

GUIDANCE FOR EVALUATING LANDFILL GAS EMISSIONS FROM CLOSED OR ABANDONED FACILITIES



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by

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Abstract

This document provides guidance to superfund remedial project managers, on-scene coordinators, facility owners, and potentially responsible parties for conducting an air pathway analysis for landfill gas emissions under the Comprehensive Environmental Response, Compensation, and Liability Act, Superfund Amendments and Reauthorization Act, and the Resource Conservation and Recovery Act. The document provides procedures and a set of tools for evaluating LFG emissions to ambient air, subsurface vapor migration due to landfill gas pressure gradients, and subsurface vapor intrusion into buildings. The air pathway analysis is used to evaluate the inhalation risks to offsite receptors as well as the hazards of both onsite and offsite methane explosions and landfill fires.

Foreword

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Sally Gutierrez, Director
National Risk Management Research Laboratory

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List of Acronyms

<u>Acronym</u>	<u>Definition</u>
ARAR	applicable or relevant and appropriate requirement
ASTM	American Society of Testing and Materials
BDT	best demonstrated technology
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CH ₄	methane
CO	carbon monoxide
CO ₂	carbon dioxide
COPCs	contaminants of potential concern
DCA	dichloroethane
DQO	data quality objectives
DRE	destruction removal efficiency
ED	exposure duration
EG	Emission Guidelines
EPA	U.S. Environmental Protection Agency
ERTC	Environmental Response Team Center
FID	flame ionization detector
FML	flexible membrane liner
GC/MS	gas chromatograph/mass spectrometer
GMPs	gas monitoring probes
GPS	Global Positioning System
H ₂	hydrogen
HAP	hazardous air pollutant
HCl	hydrogen chloride
HDPE	high-density polyethylene
HEAST	health effects assessment summary tables
Hg	mercury
HI	hazard index
HRPM	horizontal radial plume mapping
HSWA	Hazardous and Solid Waste Act
ICE	internal combustion engine
IRIS	Integrated Risk Information System
ISC3	Industrial Source Complex, Version 3

List of Acronyms (continued)

<u>Acronym</u>	<u>Definition</u>
ISCLT3	Industrial Source Complex Long Term, Version 3
LandGEM	landfill gas emission model
LBL	Lawrence Berkeley National Laboratory
LCS	laboratory control samples
LEL	lower explosive limit
LFG	landfill gas
LMOP	Landfill Methane Outreach Program
LNAPL	light nonaqueous phase liquids
MACT	maximum achievable control technology
MDL	method detection limit
MS	matrix spike
MSD	matric spike duplicate
MEK	methyl ethyl ketone
MSW	municipal solid waste
MSWLFs	municipal solid waste landfills
N ₂	nitrogen
NAPL	nonaqueous phase liquids
NCEA	National Center for Environmental Assessment
NCP	national contingency plan
NESHAP	National Emission Standards for Hazardous Air Pollutants
NMOC	nonmethane organic compounds
NRCS	Natural Resources Conservation Service
NRMRL	National Risk Management Research Laboratory
NSCEP	National Service Center for Environmental Publications
NSPS	New Source Performance Standard
O ₂	oxygen
OP-FTIR	open path fourier transform infrared
OPMs	open path monitors
OPS	optical remote sensing
OP-TDLAS	open-path tunable diode laser absorption spectroscopy
ORS	optical remote sensors
OSC	on scene coordinator
OSHA	Occupational Safety and health Administration
PC	personal computer
PCB	polychlorinated byphenyl
PID	photoionization detector
ppb	parts per billion
ppmv	parts per million by volume
POTW	publically owned treatment works
PRP	potential responsible party
PVC	polyvinyl chloride
QAPP	Quality Assurance Project Plan

List of Acronyms (concluded)

<u>Acronym</u>	<u>Definition</u>
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RfCs	reference concentrations
ROD	record of decision
RPD	relative percent difference
RPM	remedial project managers
SARA	Superfund Amendments and Reauthorization Act
SCDM	superfund chemical data matrix
SCRAM	Support Center for Regulatory Air Models
SCS	Soil Conservation Service
SFL	superfund landfill
SO ₂	sulfur dioxide
SOPs	standard operating procedures
SSL	soil screening levels
SSM	start-up shutdown malfunction
STAR	stability array
SVOCs	semi-volatile organic compounds
TBA	to be assigned
TCLP	toxicity characteristic leaching procedure
TMPs	temporary gas monitoring probes
TSDF	treatment storage and disposal facilities
UEL	upper explosive limit
UV-DOAS	ultraviolet differential optical absorption spectroscopy
VOC	volatile organic compounds
VRPM	vertical radial plume mapping

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EXECUTIVE SUMMARY

Asphyxiation and explosion are the two most commonly recognized health risks associated with landfill gas (LFG). In addition, there is concern for acute toxicity, chronic hazards, and risks associated with LFG emissions. LFG is the natural by-product of the anaerobic decomposition of biodegradable waste in landfills. LFG is a complex mixture of gases, including methane, carbon dioxide, and trace constituents of volatile organic compounds (VOC), hazardous air pollutants (HAPs), and hydrogen sulfide. Landfill gas can also contain persistent bioaccumulative toxic compounds such as mercury. Municipal solid waste (MSW) landfills are one of the largest sources of anthropogenic methane emissions. Regulations under the Clean Air Act have targeted large municipal landfills through performance based regulations for controlling LFG emissions. This guidance addresses the LFG hazards by providing interested stakeholders and decision makers with information that can be used to evaluate and mitigate potential landfill gas emissions to ensure protection of human health and the environment.

The movement of LFG in unsaturated MSW may occur through various mechanisms, including diffusion, convection, pressure gradient flow, and water-vapor transport. The characteristics of LFG (generally warmer though slightly more dense than soil air at equivalent temperatures) also impact the mechanics of the gas transport, as do the molecular weights and specific gravities of the VOCs in the LFG. Given the varying solubilities, vapor pressures, molecular weights, and specific gravities of the typical components of LFG, specific transport mechanisms will affect the migration of the respective components. Thus, migration occurs as movement of individual gaseous components and an integral excursion front. Through advective flow, LFG pressure gradients can influence the direction and rate of both LFG excursion fronts and VOC migration paths. LFG will migrate (encouraged by the natural development of positive pressures within the landfill) toward the surface and edges of the fill and into the adjoining soils.

LFG migrates from the subsurface to the atmosphere via diffusion and advection mechanisms through the soil pores, fractures, gaps and defects in the cover materials, or it is collected and discharged via vents systems that may or may not be controlled. LFG migrates underground via natural and manmade pathways. Natural pathways include fracture zones normally associated with karst topography, significant cavernous structures, dry pockets or strata of sand and gravel, and soil strata interfaces. Migrating LFG does not generally travel at a depth lower than the current groundwater table unless a manmade structure is provided. These structures include the trenches associated with all types of buried utilities (sanitary sewers,

storm sewers, electrical service lines, cable TV lines, telephone lines, and water mains). Usually the granular or aggregate bedding for these buried utilities is sufficiently porous to allow easy migration of LFG along the trench line. Ultimately the LFG will travel from the area of highest pressure via the path of least resistance, until the pressure and concentration gradient reach equilibrium with the surrounding environment.

When LFG accumulates in a trench, excavation, or other enclosed space, an extremely dangerous situation is present. Gas infrared analyzers (“sniffers”) are used to make sure that the air in the enclosed space is safe to breathe, and they are used to measure gas accumulations in monitoring probes. Gas can also accumulate in the foundations, basements, and closed rooms of nearby buildings. Such places can accumulate LFG until it exceeds the lower explosive limit (LEL). LFG migrating through soil at shallow depths tends to kill root systems, resulting in visible vegetative stress along the path of migration. Such dead or dying vegetation is typically a clear indication of migrating gas, and monitoring probes are usually installed in these areas to directly measure the amount of escaping LFG.

Emission estimating is an important step in conducting risk evaluations, obtaining permits, demonstrating compliance with regulatory limits, and designing emission control systems for solid waste landfills. There are several methods for measuring and analyzing LFG. This document presents a step-wise procedure using readily available field instruments, sampling probes placed just below the cover, routine analytical methods, and commonly used fate and transport modeling procedures. The document also presents the results of an example application of an open path Fourier transform infrared spectroscopy (OP-FTIR) emission measurement method. The OP-FTIR was used in conjunction with a radial plume mapping technique in order to estimate the emission rates and establish ambient air concentrations. Figure 1 presents a flow chart that illustrates the information gathering and decision-making process described in the guidance.

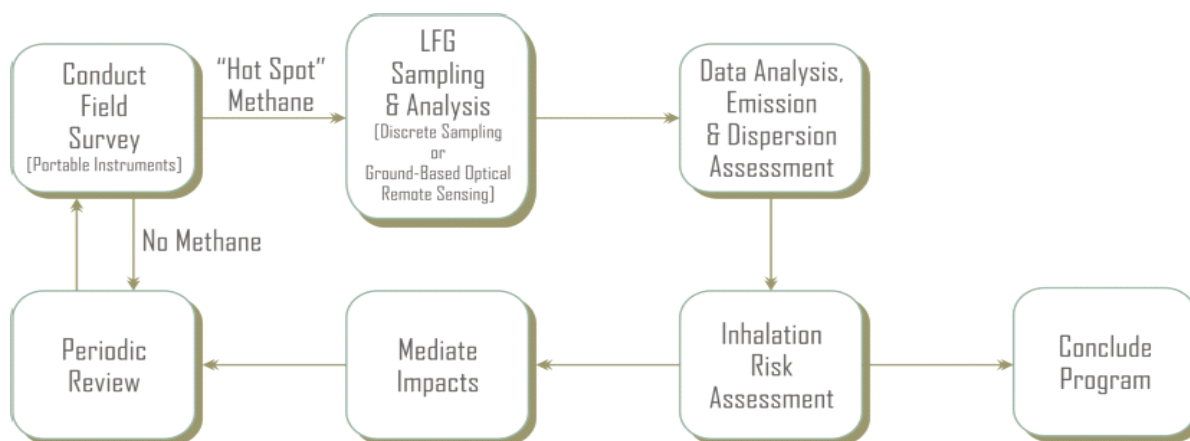


Figure ES-1. Simplified Data Gathering and Decision-Making Flow Chart for the Guidance for Evaluating Landfill Gas Emissions from Closed or Abandoned Facilities.

Emissions from Closed or Abandoned Facilities

This document presents site investigators, risk managers, and design engineers with procedures and methodologies that may be used to estimate LFG emissions and their resulting ambient air concentrations. The usefulness of this document was demonstrated at three study sites that are illustrative of the techniques discussed herein. It is recognized that each technique has advantages and disadvantages that must be taken into account. Decision makers must balance their need for definitive site-specific information with that derived by generic fate and transport models. The field screening, sampling, and modeling procedures were used at three sites—Rose Hill Regional Landfill in South Kingston, Rhode Island; Bush Valley Landfill in Abingdon, Maryland; and the Municipal Landfill Superfund Site located in Somersworth, New Hampshire. At the third site, ground-based optical remote sensing was used in addition to serpentine pattern sampling.

