly proportional tot he soil vapor concentration, the emission rate will increase as saturation concentration increases.
Diffusion Coefficient	Compounds with high overall diffusion coefficients will be emitted at higher rates than those with lower diffusion coefficients via increased transport, on a relative basis. The overall diffusion coefficient may be comprised of diffusion through the soil-water interface, soil-air interface, soil, water, air, and soil vapor.
Molecular Weight	Lower molecular weight compounds typically have higher volatilization and diffusion coefficients. Other compound characteristics may predominate. Molecular weight is used to determine diffusion rates in some predictive models.
Partial Pressure of Constituents	High partial pressure increases the emission rate of a species by increasing its soil vapor concentration.
Weight Fraction	An effect similar to partial pressure, it is used as an input to some predictive models. Not as important as Henry's Law constant.
Combination of Constituents	This increases the complexity of the emissions process and determines the emission rate. It may change over time as more volatile species are lost.
Concentration of Waste	Increasing waste concentration increases the emission rate for dilute wastes by increasing the vapor pressure and, therefore, vapor concentration.
Henry's Law Constant	This is used to determine diffusion coefficients. A high Henry's Law constant produces a higher diffusion rate.

(Continued)

Property	Effect
Porosity	One of the controlling factors for diffusion through the soil. Emission rates typically increase with increasing soil porosity. Total porosity, i.e., dry soil, may represent worst-case conditions for predictive models. Air-filled porosity may be more a realistic parameter for many sites.
Adsorption/Absorption Properties of Soil	Soil with high sorption properties will reduce the vapor density of the sorped compounds and, therefore, the emission rate. The effect may be minimal where high waste concentrations saturate the sorption sites. The effect may be reversed causing increased emissions.
Soil Moisture	Its effect varies. High moisture will reduce the air-filled porosity, with pores being filled under worst-case conditions and, therefore, should reduce the emission rate. Moisture may be preferentially adsorped by the soil, releasing volatiles and increasing the emission rate. Drying of soil may increase available sorption sites. Moisture is required for the wick effect.
Wick Effect	Soil moisture may draw waste constituents to the surface through the soil pores. This process can increase the concentration of the constituents at the surface and, therefore, increase the emission rate.
Particle Size Distribution	This affects the total soil porosity and soil pore continuity. Increased soil pore continuity increases the emission rate. A higher percent of fines will typically increase particulate emissions.
Organic Content of Soil	High organic content will increase the sorptive characteristics of the soil and reduce the emission rate. High organic content also will increase microbial action.
Microbial Activity	Its effect varies. It may reduce the emission rate by biological reduction of the waste present. It also may increase the emission rate due to gas formation which carries volatile species to surface.

(Continued)

Property	Effect
Depth of Landfill Cover	Emission rates decrease with increasing depth (thickness) of cover as the diffusion path increases. For an open dump or landfill, the cover thickness is zero.
Compaction of Landfill Cover	Increasing compaction reduces the soil porosity and disrupts continuity of the soil pores, thereby, reducing the emission rate.
Ground Cover	Soil cover, typically vegetation, will reduce particulate emissions by reducing the erodability of the soil. It also will help hold soil moisture, which reduces the air-filled porosity and reduces volatile emissions.
Size of Landfill/Lagoon	The emission rate is directly proportional to the size of the landfill or lagoon.
Amount of Exposed Waste	Emission will increase when waste is exposed at the surface, both due to volatilization and wind erosion.
Water Depth in Lagoon	Water overlying waste will act as a cover. Diffusion through water may control the emission rate.
Aeration of Lagoons	Aeration increases emission of volatile and particulates with increasing volume of air used and/or agitation. The effect is due to air stripping of volatiles and bulk transport of liquid particles.
Temperature	Increasing temperature increases the volatilization rate for organic species and, therefore, the emission rate. Increasing temperature reduces soil moisture, increasing air-filled porosity and the emission rate.
Wind	Wind removes the volatilized compound concentration in the boundary layer over the site, maintaining the driving force for volatilization. Increasing wind speed reduces the boundary layer over the site. Wind causes turbulence within the boundary layer, providing the driving force for surface soil/waste erosion and increasing particulate emission rate.

Property	Effect
Cloud Cover	Increased cloud cover reduces solar heating of the surface and, therefore, the volatilization rate from surface. It also affects wind stability.
Precipitation	Emissions are reduced by reducing the air-filled soil porosity. It may increase landfill emission by displacing soil vapor from soil voids. It may increase surface water and air emissions by floating waste constituents to the surface. Precipitation increases agitation of the lagoon surface, potentially increasing emissions, but it also increases water depth over waste in the lagoon.
Humidity	Increasing partial pressure of water vapor in air reduces the capacity for some types of volatilized material. It may reduce air-filled soil porosity.
Barometric Pressure	Changing barometric pressures cause bulk flow of soil vapor into/out of soil. The overall net effect is to increase the emission rate. The effect increases with frequency and scale of barometric changes.

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