1. Introduction

The purpose of this guidance document is to provide the remedial project manager (RPM), the on-scene coordinator (OSC), and potentially responsible parties (PRPs) with a set of procedures and tools for evaluating the health and safety impacts of landfill gas (LFG) emissions from closed or abandoned co-disposal landfills under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); the Superfund Amendments and Reauthorization Act (SARA); and the Resource Conservation and Recovery Act (RCRA). The procedures and methodologies described in this document are summarized in Table 1-1.

Table 1-1. Idealized Procedures and Methodologies for Evaluating the Significance of Landfill Gas Emissions

Procedure	Methodology
1	Collect historic data to assist in planning sampling and analysis activities.
2	Develop quality assurance project plan. Identify applicable or relevant and appropriate requirements (ARARs) and determine regulatory requirements. Establish target analyte (chemical of potential concern) list. Select analytical methods to be used. Determine if off site sampling and analysis needs to be included in the effort.
3	Develop a sample grid to cover the landfill and adjacent areas of concern. Grid size varies according to homogeneity of landfill contents and economics associated with collecting and analyzing LFG. Offsite sampling may be needed to determine if LFG is migrating below the surface or if vapors from contaminated groundwater is migrating through the soils and potentially entering into buildings.
4	Choose option A or B: (A) Use field instruments to identify hot spots emitting methane (CH ₄) and non-methane organic compounds (NMOCs); or (B) Use remote optical scanning system to identify hot spots and to generate emission rate information and resulting ambient air concentration data. The choice is largely determined by economics, time criticality, and availability of equipment and expertise.
5	If following option A: Determine the minimum number of areas (parcels) of nearly homogeneous emissions required to normalize the emissions from the landfill surface. Non-parametric statistical procedures (e.g., Wilcoxon, Mann-Whitely) and geographical isopleth plotting software are used to make this determination.

continued

- 6 If following option A: Use rank order statistics to identify hot spot locations (highest NMOC/CH₄ concentration) for each parcel. Collect subsurface LFG samples from each parcel hot spot. Samples may need to be collected from active and passive vents and from the landfill surface. Surface sampling is accomplished by making a hole (e.g., slam bar, geoprobe) through the landfill cover and by placing an extraction tube into the hole and by collecting samples (bag or canister) for laboratory analysis. Sample extraction ports are used to collect samples from the vents. Exercise care not to cause ambient air to enter the LFG sample. Repair holes and close ports as appropriate.
 - 7 If following option A: Use landfill emission estimating model (e.g., LandGEM, LANDFILL) to estimate emission rate for each parcel;
 - 8 If following option A: Use dispersion and deposition models (e.g., ISC3, Screen, AERMOD, etc.) to estimate the ambient air concentration at each receptor location of concern.
 - 9 Compare the predicted concentrations with the target air concentration to satisfy both the prescribed risk level and target hazard index.
-

A co-disposal landfill is defined as a landfill in which both municipal solid waste (MSW) and hazardous or toxic wastes have been deposited. The MSW fraction is the most significant quantity both volumetrically and on a weight basis. Municipal landfills constitute approximately 20 percent of all sites on the Superfund National Priorities List. LFG is produced by the breakdown of household garbage by bacteria and typically consists of 40 to 60 percent carbon dioxide (CO₂), 45 to 60 percent methane (CH₄), and trace constituents which include volatile organic compounds (VOCs), and hazardous air pollutants (HAPs). Landfill gas can also contain (1) persistent bioaccumulative toxic compounds such as mercury, (2) ammonia, (3) oxygen (O₂) and nitrogen (N₂) from air infiltration, (4) carbon monoxide (CO), and (5) hydrogen sulfide (H₂S). Nonmethane organic compounds (NMOCs) include trichloroethylene, benzene, and vinyl chloride. Usually, gas production begins within a year of waste placement and may continue for as long as 50 years after landfill closure. Maximum gas production ranges from less than 0.2 to more than 0.5 m³ per kg of solid waste. The actual rate of gas production is a function of refuse composition, age (or time since emplacement), climate, moisture content, particle size and compaction, nutrient availability, and buffering capacity. Reported production rates vary from 0.0007 to 0.0080 m³ per kg-yr. Generally, for any given cell, these production rates peak during the first or second year following waste placement and decline thereafter. In an active landfill, because of the sequential nature of the operations, each cell will be in a different stage of decomposition and will be generating gas at a different rate. As more waste is added, however, the total gas production rate increases. In general, it is expected that total gas production will rise rapidly during the operating years, and then fall off after closure.

Numerous investigations have been conducted to characterize LFG emissions, and significant variation in LFG composition has been observed. More than fifty different VOCs—including simple alkanes, olefins, aromatics, and a wide array of chlorinated compounds—have been identified in LFG. These VOCs include a number of known or suspected carcinogens (such as benzene and vinyl chloride). The VOC concentrations range from a few parts per billion (ppb) to tens of thousands of ppb. LFG, including CH₄, can easily move through permeable soils like those present at many closed and uncontrolled landfill sites.

Emissions from Closed or Abandoned Facilities

These gases usually move from areas of high pressure (at depth within the landfill) to areas of low pressure (surficial soils and atmosphere), but it is often difficult to predict specific patterns of gas movement. Under certain conditions, LFG can migrate laterally for long distances from the landfill. An often used rule of thumb is that it may migrate up to 1000 feet, but there are documented cases where LFG has traveled in the subsurface for more than 2000 feet. Structures within this distance may require additional evaluations and precautions to protect them from LFG accumulation. LFG will migrate along all possible pathways, favoring those that present the path of least resistance. Utility trenches, sanitary and storm sewers, and building footers are the most common pathways allowing long distance transport. Knowledge of the landfill's, geometry, design, and operating characteristics as well as the local geology, hydrology, and land uses is helpful in evaluating and understanding gas migration and emission phenomena.

High concentrations of LFG occur most commonly in landfills that contain municipal garbage and have an impermeable or nearly impermeable cover. The cover traps these gases, prevents them from escaping upward, and causes them to move either into a gas collection and control system or laterally into adjacent, off-site areas. Highest CH₄ concentrations occur in the warmer summer months, and concentrations are higher during the heat of the day compared to measurements taken during morning hours. LFG levels in soils tend to be higher during dry periods and lower after significant rainfall events. Associated with high methane production are increases in CO₂ and hydrogen sulfide and decreased amounts of O₂.

Human exposure to LFG is not typically addressed during the remedial investigation phase because containment of the landfill mass and treatment of the LFG is the presumptive remedy, although this presumptive remedy does not address exposure pathways outside the source area. Hence, risk assessment and other exposure pathway analyses, as appropriate, may be used to address offsite migration of LFG. Historically, control of LFG has been performed either to minimize the potential for LFG explosive hazards or to avoid negatively impacting the selected cap (i.e., pressures exerted against the cap) rather than an assessment of human exposure during baseline conditions (undisturbed) and during remediation. Recent consideration of alternative caps and subsurface natural attenuation may actually increase the potential to release toxic LFG constituents to the atmosphere. Permeable caps are designed to allow water to infiltrate and to allow gases to release to the atmosphere. However, this also minimizes gas capture, resulting in larger fugitive loss of emissions.

1.1 What Is Landfill Gas?

LFG is generated by the decomposition of organic municipal solid wastes such as garbage, garden wastes, and paper products. This process may continue for 20 to 50 years after initial dumping of the MSW. At near steady-state conditions, LFG is typically composed of approximately 55 percent CH₄, 40 percent CO₂, 5 percent N₂, and smaller amounts of NMOCs such as benzene, vinyl chloride, chloroform, 1,1-dichloroethene, carbon tetrachloride, and other NMOCs. In addition, non-organic species such as hydrogen sulfide and vapor phase mercury are often found in LFG. Table 1-2 presents volumetric and characteristic information for a typical LFG.

Table 1-2. "Typical" Landfill Gases, Their Percent by Volume, and Their Characteristics

Component	Percent by Volume	Characteristic
CH ₄	45 to 60	CH ₄ is a naturally occurring, colorless, and odorless gas. Its concentration in ambient air is 0.0002%. Landfills are the single largest source of U.S. man-made methane emissions.
CO ₂	40 to 60	CO ₂ is a colorless and slightly acidic gas that occurs naturally at a small concentration (0.03%) in the atmosphere.
N ₂	2 to 5	N ₂ comprises approximately 79% of the atmosphere. It is odorless, tasteless, and colorless.
O ₂	0.1 to 1	O ₂ comprises approximately 21% of the atmosphere. It is odorless, tasteless, and colorless.
Ammonia	0.1 to 1	Ammonia is a colorless gas with a pungent odor. Atmospheric concentrations are less than 0.0001%.
NMOCs	0.01 to 0.6	NMOCs are organic compounds (i.e., compounds that contain carbon) excluding methane. NMOCs may occur naturally or be formed by synthetic chemical processes.
Sulfides	0 to 1	Sulfides (e.g., hydrogen sulfide, dimethylsulfide, mercaptans) are naturally occurring gases that gives the landfill gas mixture its rotten egg smell. Sulfides can cause unpleasant odors even at very low concentrations. Ambient air concentrations are less than 0.001%.
Hydrogen	0 to 0.2	Hydrogen is an odorless and colorless gas. Atmospheric concentrations are less than 0.00005%.
CO	0 to 0.2	CO is an odorless and colorless gas. Atmospheric concentrations are less than 0.00001%.

Co-disposal LFG typically includes higher NMOC vapor concentrations when compared to an MSW landfill that has not received any significant quantity of toxic or hazardous compounds.

1.2 What Are the Routes of Human Exposure?

Human exposure to LFG occurs through three primary pathways: (1) release of LFG to ambient air, (2) subsurface vapor migration by convection and subsequent indoor vapor infiltration, and (3) indoor vapor infiltration from contaminated groundwater below buildings. Release of LFG to ambient air is most prevalent when a permeable cover is used or when the cover has been breached either intentionally or unintentionally. Under such conditions, the internal pressure transports the gas to the surface or through passive vents to the outside air. Human exposure may occur onsite and offsite as a function of the actual emission rate and atmospheric dispersion. The significance of the human exposure is determined by the chemical's toxicity and concentration as well as by the duration and frequency of exposure. Duration and frequency of exposure are functions of the LFG emission rate, the atmospheric dispersion, and human life style.

When an impermeable or nearly impermeable cover exists or when a permeable cover is

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either overlain by snow or nearly saturated with moisture, horizontal (lateral) subsurface vapor migration may be the path of least resistance. The rate and extent of lateral vapor migration is a function of the landfill's internal pressure and the permeability of the surrounding media. LFG that has migrated laterally from the landfill may be discharged into ambient air and buildings when the vertical vapor permeability is greater than the horizontal vapor permeability.

If contaminated landfill leachate is allowed to commingle with groundwater and/or if the LFG contaminant vapor phase concentration is greater than the aqueous solubility, a plume of contaminated groundwater may be generated that will move through the subsurface in a direction that is hydraulically down gradient. The groundwater plume may move in a direction that is different than the LFG plume. The contaminated groundwater will off gas when the contaminant soil vapor pressure is lower than that found in the groundwater in accordance with Henry's law. The released vapor will migrate towards the surface until equilibrium is achieved or until an atmospheric release occurs.

1.3 Human Health and Safety Concerns

Human health concerns are a function of the exposure to the toxic constituents of LFG. A list of toxic compounds often found in the LFG of MSW landfills is given in Table 1-3 (U.S. EPA, 1997a). *These toxic compounds should not be considered the only possible toxic constituents, but the constituents that are typically target analytes during LFG testing or are considered hazardous air pollutants (HAPs) under the Clean Air Act (CAA) or are monitored for under a State program.* Additional toxic constituents could be present depending on the disposal history of the landfill—e.g., other industrial organic compounds, herbicides, pesticides, polychlorinated biphenyls (PCBs), mercury, etc.

Table 1-3. Contaminants of Potential Concern Commonly Found in LFG ^a

1,1,1-Trichloroethane (Methyl Chloroform)	1,1,2,2- Tetrachloroethene
1,1-Dichloroethane (ethylidene dichloride)	1,1-Dichloroethene (vinylidene chloride)
1,2-Dichloroethane (ethylene dichloride)	1,2-Dichloropropane (propylene dichloride)
Acetone	Acrylonitrile
Benzene	Bromodichloromethane
Carbon disulfide	Carbon tetrachloride
Chlorobenzene	Chloroethane
Chlorofluorocarbons	Chloroform
Chloromethane	Dichlorobenzene
Dichloromethane (Methylene Chloride)	Hexane
Hydrogen sulfide	Methyl ethyl ketone
Methyl isobutyl ketone	Methyl mercaptans
Tetrachloroethylene (perchloroethylene)	Toluene
Trichloroethylene	Vinyl chloride
Xylenes	

^a Constituents associated with carcinogenic and/or chronic noncarcinogenic health effects that are routinely measured;
Source: SWANA 2000.

Although the source of this information is the U.S. Environmental Protection Agency (EPA) *Compilation of Air Pollutant Emission Factors, AP-42, 5th Edition, Supplement C* (AP-42) section on MSW landfills, the background information for this section contains data from sites with and without known co-disposal of hazardous wastes. Therefore, although Table 1-3 should not be considered a complete list of all contaminants of potential concern (COPCs) contained in LFG, the listed constituents have significant potential to be found at sites where co-disposal has taken place. If there is historical evidence indicating that other industrial chemicals, pesticides, herbicides, or other substances have been disposed of at a site, these should be added to the list of COPCs.

Methane is a flammable, potentially explosive gas that is combustible only under specific conditions (i.e., the right combination of CH₄ and O₂ plus a source of ignition). Methane is explosive at concentrations that range from the lower explosive limit (LEL) of 5 percent to the upper explosive limit (UEL) of 15 percent CH₄ per volume of air. This corresponds to CH₄ concentrations of 10,000 to 30,000 parts per million by weight (ppmw). There have been at least 30 reported cases of explosions associated with LFG, causing property damage and killing or injuring nearby residents or workers. At concentrations below the LEL, the CH₄/air mixture is too dilute (CH₄ concentrations are too low) to ignite. If a source of ignition is available any concentration between the LEL and the UEL will allow combustion. Methane concentrations above the UEL (> 15%/v) are too rich (O₂ levels are too low) to support combustion. To sustain a flame, O₂ levels have to be at or above 19 percent.

Landfill fires and the accumulation of explosive levels of CH₄ within onsite and offsite buildings is the primary LFG safety concern. Landfill fires can occur from the excessive influx of ambient air into the landfill wastes. As ambient air infiltrates the landfill wastes, the CH₄ concentration may be locally diluted to levels below the UEL and above the LEL. Typically, the source of ignition is the establishment of aerobic conditions (composting) in the upper reaches of the landfill wastes. The aerobic composting can generate enough heat to cause the CH₄ to autogenously ignite. Aerobic conditions are a direct result of ambient air infiltration due to excessive vacuum applied to LFG extraction wells, landfill cover separations, and natural diffusion of ambient air through permeable cover materials.

Lateral and subsequent vertical migration of LFG into buildings can also occur. If the landfill does not incorporate impermeable liners on the sides and bottom, and the wastes are still generating CH₄, subsurface vapor migration can occur beyond the property boundaries. This may be especially problematic where native soils are relatively permeable (e.g., sands) and offer little resistance to vapor flow. Favorable conditions for subsurface migration also include an impermeable surface boundary such as pavement or when surface soils are frozen. Under these conditions, the horizontal vapor permeability of the soil is greater than the vertical permeability, and LFG may migrate a considerable distance and at different depths until the gas reaches equilibrium or until it discharges to the atmosphere. As with landfill fires, if the CH₄ concentration in the building is between the LEL and the UEL, all that is required for an explosion is a source of ignition (e.g., pilot light, electrical motor spark, static electricity, stoves, and ranges, etc.).

This guidance document provides both modeling approaches and measurement procedures

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for estimating the extent of subsurface vapor migration of LFG. The modeling approaches cover theoretical vapor transport as a function of pressure-driven flow in soils. The measurement procedures cover sampling methods for measuring LFG concentrations above the landfill, at the property boundaries, and towards potentially affected buildings. In addition, monitoring methods are provided for determining the concentrations of CH₄ and COPCs in soil gas under affected buildings and in building air.

1.4 ARARs Specific to Landfill Gas Emissions

Applicable or relevant and appropriate requirements (ARARs) as defined in the National Contingency Plan (NCP) may include: (1) chemical-specific, (2) location-specific, and (3) action-specific statutory requirements. These requirements include those established by the U.S. EPA and other Federal agencies and those established by the state in which any release occurs, if the State's standards are promulgated, more stringent than the Federal standards, and are identified in a timely manner. *Applicable requirements* are Federal or state requirements that “specifically address a hazardous substance, pollutant, contaminant, remedial action, location, or other circumstance found at a CERCLA site” (NCP Sec. 300.5). *Relevant and appropriate requirements* are Federal or State laws that, while not applicable, “address problems or situations sufficiently similar to those encountered at the CERCLA site that their use is well suited to the particular site.” (NCP Sec. 300.5). For the air pathway, ARARs are typically classified as either chemical-specific or action-specific and can be divided further into either Federal or State ARARs.

1.4.1 Federal Air Pathway ARARs

Federal air pathway action-specific ARARs include the New Source Performance Standards (NSPS) and the Emission Guidelines (EG) for MSW Landfills under the Clean Air Act (CAA); process and remedial technology emission limits under Subtitle D of RCRA; and RCRA Subtitle C requirements for explosive gases control.

The NSPS for MSW landfills is applicable only for “new” landfills that began construction, modification, or reconstruction on or after May 30, 1991. Modifications can include lateral and vertical expansions of the landfill. The EG for MSW landfills is applicable for “existing” landfills that accepted waste on or after November 8, 1987. In addition, both the NSPS and the EG are applicable only for relatively large landfills with NMOC annual emissions above 50 megagrams per year. The NSPS may be an ARAR if the Superfund landfill (SFL) is a subsection of a “new” landfill still accepting waste. In most cases, however, the EG—Section 111(d) Plan—is more likely to constitute the major action-specific ARAR for landfills no longer accepting waste. EPA has determined that although the EG may not be applicable for a given site because it does not meet the waste acceptance cutoff date, the EG may still be relevant and appropriate if the landfill design capacity cutoff value (2.5 million Mg or 2.5 million m³) and NMOC annual emission cutoff value (50 Mg/yr) are met or exceeded. The substantive requirements of the NSPS and EG include installation of a LFG capture system and emission control requirements as well as monitoring requirements.

Promulgated EG under 40 CFR Part 60 are not enforceable by either EPA or the States. To

be enforceable, Section 111(d) of the CAA requires that the EG requirements be stipulated in either a Federal or an approved State implementation plan, codified in 40 CFR Part 62. The Federal plan acts as an enforceable place holder until EPA approves the State plan. There should be no fundamental difference in the requirements of the Federal plan and an EPA approved State plan. This is discussed further in Chapter 4, Section 4.1.

Air pathway rules for the treatment or disposal of hazardous wastes may be applicable or relevant and appropriate requirements under specific circumstances. LFG is not a hazardous waste. If, however, solid wastes are excavated and/or treated, or if a liquid waste stream is treated, the air emission standards for process vents, equipment leaks, containers, tanks, and surface impoundments may apply. Liquid waste streams such as leachate may be considered hazardous waste if precipitation has percolated through land disposal wastes comprised of more than one restricted waste classified under RCRA Part 261. Even if landfill records are lacking that determine if specific restricted waste streams have been deposited in a landfill, the leachate would have to undergo the toxicity characteristic leaching procedure (TCLP) and other RCRA characteristic waste tests as specified in 40 CFR §261.20 through §261.24. If the leachate fails one or more of these tests, it is considered a RCRA characteristic hazardous waste. The characteristic waste tests would also apply to any collected LFG condensate. If the leachate or condensate is considered a listed or characteristic hazardous waste and is treated (e.g., by air stripping) or disposed of (e.g., by burning in an enclosed flare), the RCRA rules governing treatment and/or incineration of hazardous waste may apply.

Finally, RCRA Part 258 specifies the control requirements for explosive gases at new MSW landfills, existing MSW landfills, and lateral expansions of existing MSW landfills. These requirements are considered ARARs and include the establishment of a routine CH₄ monitoring program to detect whether the LFG CH₄ concentrations within facility structures exceed 25 percent of the LEL or exceed the LEL at the property boundary. At 25 °C, the LEL of CH₄ in air is approximately 5 percent. If one or both of these levels are exceeded, the rules require the owner or operator of the landfill to immediately take steps to protect human health and to implement a remediation plan. The Federal ARARs mentioned above are discussed in greater detail in Chapter 4 of this document. There is no national engineering or building code for the design or construction for LFG control systems.

1.4.2 State Air Pathway ARARs

State air pathway ARARs may include a variety of action-specific and chemical-specific regulatory requirements. State air pathway ARARs may include emission limits based on an emission rate (e.g., pounds per hour) or based on a stack concentration (e.g., parts per billion by volume). These limits may be pollutant-specific or apply to a specified chemical class (e.g., NMOC). State ARARs may also include ambient air standards for the traditional “criteria” pollutants such as particulate matter and sulfur dioxide (SO₂) or may be risk-based ambient air standards for specific carcinogenic and noncarcinogenic pollutants. State rules may also dictate the type and frequency of CH₄ monitoring programs at MSW landfills and may include nuisance or odor regulations designed to prevent the excessive release of malodorous compounds. Finally, landfill monitoring or sampling requirements may be more stringent than those of the Federal EG Part 258 rules.

1.5 Potential Landfill Problem Areas

The following are potential air pathway problem areas particular to both MSW and co-disposal landfills that should be carefully considered. Other potential areas of concern for the air pathway may be present at a given site due to site-specific factors.

1.5.1 Landfill Cover Emissions

In some cases, the landfill may be capped with a simple soil cover. In addition, a passive vent system may also be employed to vent LFG to the atmosphere. Under this scenario, the majority of the landfill gas may be emitted through cracks and gaps in the cover or directly through the soil and not necessarily through the passive vents. In this type of situation, the radius of influence of a passive vent is relatively small whereas the transport of landfill gas is multi-dimensional and will take the path of least resistance. In such cases, exposure to emissions of LFG into ambient air are likely to be the greatest at the landfill perimeter. This may be especially problematic if relatively high concentrations of toxic NMOCs in the LFG are located in perimeter sections of the landfill near potential receptors.

1.5.2 Risks Due To Indoor Vapor Intrusion

Subsurface lateral migration of LFG is a potential exposure pathway. Lateral migration may be especially problematic when surface soils are frozen or when surrounding areas are paved. These situations result in a higher subsurface pressure gradient and, thus, longer transport distances. If indoor air concentrations are found to be below the LEL of CH₄, this pathway cannot be dismissed simply because an explosive detonation or fire cannot occur. Although the risk of a CH₄ explosion does not exist below the LEL, the vapor concentrations of the toxic LFG constituents may still be unacceptable. For example, the 1-in-1,000,000 risk-based residential air concentration of vinyl chloride is approximately 0.072 mg/m³. Given a typical residential building air exchange rate and a relatively small subsurface vapor intrusion rate, an indoor air concentration of vinyl chloride greater than 0.072 mg/m³ is possible even if the methane concentration of the LFG entering the house is less than the LEL.

1.5.3 Landfill Fires and Explosions

Landfill fires and explosions occur when ambient air infiltrates the landfill wastes providing enough oxygen to support combustion and locally diluting the CH₄ concentration below the UEL. Air infiltration can occur by various means. Landfill subsidence can cause cap or cover slippage leaving air infiltration gaps or can actually expose the waste to ambient air. In addition, active gas collection systems purge LFG from the landfill by drawing a vacuum at each collection well. If the landfill cover leaks at the point of penetration of one or more collection wells, ambient air can be drawn down the annulus of the well and into the wastes.

1.5.4 Emissions of Toxic LFG Constituents

Co-disposal landfills are typically remediated under the Superfund program because of the hazardous or toxic wastes that have been deposited in the landfill. These wastes may contain constituents that become part of the LFG but at levels which are below the detection limit of

the field instruments commonly used to detect VOC. For example, PCBs or other extremely toxic compounds may have been dumped within a given landfill. In such cases, LFG sampling and analytical procedures capable of detecting these types of compounds should be employed.

1.6 Document Organization

The remainder of this document is divided into five chapters and appendices. Chapter 2 covers the generation of LFG as well as techniques for assessing the ambient air impacts from LFG emissions under baseline or uncontrolled conditions. Chapter 3 discusses subsurface vapor migration of LFG. Techniques are provided for assessing the extent of pressure-driven subsurface vapor migration beyond the site boundary and possible vapor intrusion into buildings. In addition, procedures are discussed for assessing possible subsurface vapor intrusion into buildings as a result of contaminated groundwater. Chapter 4 provides a more detailed description of Federal and State air pathway ARARs including the CAA NSPS and EG for MSW landfills. This chapter also discusses the individual rules under RCRA and general State rules that may be ARARs. Chapter 5 covers LFG capture and control systems commonly in use at both Superfund and MSW landfills under RCRA Subtitle D. Appendix A provides sampling and analytical methods for determining: (1) the composition of LFG, (2) the concentrations of LFG constituents in ambient air, and (3) the concentrations of LFG constituents in indoor air as a result of indoor vapor intrusion. Appendix B contains a Generic Quality Assurance Project Plan (QAPP). Appendix C includes a discussion of the methodology and statistical procedures used to determine if the landfill emission can be characterized as homogeneous.

2. Landfill Gas Generation and Transport

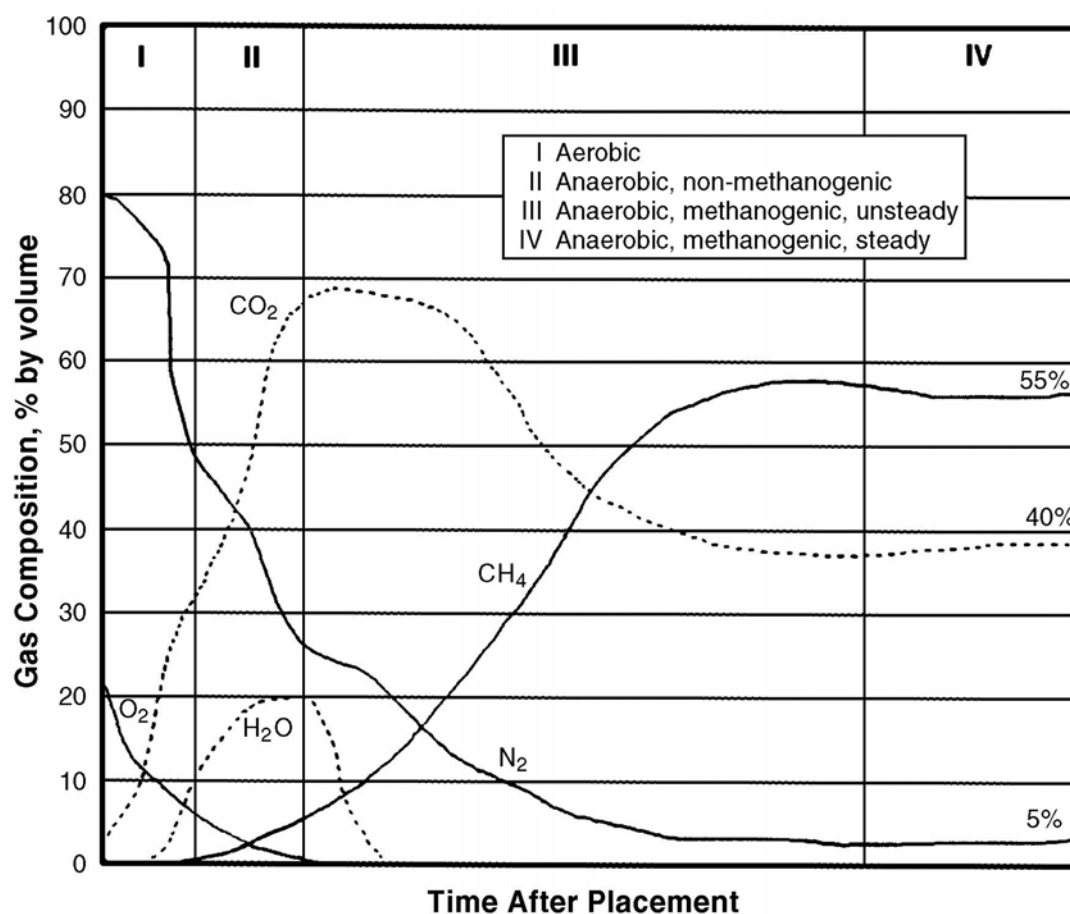
This chapter covers the generation of LFG within MSW and co-disposal landfills as well as the emissions of toxic constituents in landfill gas. Modeling concepts and procedures are also introduced for estimating the emissions of LFG and the individual emissions of hazardous or toxic LFG constituents. Modeling procedures are also provided for dispersing LFG COPCs in ambient air and for estimating exposure point air concentrations. Finally, ambient air sampling is discussed for measuring air concentrations at potential exposure points.

2.1 Landfill Gas Generation

CH₄ and CO₂ are the primary constituents of LFG and are produced by microorganisms within the landfill under anaerobic conditions. Carbohydrates from paper, cardboard, and other waste material, which form the major components of refuse, are decomposed initially to sugars, then mainly to acetic acid, and finally to CH₄ and CO₂ (U.S. EPA, 1997a).

LFG generation, including rate and composition, proceeds through four characteristic phases throughout the lifetime of a landfill. Figure 2-1, from the *Emission Factor Documentation for AP-42, Section 2-4, Municipal Solid Waste Landfills* (U.S. EPA, 1997a), is a graphical representation of typical LFG evolution. Bacteria decompose landfill waste in four phases. The composition of the gas produced changes with each of the four phases of decomposition. Landfills often accept waste over a 20- to 30-year period, so waste in a landfill may be undergoing several phases of decomposition at once. This means that older waste in one area might be in a different phase of decomposition than more recently buried waste in another area.

During the first phase of decomposition, aerobic bacteria—bacteria that live only in the presence of oxygen—consume O₂ while breaking down the long molecular chains of complex carbohydrates, proteins, and lipids that comprise organic waste. The primary byproduct of this process is carbon dioxide. Nitrogen content is high at the beginning of this phase but declines as the landfill moves through the four phases. Phase I continues until available O₂ is depleted. Phase I decomposition can last for days or months, depending on how much O₂ is present when the waste is disposed of in the landfill. Oxygen levels will vary according to factors such as how loose or compressed the waste was when it was buried.



Note: Time scale (total time and phase duration) of gas generation varies with landfill conditions (i.e., waste composition and anaerobic state).

Figure 2-1. Landfill Gas Evolution (Tchobanoglous et al., 1993)

Phase II decomposition starts after the O_2 in the landfill has been used up. Using an anaerobic process (a process that does not require oxygen), bacteria convert compounds created by aerobic bacteria into acetic, lactic, and formic acids and alcohols such as methanol and ethanol. The landfill becomes highly acidic. As the acids mix with the moisture present in the land-fill, they cause certain nutrients to dissolve, making nitrogen and phosphorus available to the increasingly diverse species of bacteria in the landfill. The gaseous byproducts of these processes are carbon dioxide and hydrogen. If the landfill is disturbed or if O_2 is somehow introduced into the landfill, microbial processes will return to Phase I.

Phase III decomposition starts when certain kinds of anaerobic bacteria consume the organic acids produced in Phase II and form acetate, an organic acid. This process causes the landfill to become a more neutral environment in which methane-producing bacteria begin to establish themselves. Methane- and acid-producing bacteria have a symbiotic, or mutually beneficial, relationship. Acid-producing bacteria create compounds for the methanogenic bacteria to consume. Methanogenic bacteria consume the carbon dioxide and acetate, too much of which

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would be toxic to the acid-producing bacteria.

Phase IV decomposition begins when both the composition and production rates of landfill gas remain relatively constant. Phase IV landfill gas usually contains approximately 45 to 60 percent CH_4 by volume, 40 to 60 percent CO_2 , and 2 to 9 percent other gases, such as sulfides. Gas is produced at a stable rate in Phase IV, typically for about 20 years; however, gas will continue to be emitted for 50 or more years after the waste is placed in the landfill. Gas production might last longer, for example, if greater amounts of organics are present in the waste, such as at a landfill receiving higher than average amounts of domestic animal waste.

The first phase is aerobic (i.e., while O_2 is available), and the primary gas produced is CO_2 . The second phase is characterized by O_2 depletion, resulting in an anaerobic environment where large amounts of CO_2 and some hydrogen (H_2) are produced. In the anaerobic third phase, CH_4 production begins, with an accompanying reduction in the amount of CO_2 produced. Nitrogen content is initially high in LFG in the aerobic first phase and declines sharply as the landfill proceeds through the anaerobic second and third phases. In the fourth phase, gas production of CH_4 , CO_2 , and N_2 becomes fairly steady. The phase, duration, and timing of gas generation vary with landfill conditions (i.e., waste composition, cover materials, moisture content, temperature, pH, etc.) and may also vary with climatic conditions such as precipitation rates and temperatures.

Emissions of NMOCs, including COPCs, result from NMOCs originally contained in the land filled waste and from their creation from biological processes and chemical reactions within the landfill. For example, benzene may be a component of petroleum-derived solvents, whereas vinyl chloride is typically formed from the breakdown of chlorinated solvents, such as trichloroethylene, trichloroethane, and perchloroethylene.

The rate of LFG emissions is governed by gas production and transport mechanisms. Production mechanisms involve the production of the emission constituent in its vapor phase through vaporization, biological decomposition, or chemical reaction. Production mechanisms are affected by a variety of factors.

Vaporization is affected by the concentration of the individual compounds in the landfill, the physical properties of the individual compounds, and the specific landfill conditions (i.e., temperature and confining pressure). Biological decomposition of liquid and solid compounds into other chemical species depends on:

- Nutrient availability for micro-organisms,
- Waste composition,
- The age of the landfill,
- Moisture content,
- pH,
- Temperature,
- O_2 availability,
- Exposure to certain biological activity-inhibiting industrial wastes.

Accurate quantification of the impacts of any of these factors on LFG production is not

possible with the current state of knowledge. Chemical reactions are dictated by the composition of the waste, temperature, and moisture content in the landfill.

Temperature, age of the refuse, and pH also affect landfill gas production. A pH of 6.6 to 7.4 is thought to be optimal for CH₄-generating microorganisms (methanogens). Temperature affects microbial activity within the landfill, which in turn affects the temperature of the landfill. The internal temperature of the landfill tends to be self-regulating because anaerobic decomposition can typically heat the landfill interior to approximately 90 to 120 °F. Warm landfill temperatures favor CH₄ production, which may be affected by seasonal temperature fluctuations in cold climates where the landfill is shallow and sensitive to ambient temperatures.

Transport mechanisms involve the transportation of volatile constituents in the vapor phase to the surface of the landfill, through the air boundary layer above the landfill, and into the atmosphere. There are two major mechanisms that enable transport of a volatile constituent in its vapor phase: molecular diffusion and LFG convection (U.S. EPA, 1997a).

As with production mechanisms, transport mechanisms are affected by a variety of factors. Molecular diffusion through a soil cover is influenced by the soil porosity, soil moisture content, the existing concentration gradient, the diffusivity of the constituent, and the thickness of the soil. Molecular diffusion through the air boundary layer is affected by the wind speed, concentration gradient, and diffusivity of the constituent.

LFG convection occurs due to pressure changes within the landfill that are influenced by nutrient availability for bacteria, waste composition, moisture content, landfill age, temperature, pH, O₂ availability, presence of a gas collection system, and biological activity-inhibiting wastes (i.e., industrial wastes). Displacement of LFG due to compaction and settlement depends on the degree of compaction, waste compatibility, and overburden weight (settlement). Displacement can also occur through other mechanisms. Displacement can be influenced by changes in atmospheric pressure. Displacement due to water table fluctuations is affected by the presence of a liner, rate of evaporation, rate of precipitation, and the horizontal versus the vertical permeability (U.S. EPA, 1997a).

Spatial and temporal variability are considered to be important relative to sampling. Landfills are known to exhibit large variations in gas production from one area to the next. The focus of the recommended sample design is to maximize the spatial coverage by collecting LFG information from all vents and on-site structures and from locations that are established by using a systematic 30-m by 30-m sampling grid that is defined by the landfill cover and extends to 30 meters beyond the landfill boundary. This systematic screening technique is designed to identify “hot spot” locations for both methane and NMOC. The screening results will be used to identify locations that will be sampled for the COPCs. Depending on the landfill cover material, it is assumed that the landfill vents will have higher LFG concentrations, and their impact on the ambient air will be greater than the impacts derived from the surface emissions. The sample design assumes that the emissions from the locations with the highest NMOC concentration within each homogeneous area will adequately characterize the total landfill emissions.

The sample design assumes that the proximity of off-site structures to the landfill boundary is the dominant risk driver for subsurface vapor intrusion into off-site buildings via pressure gradients. This assumption may be invalid if there are interceptors, diversion structures, barriers, geologic faults, or preferential vapor pathways between the landfill and the building.

2.2 Estimation of Ambient Air Impacts

One of the primary routes of human exposure to LFG is inhalation of COPCs in ambient air. In addition, compliance with Federal and State air pathway ARARs, as appropriate, must also be assessed.

An assessment of ambient air impacts necessarily begins with an estimate of the LFG emissions of NMOCs and COPCs. Under baseline conditions, LFG emissions typically occur at or near ground-level through any existing cover or landfill vents. Atmospheric dispersion of these types of emission sources results in maximum offsite impacts at the perimeter of the landfill. It is therefore necessary to estimate the spatial variability of emissions across the areal extent of the landfill.

If the landfill employs uncontrolled vents, each vent will be sampled separately. If vents are not employed or if the area of influence for the vents is not adequate, LFG concentrations will be delineated using a superimposed grid system. The number of sampling points will be determined as a function of the landfill size, homogeneity of its contents, and the amount of resources available for sampling and analysis activities. As long as there is no flexible membrane liner (FML) soil gas sampling will be conducted approximately one meter below any landfill cover using either a slam-bar or a Geo-probe depending on equipment availability and soil properties. If there is an FML, arrangements must be made to make repairs or to use an alternative sampling technique, such as open path Fourier transform infrared spectroscopy (OP-FTIR), to estimate the emission rates.

The number of samples that must be obtained to estimate the mean concentration of an area depends strongly on the heterogeneity of the chemical distribution. Thus, for an area with uniform distribution, few samples are needed to provide good characterization. Conversely, an area with widely variable distribution would require a great number of samples. For landfills with nonuniform distribution, the total number of samples can be reduced by subdividing the area into zones with similar levels of contamination and variability, age, volume, and surface area. The objective of the screening effort is to identify the areas with near homogeneous NMOC concentration. The Wilcoxon rank sum test (also known as Mann-Whitney test) will be used to determine if there is an area with a higher mean concentration when compared to the entire landfill. A grid density of 1 per 900 square meters (30×30 meter grid) is recommended as point of departure. A higher density may be warranted if portions of the landfill are known to differ significantly from one area to the next over a short lateral distance. On the other hand, if the landfill is very large or the operating history indicates that what is buried in one area is similar to that buried in another, a large grid may be needed in order to reduce the costs and expenses associated with the characterization effort.

Emission estimating is an important step in conducting risk evaluations, obtaining permits,

demonstrating compliance with regulatory limits, and in designing emission control systems for solid waste landfills. There are several methods for measuring and analyzing LFG. The chemical concentration may be determined via: (1) sampling at active and passive vents; (2) using probes placed just below the cover; (3) OP-FTIR; (4) open path tunable diode laser methods; (5) flux chamber methods; and (6) passive adsorption concentration gradient methods. This document presents a step-wise procedure using readily available field instruments, sampling probes placed just below the cover, routine analytical methods, and commonly used fate and transport modeling procedures. The document also presents the results of an example application of an open path OP-FTIR emission measurement method. The OP-FTIR was used in conjunction with a radial plume mapping technique to estimate the emission rates and to establish ambient air concentrations.

This document provides site investigators, risk managers, and design engineers with procedures and methodologies that may be used to estimate LFG emissions and resulting ambient air concentrations. The usefulness of this document was demonstrated at three study sites that are illustrative of the techniques discussed herein. It is recognized that both techniques—screening/sampling/modeling and optical remote scanning—have advantages and disadvantages that must be taken into account. Decision makers must balance their need for definitive site-specific information with that derived by generic fate and transport models. The technique using field screening, sampling, and modeling procedures were used at two sites: Rose Hill Regional Landfill, South Kingston, Rhode Island, and Bush Valley landfill in Abingdon, Maryland. Both techniques were implemented at the Municipal Landfill Superfund Site located in Somersworth, New Hampshire. Both techniques that are illustrated in the guidance have been shown to be viable.

2.2.1 The Technique Using Probes Placed Just Below the Surface

This process is initiated with a first round of air sampling (screening) across the face of the landfill using portable instruments as discussed in Appendix A. This is typically accomplished using either biased (based on foreknowledge) or unbiased (randomly selected) grid sampling depending on any previous knowledge of emission patterns or the spatial distribution of wastes. If the landfill is covered by an impermeable membrane, this type of sampling is still appropriate because the cover's integrity may have been compromised by differential settling, improper installation, or unexpected surface activities such as rolling heavy equipment across it or construction of structures and buildings. Screening level sampling uses portable instruments that can detect total organic compounds (including CH₄) and instruments that detect total organics but are insensitive to CH₄. From these data, the surface of the landfill and any passive vents can be analyzed for emissions of both CH₄ and NMOCs. These screening data also provide information necessary to partition the surface of the landfill into areas of lesser emission variability using the Wilcoxon statistical procedures. Hot spots are identified by using the Wilcoxon statistical procedures (described elsewhere). Below the cover, LFG samples are collected at hot spots for each nearly homogeneous areas of the landfill. The NMOC emissions are used to estimate average or upper bound (e.g., 90th percentile) emissions of individual COPCs for each area. It is important to understand that the extent of CH₄ and NMOC emissions may not correlate at a given location. That is, NMOC emissions may be higher or lower in relation to CH₄ emissions as a function of where the hazardous or toxics wastes were dumped.

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Therefore, second-round sampling locations should be based on the screening data for NMOCs. Second-round sampling involves methods for determining the LFG concentrations of individual COPCs. These concentrations can then be used to estimate landfill emissions based on modeling. Appendix A provides information on sampling and analytical techniques that may be used.

With data on the spatial distribution of LFG concentrations of COPCs, the analyst can use these data as input values for emissions modeling. Estimated COPC emissions are then dispersed in ambient air using either screening-level or refined atmospheric dispersion models to estimate exposure point air concentrations for both onsite and offsite receptors as applicable. These estimates of ambient air concentrations are then used to estimate human health risks and to determine compliance with any air pathway ARARs for baseline conditions.

Figure 2-2 provides a general flow chart for estimating through modeling the ambient air impacts from baseline emissions of LFG. Details of the flow chart are discussed in the subsequent sections of this Chapter. As an alternative, air impacts can also be assessed using ambient air sampling techniques. Section 2.2.5 provides guidance on estimating air impacts from emissions of LFG COPCs. Appendix A provides information on sampling and analytical procedures for ambient air sampling.

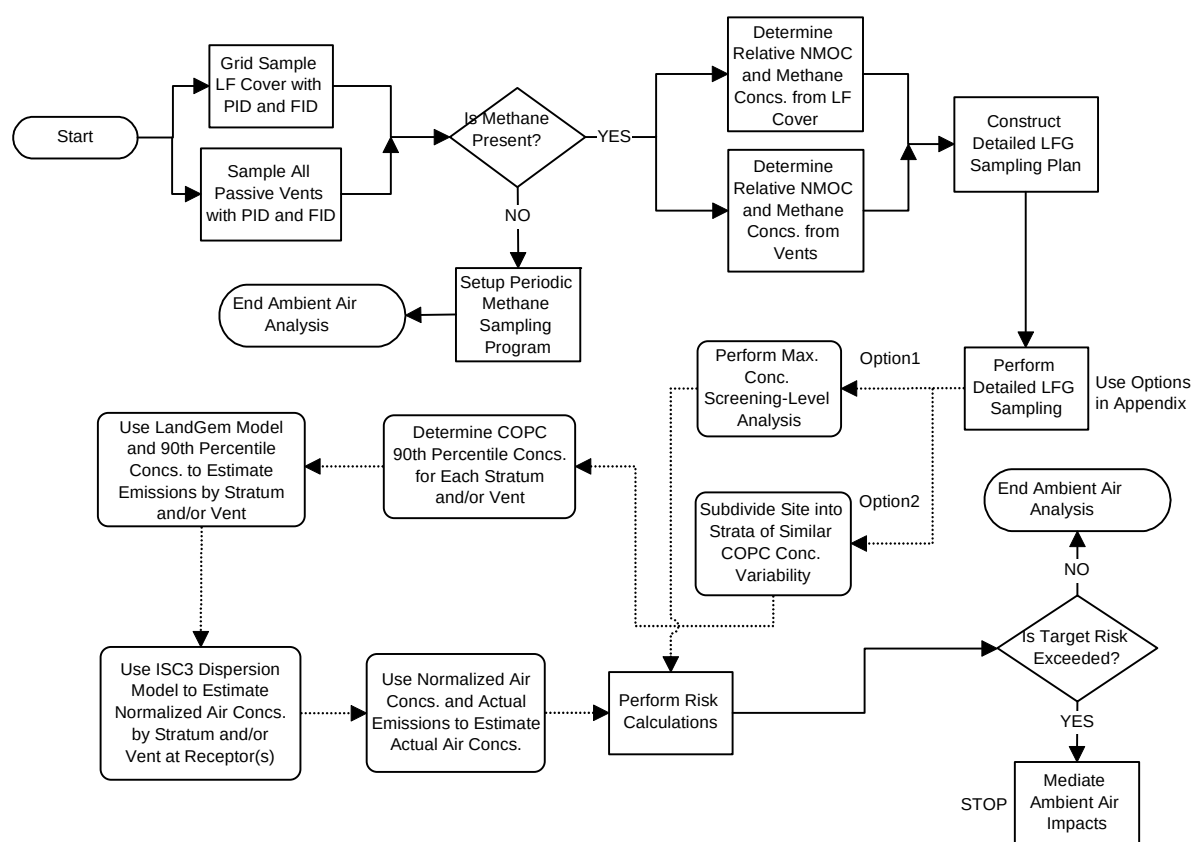


Figure 2-2. Flow Chart for Assessing Air Impacts by Modeling.

2.2.1.1 Estimating Uncontrolled Landfill Gas Emissions

The recommended methods for estimating emissions of LFG constituents at Superfund landfills (SFLs) are the same as those developed for MSW landfills and published in AP-42 (U.S. EPA, 1997a, 1997b). Alternative methods using OP- FTIR and optical remote sensing radial plume mapping techniques are discussed in Appendix A. To estimate uncontrolled emissions of the various constituents present in LFG, total LFG emissions must first be estimated. Uncon-trolled CH₄ emissions are estimated with a theoretical first-order kinetic model of CH₄ production. This model is known as the Landfill Gas Emissions Model (LandGEM). A version of LandGEM for the personal computer (PC) can be downloaded from EPA's website at <http://www.epa.gov/ttn/catc/products.html#rblsoftware> (accessed September 2005). A user's manual is also available on this website. It should be noted that the LandGEM model described in this document has been modified. The Beta version is PC-based software for estimating emissions of CH₄, CO₂, NMOCs, and HAPs from municipal solid waste landfills.

There are two sets of default values in LandGEM. One, the CAA set, is based either on the NSPS requirements for emissions to the atmosphere from new municipal solid waste landfills or on the Federal EG for emissions from existing landfills. These regulations and guidelines are contained in the *Code of Federal Regulations*, Title 40, Part 60, (40CFR60) Subparts WWW and Cc, respectively. This set of default values produce conservative emission estimates that can be used to determine the applicability of Federal regulations or guidelines to the landfill being evaluated. For more information on the assumptions used in the model and the CAA default set, see the background information document (U.S. EPA, 1991) or public docket (A-88-09) for the landfill NSPS and guidelines.

The other set of values, the AP-42 set, is based on emissions factors in EPA's guidance document, *Compilation of Emission Factors, Fifth Edition, AP-42* (U.S. EPA, 1997b). This set of default values is less conservative than the CAA set and can be used to produce typical emission estimates in the absence of site-specific test data. The AP-42 values used in this Beta version of LandGEM have been revised and are available for public comment. Once AP-42 revisions have been published as final, the AP-42 default set in LandGEM will be revised accordingly, and the final version of the model will be issued. Although this is a Beta version and subject to additional testing, all software components of LandGEM are fully functional.

LandGEM can be used to estimate mass emissions of NMOCs to assess applicability of a site with regards to the NSPS and EG. The model can also be used to estimate mass emissions of the COPCs by using either default or user-specified LFG concentration data. The following discussion provides details on the equations and underlying data used in LandGEM (and documented in AP-42) to estimate LFG emissions.

The equation used to estimate the generation rate of CH₄ within LandGEM is

$$Q_{CH_4} = \sum_{i=1}^n \sum_{j=0.1}^1 kL_0 \left(\frac{M_i}{10} \right) e^{-kt_{ij}} \quad 2-1$$

where:

Q_{CH_4} = annual CH₄ generation during the year of the calculation in cubic meters per year,

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i = 1 year time increment,
 n = (year of the calculation) - (initial year of waste acceptance),
 j = 0.1 year time increment,
 k = methane generation rate in reciprocal years,
 L_0 = potential methane generation capacity in cubic meters per megagram,
 M_i = mass of waste accepted in the i^{th} year in megagrams,
 t_{ij} = age of the j^{th} section of waste mass M_i accepted in the i^{th} year (decimal years, e.g., 3.2 years).

LandGEM provides a mass emission rate that is used in a dispersion model to provide ambient concentrations. Other fates may exist for the gas generated in a landfill, including capture and microbial degradation within the landfill's surface layer. Currently, there are no data that adequately address this fate. It is generally accepted that the bulk of the gas generated will be emitted through the cover materials or cracks and other openings in the landfill surface, taking the path of least resistance. Some oxidation will occur as gas diffuses through the soil cover, but this is typically thought to be less than 10%.

Site-specific landfill information is generally available for the variables M_i , c , and t . When refuse acceptance rate information is scant or unknown, M_i can be determined by dividing the mass of refuse in-place by the age of the landfill. The average annual acceptance rate should only be estimated by this method when there is inadequate information available on the actual average acceptance rate.

To determine the amount of waste in place, an estimate of the volume of the landfill must be made. Often information on the area of the landfill can be obtained from topographic maps, aerial maps, or previous surveys of the waste boundaries. The depth of the landfill can be determined from surveys (e.g., borings) of the waste depth. In some cases, topographic maps may be useful in estimating waste depth. Because the density of the waste is difficult to establish, a recommended value of 625 kg/m³ (1,800 lb/yd³) should be used (NSWMA, 1985). This value is based on MSW that has undergone compaction and some degree of degradation and settling.

If there are data on the fraction of nondegradable wastes for a site, this waste mass can be excluded from the calculation of M_i . This issue is significant for SFLs, because the potential exists for disposal of large portions of nondegradable waste. Nondegradable waste includes concrete, brick, stone, glass, piping, plastics, and metal objects. The time variable, t , includes the total number of years that the waste has been in-place including the number of years that the landfill has accepted waste and, if applicable, has been closed.

Values for L_0 and k must be estimated. Estimation of the potential CH₄ generation capacity of refuse (L_0) is generally treated as a function of the moisture and organic content of the refuse. Estimation of the CH₄ generation constant (k) is a function of a variety of factors, including moisture, pH, temperature, other environmental factors, and landfill operating conditions. Specific CH₄ generation constants can be estimated by the use of EPA Reference Method 2E (40 CFR Part 60 Appendix A); however, default values are often used.

LandGEM includes both regulatory default values and recommended AP-42 default values for L_0 and k . The regulatory defaults were developed for the purposes of determining the applicability of the NSPS/EG. As a result, LandGEM contains conservative L_0 and k default values in order to protect human health, to encompass a wide range of landfills, and to encourage the use of site-specific data.

LandGEM also contains the AP-42 defaults that are recommended for use in assessing SFL emissions. A default k value of 0.04/yr should be used for areas receiving 25 in (63.5 cm) or more of rain per year, but a default k value of 0.02/yr should be used in drier areas (less than 25 in/yr). An L_0 value of 100 m³/Mg-refuse (3,530 ft³/ton) is appropriate for most landfills. Although the recommended default k and L_0 values are based on the best fit to 21 different landfills, the predicted CH₄ emissions ranged from 38 to 492 percent of the actual emissions and exhibited a relative standard deviation of 0.85.

It should be emphasized that in order to comply with the NSPS or EG, the regulatory default values for k and L_0 must be applied as specified in the final rule. The regulatory default values of k and L_0 are 0.05/yr and 170 m³/Mg, respectively.

When gas generation reaches steady-state conditions, LFG consists of approximately 40 percent by volume CO₂, 55 percent CH₄, 5 percent N₂ (and other gases), and trace amounts of NMOCs. Therefore, the estimate derived for CH₄ generation using LandGEM can also be used to represent CO₂ generation. The sum of the CH₄ and CO₂ emissions is a reasonable estimate of total LFG emissions. If site-specific information is available to suggest that the CH₄ content of LFG is not 55 percent, then the site-specific information should be used, and the CO₂ emissions estimate should be adjusted accordingly.

Most of the NMOC emissions result from the volatilization of organic compounds contained in the landfilled waste and subsequent transport in the LFG. The current version of the LandGEM model contains a regulatory default concentration value for total NMOC of 4,000 part per million by volume (ppmv), expressed as hexane. Available data, however, show that there is a considerable range for total NMOC values from landfills. The regulatory default value for NMOC concentration was developed for regulatory compliance purposes. For emissions inventory purposes, site-specific information should be taken into account when determining the total NMOC concentration (i.e., using EPA Reference Methods 25C or 18 found in 40 CFR 60, Appendix A).

If a site-specific NMOC concentration is available, it must be corrected for air infiltration which can occur by two different mechanisms: LFG sample dilution and air intrusion into the landfill. These corrections require site-specific data for the LFG CH₄, CO₂, N₂, and O₂ content (i.e., from EPA Reference Method 3C found in 40 CFR 60, Appendix A). If the ratio of N₂ to O₂ is less than or equal to 4.0 (as found in ambient air), then the total pollutant concentration is adjusted for sample dilution by assuming that CO₂ and CH₄ are the primary (100 percent) constituents of LFG, and the following equation is used:

$$C_p(\text{corrected}) = \frac{C_p}{C_{CO_2} + C_{CH_4}} \quad 2-2$$

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where:

- C_P = COPC Concentration in LFG in parts per million by volume,
- C_{CO_2} = CO_2 concentration in LFG in parts per million by volume,
- C_{CH_4} = CH_4 concentration in LFG in parts per million by volume.

If the ratio of N_2 to O_2 concentrations is greater than 4.0, the total pollutant concentration should be adjusted for air intrusion into the landfill by using Equation 2-2 and adding the concentration of N_2 (i.e., C_{N_2}) to the denominator. Values for C_{CO_2} , C_{CH_4} , C_{N_2} , and C_{O_2} can be obtained using EPA Reference Method 3C.

To estimate emissions of NMOCs or other COPCs, the equation that should be used is

$$Q_P = 1.82 Q_{CH_4} \times \frac{C_P}{10^6} \quad 2-3$$

where:

- Q_P = Emission rate of COPC in cubic meters per year,
- Q_{CH_4} = CH_4 generation rate in cubic meters per year (e.g., from LandGEM),
- C_P = COPC Concentration in LFG in parts per million by volume,
- 1.82 = Multiplication factor (assumes that 55% of LFG is CH_4 and 45% is CO_2 , N_2 , and other constituents),
- 10^6 = Constant to correct units as parts per million by volume.

Uncontrolled mass emissions per year of NMOC (as hexane), CO_2 , CH_4 , and COPCs can be estimated by

$$UM_P = Q_P \times \left[\frac{MW_P \times 1 atm}{R \times 1,000 \times (273 + T)} \right] \quad 2-4$$

where:

- UM_P = Uncontrolled mass emissions of COPC in kilograms per year,
- MW_P = Molecular weight of COPC in grams per gram-mole,
- Q_P = NMOC emission rate of COPC in cubic meters per year,
- T = Temperature of landfill gas in degrees Celsius,
- R = Gas constant ($8.205 \times 10^{-5} \text{ m}^3\text{-atm/gmol-K}$),
- 1,000 = Constant to convert grams to kilograms.

This equation assumes that the operating pressure of the system is approximately 1 atmosphere. If the temperature of the LFG is unknown, a temperature of 25 °C (77 °F) is recommended.

Table 2-1 lists the AP-42 default LFG concentrations for several common COPCs. It is important to note that the COPCs listed in Table 2-1 are not the only compounds likely to be present in LFG. The listed COPCs are those that were identified through a review of the available literature. The reader should be aware that additional compounds are likely to be present, such as those associated with consumer or industrial products.

Table 2-1. Default Concentrations for Landfill Gas Copcs ^a

COPC	CAS Number	Molecular Weight	Concentration (ppmv)	
			AP-42 Default	90 th Percentile
1,1,1-Trichloroethane (methyl chloroform)	71-55-6	133.42	0.48	3.82
1,1-Dichloroethene (vinylidene chloride)	120-82-1	96.94	0.20	15.1
1,2-Dichloroethane (ethylene dichloride)	107-06-2	98.96	0.41	32.0
Acrylonitrile	107-13-1	53.06	6.33	28.3
Benzene	71-43-2	78.11	11.1	92.6
Carbon tetrachloride	56-23-5	153.84	0.004	0.22
Chlorobenzene	108-90-7	112.56	0.25	9.92
Chlorofluorocarbons ^c (as dichlorodifluoromethane)	na ^d	120.91	19.7	56.0
Chloroform	67-66-3	119.39	0.02	2.11
Dichlorobenzene ^e	106-46-7	147.00	0.21	0.33
Dichloromethane (methylene chloride)	75-09-2	84.94	14.3	45.6
Ethyl chloride	75-00-3	64.52	1.25	6.51
Ethylene dibromide	106-93-4	187.88	0.001	0.001
Hydrogen sulfide	7783-06-4	34.08	35.5	81.3
Mercury (total) ^f	7439-98-7	200.61	2.92×10^{-4}	0.001
Perchloroethylene (tetrachloroethylene)	127-18-4	165.83	3.73	15.1
Toluene	108-88-3	92.13	165	380
Trichloroethylene (trichloroethene)	79-01-6	131.38	2.82	7.88
Vinyl chloride	75-01-4	62.50	7.34	18.6
Xylenes (all isomers)	133-20-7	106.16	12.1	77.9

^a Source: EPA, 1997a.^b Constituents associated with carcinogenic or chronic non-carcinogenic health effects which are routinely measured.^c Concentrations derived from four chlorofluorocarbons commonly found in LFG.^d na = not applicable^e Source tests did not indicate whether this compound was the para- or ortho- isomer. The para isomer is a Title III-listed HAP.^f No data were available to speciate total Hg into the elemental and organic forms.

Warning: AP-42 undergoes periodic review and updates are published after the peer review process is completed. A work group has been established to review Section 2.4 - Municipal Landfill. Readers are cautioned to check for updates.

As shown from the equations presented above, developing uncontrolled emission rates for one or more COPCs can be a time-consuming process. Hence, it is recommended that the LandGEM program be used to quickly develop these estimates. Figure 2-3 is an example of output from LandGEM. This example is for vinyl chloride emissions; however, estimates for total NMOCs and for other COPCs can also be generated by LandGEM. The example shown in Figure 2-3 is for a landfill that began accepting wastes in 1969 and closed in 1980. The vapor concentration of vinyl chloride in the LFG was measured for site-specific conditions. CH₄

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generation (and thus vinyl chloride emissions) is estimated to peak in 1980 and continue well beyond the year 2268 (as stated above, all of the CH₄ generated and associated COPCs are assumed to be emitted). Figure 2-4 is a graphical example of the data shown in Figure 2-3.

Figure 2-3. Sample Output from the LandGEM Model

Model Parameters			
Lo : 100.00 m ³ / Mg			
k : 0.0400 1/yr			
NMOC : 595.00 ppmv			
Methane : 50.0000 % volume			
Carbon Dioxide : 50.0000 % volume			
Air Pollutant : Vinyl Chloride (HAP/VOC)			
Molecular Wt = 62.50 Concentration = 7.340000 ppmV			
Landfill Parameters			
Landfill type : Co-Disposal			
Year Opened : 1969 Current Year : 1999 Closure Year: 1980			
Capacity : 792000 Mg			
Average Acceptance Rate Required from			
Current Year to Closure Year : 0.00 Mg/year			
Model Results			
Vinyl Chloride (HAP/VOC) Emission Rate			
Year	Refuse In Place (Mg)	(Mg/yr)	(Cubic m/yr)
1970	7.200E+04	1.099E-02	4.228E+00
1971	1.440E+05	2.155E-02	8.290E+00
1972	2.160E+05	3.170E-02	1.219E+01
1973	2.880E+05	4.144E-02	1.594E+01
1974	3.600E+05	5.081E-02	1.955E+01
1975	4.320E+05	5.981E-02	2.301E+01
1976	5.040E+05	6.845E-02	2.633E+01
1977	5.760E+05	7.676E-02	2.953E+01
1978	6.480E+05	8.474E-02	3.260E+01
1979	7.200E+05	9.241E-02	3.555E+01
1980	7.920E+05	9.977E-02	3.838E+01
1981	7.920E+05	9.586E-02	3.688E+01
1982	7.920E+05	9.210E-02	3.543E+01
.	.	.	.
1998	7.920E+05	4.857E-02	1.868E+01
1999	7.920E+05	4.666E-02	1.795E+01
2000	7.920E+05	4.483E-02	1.725E+01
.	.	.	.
2266	7.920E+05	1.073E-06	4.128E-04
2267	7.920E+05	1.031E-06	3.967E-04
2268	7.920E+05	9.907E-07	3.811E-04

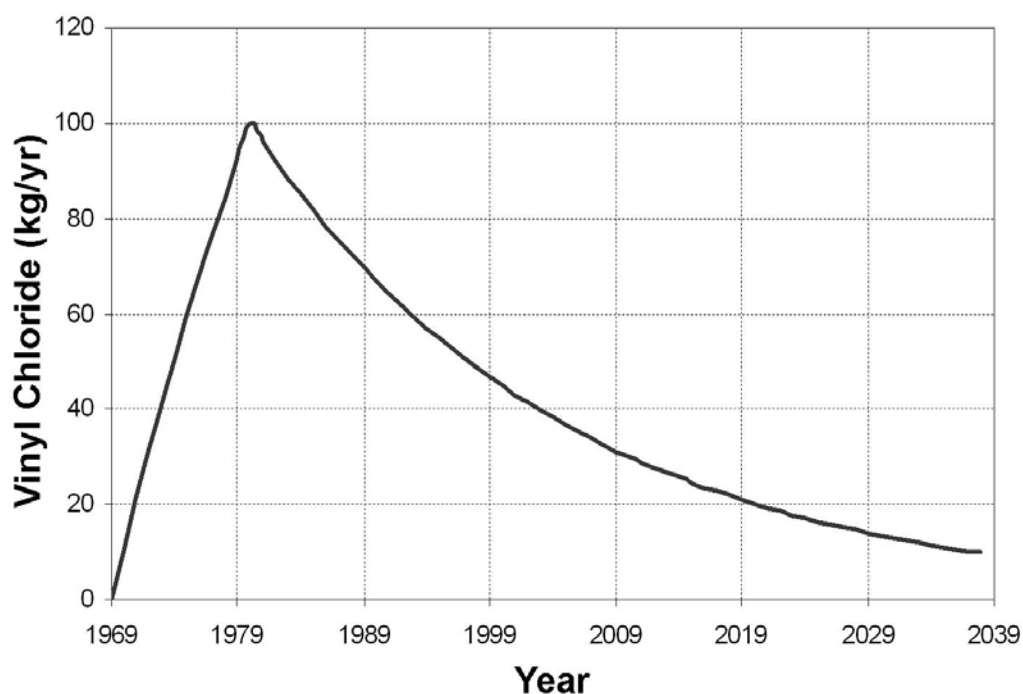


Figure 2-4. Example COPC Emission Estimates Produced by LandGEM.

2.2.1.2 Measuring LFG Constituent Concentrations

The constituents of LFG include CH_4 , CO_2 , N_2 , O_2 , NMOCs, and individual COPCs. These LFG constituents may need to be measured for a variety of purposes. To establish whether the CAA NSPS or EG controls are applicable to a specific landfill, the NMOC maximum annual emissions must be greater than or equal to 50 Mg/yr. In a Tier I analysis, the LandGEM model is used to estimate these emissions with a landfill gas NMOC concentration set equal to the regulatory default value of 4,000 ppmv, expressed as hexane. A Tier I analysis further specifies that the CH_4 generation rate constant (k) and the CH_4 generation potential (L_0) be set equal to the regulatory default values of 0.05 /yr and 170 m^3/Mg , respectively. If the maximum annual NMOC emission rate is greater than or equal to 50 Mg/yr and the design capacity and applicability cutoff dates are triggered, the landfill may be subject to the NSPS or EG. A Tier II analysis allows for a site-specific determination of the landfill gas NMOC concentration. This value is determined using EPA Reference Methods 25C or 18. The NMOC concentration (as well as the concentrations of COPCs), however, must then be corrected for any air infiltration using Equation 2-2. This equation requires the site-specific LFG concentrations of CH_4 , CO_2 , N_2 , and O_2 as determined by EPA Reference Method 3C.

To determine the LFG concentrations of three reduced sulfur species on the CAA HAP list (carbonyl sulfide, captan, and carbon disulfide), EPA Reference Method 15 can be used. The LFG concentrations of mercury (Hg) can be determined using EPA Method IO-5. EPA Reference Methods 3C, 25C, and 15 can be found in Appendix A of 40 CFR 60; EPA Method IO-5 can be found in the *Compendium of Methods for the Determination of inorganic Compounds in Ambient Air*, EPA/625/R-96-010a, June 1999.

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The LFG concentrations of the volatile constituents found in Table 1-1, as well as of other volatiles, can be determined using EPA Compendium Method TO-15 as found in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition*, EPA/625/R-96-010b, January 1999. These analytical methods are associated with whole air sampling methods such as the use of specially treated canisters. Appendix A details several sampling and analytical methods pertinent to the determination of LFG constituent concentrations sampled within the landfill wastes, at the landfill property boundary, and within a LFG collection system. Appendix A also provides sampling and analytical methods for determining ambient air concentrations and indoor air concentrations of LFG COPCs.

With a determination of site-specific LFG concentrations of COPCs and NMOCs, the LandGEM model may be used to estimate more accurate annual emissions of these pollutants. This allows for a more confident determination as to the maximum annual NMOC emissions for NSPS/EG applicability. It also allows for a site-specific estimate of COPC emissions and thus an evaluation of the resulting risks, as well as an evaluation of compliance with State or local air pathway ARARs specific to baseline or uncontrolled conditions.

2.2.1.3 Estimating Time-Averaged Emission Rates

The LandGEM model will not only produce an estimate of the annual CH₄ emission rate from a given landfill, but will also produce a similar annual emissions profile for specified COPCs as depicted in Figure 2-4. For risk evaluation purposes, however, what is usually required is a time-averaged emission rate. An estimation of the time-averaged emission rate can be accomplished by using a trapezoidal approximation of

$$\langle E \rangle = \frac{1}{ED} \int_0^t E_{(t)} dt \quad 2-5$$

where:

- $\langle E \rangle$ = Time-averaged emission rate in megagrams per year,
- ED = Exposure duration in years,
- $E_{(t)}$ = Emission rate at time t from LandGEM in megagrams per year,
- t = Time in years.

The trapezoidal approximation of the integral in Equation 2-5 is calculated by

$$\langle E \rangle = \frac{1}{ED} \left[\frac{h}{2} (E_0 + 2E_1 + 2E_2 + \cdots + 2E_{n-1} + E_n) \right] \quad 2-6$$

where:

- h = Time-step interval in years ($h = 1$ yr),
- $E_{0,1,2 \dots n}$ = Emission rate at the end of the first year (E_0) and each succeeding year from LandGEM in megagrams per year,
- n = Number of time-steps ($n = ED$).

Equation 2-6 may be entered into a spreadsheet program such as Microsoft Excel by

$$< E > (1/ED) * \left((h/2) * (E_0 + 2 * SUM(E_1:E_{n-1}) + E_n) \right) \quad 2-7$$

For example, if the exposure duration (ED) were 30 years and the annual emissions of vinyl chloride were used from Figure 2-3 for the years 1999 through 2028, the time-averaged emissions calculated by Equation 2-6 over this 30 year period would be 2.670×10^{-2} Mg/yr. This time-averaged emission rate may then be entered into an atmospheric dispersion model to estimate the average exposure point air concentration of vinyl chloride at a specified onsite or offsite receptor. With an estimate of the average ambient air exposure point concentration, the incremental cancer risk for exposure to vinyl chloride in ambient air can be calculated.

If we assume that the areal extent of the landfill is approximately 16 acres configured as a square and that the LFG emissions are homogeneously distributed, a screening-level dispersion modeling analysis yields an estimate of the offsite maximum annual average air concentration equal to 0.17 mg/m^3 . For carcinogenic contaminants and residential exposure assumptions, the incremental risk is calculated by

$$Risk = \frac{URF \times EF \times ED \times C_A}{AT_c \times 365 \text{ days / yr}} \quad 2-8$$

where:

- URF = Unit risk factor for vinyl chloride [$4.4 \times 10^{-6} (\text{mg/m}^3)^{-1}$],
- EF = Exposure frequency (350 days/yr),
- ED = Exposure duration (30 yr),
- C_A = Annual average ambient air concentration (0.17 mg/m^3)
- AT_c = Averaging time for carcinogens (70 yr).

Therefore, the incremental cancer risk associated with 30 years of residential exposure to vinyl chloride is

$$Risk = \frac{4.4 \times 10^{-6} \times 350 \times 30 \times 0.17}{70 \times 365} = 3.1 \times 10^{-7}$$

The result of the preceding risk evaluation example indicates that the incremental cancer risk from offsite residential exposure to vinyl chloride might be acceptable (i.e., less than 1 in 1,000,000).

2.2.1.4 Atmospheric Dispersion Modeling

With an estimate of the time-averaged emission rate of each COPC, atmospheric dispersion models may be used to estimate the exposure point ambient air concentrations at actual receptors or at theoretical receptors when evaluating future land-use scenarios. Atmospheric dispersion models may be generally divided into screening-level and refined models. Screening-level models require a minimum of site-specific input data. The results of screening-level

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models, however, exhibit a relatively high degree of uncertainty. These types of models evaluate transport and dispersion of pollutants in a conservative manner relying on “worst-case” estimates of air concentrations. Refined dispersion models, however, are constructed to better represent simulations of actual air dispersion events for site-specific conditions.

2.2.1.4.1 *Screening-Level Dispersion Modeling*

Screening-level dispersion models can be used in a first-tier evaluation of risk or for an evaluation of compliance with air pathway ARARs. In such evaluations, exposure point concentrations are generated that represent worst-case dispersion conditions producing the highest air concentrations and thus the most health protective exposure assessments. Tier I exposure assessment dispersion modeling consists of simplified calculation procedures designed with sufficient health protective to allow a determination of whether an emission source (1) is clearly not an air quality threat or (2) poses a potential threat that should be examined with more sophisticated estimation techniques. Screening-level models provide short-term maximum air concentration estimates. These short-term estimates can be converted to long-term (e.g., annual) maximum air concentration estimates that can be used to characterize lifetime cancer and chronic noncancer health risks. In addition, the screening-level estimates can be converted to the averaging time appropriate to most air pathway air concentration ARARs (e.g., 8 h, 24 h, etc.) using EPA recommended conversion factors.

The EPA SCREEN3 computer program is a commonly used screening-level dispersion model. The program is a PC-based software application that uses a steady-state Gaussian plume model and is distributed through the EPA’s Support Center for Regulatory Air Models (SCRAM) website at http://www.epa.gov/scram001/dispersion_screening.htm (accessed August 2005). As of this writing, the version of the program dated (96043) is the current version of SCREEN3 and is available as a stand-alone program. A user’s guide for SCREEN3 can also be downloaded from the SCRAM website.

The SCREEN3 model is written as an interactive program that can be executed by typing “SCREEN3” at the command prompt from any directory that contains the SCREEN3.EXE executable file or by clicking on the SCREEN3.EXE icon in Windows. The program then prompts the user for input data on the site or emission source to be modeled. Once all required data are input, the model will estimate the maximum 1-h average air concentration at the user-specified receptors. SCREEN3 can estimate air concentrations for four different types of emission sources: (1) “point sources,” or stacks; (2) “area sources,” or emission sources that consist of homogeneously distributed emissions at the surface of a two-dimensional area; (3) “volume sources,” or fugitive emissions from buildings or roof monitors; and (4) “flares” such as open, candlestick flares. SCREEN3 can estimate air concentrations from only one emission source for each modeling run. If multiple sources must be modeled, a separate run must be made for each source and the air concentrations added together to determine the combined air concentration at the receptor of interest.

The SCREEN3 model estimates the maximum 1-h average air concentration based on worst-case meteorology. That is to say, the program will search through a predefined number of wind directions and atmospheric stability classes to find the combination that generates the maximum air concentration at the specified distance from the source. For area sources,

SCREEN3 also provides an option for specifying the wind direction with respect to the long axis of a rectangular emission source. This option may be used to estimate the air concentration at a particular receptor location relative to the area. Descriptions of the atmospheric stability classes and meteorological data used for screening estimates can be found in U.S. EPA, 1992a.

The emission rate and other site-specific data, must be entered into the model. Two options are available. The first is to enter the actual emission rate in units of mass rate per unit area (grams per square meter second) for area sources, and mass rate (grams per second) for point sources and flares. This means that a separate modeling run will be necessary for each pollutant of interest. The second emission input option is to enter a unity emission rate (i.e., 1 g/m²-s or 1 g/s). SCREEN3 will generate a normalized air concentration (e.g., milligram per cubic meter for each gram per second, or milligram per cubic meter for each gram per square meter second) at the receptor. The normalized air concentration is also referred to as a “dispersion coefficient”. The advantage to this approach is that only one modeling run is required for a given emission source. The actual air concentration of each pollutant of interest is then obtained as the product of the dispersion coefficient and the actual emission rate.

Dispersing Area Emission Sources

LFG emissions from the surface of a landfill can be considered “area” emission sources. If the emission rate of the pollutant of interest is homogeneously distributed across the areal extent of the landfill, only one modeling run is required. If surface emissions are significantly heterogeneous, however, multiple model runs may be necessary. Appendix C presents the statistical procedures that may be used to determine if the landfill areas are homogeneously distributed. Figure 2-5 illustrates the surface of a generic landfill where the variability in the estimated emissions of benzene is considerable. This spatial distribution may be due to the distribution of benzene in the LFG, the varying ages of different landfill cells, or both. The areal extent of the landfill has, therefore, been divided into three different parcels of land based on the different estimated emission rates. In this case, the emission rate of benzene from each parcel must be dispersed using a separate SCREEN3 run. Inputs for each model run include the dimensions

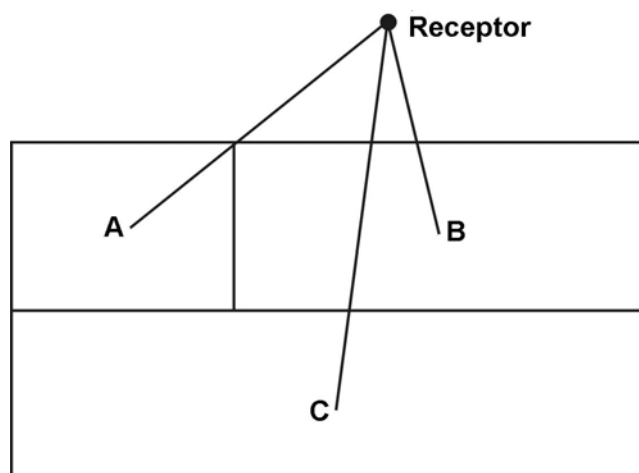


Figure 2-5. Example of Multi-Parcel Area Emission Source.

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of the parcel, the distance from the center of the parcel to the receptor, and a unity emission rate of $1 \text{ g/m}^2\text{-s}$. This results in three dispersion coefficients (normalized air concentrations) as can be seen in Table 2-2. Each dispersion coefficient is multiplied by the actual parcel-specific emission rate of benzene to yield the actual 1-h average air concentration at the receptor. The combined 1-h average air concentration is then the sum of the values from all three parcels.

Table 2-2. Example of SCREEN3 Results for Multi-Parcel Emission Source.

Parcel	Dispersion Coefficient (mg/m^3 per $\text{g/m}^2\text{-s}$)	Benzene Emission Rate ($\text{g/m}^2\text{-s}$)	Actual Air Concentration (mg/m^3)
A	1.626×10^6	1.950×10^{-6}	3.17
B	3.317×10^7	1.065×10^{-7}	3.53
C	3.404×10^7	1.320×10^{-8}	4.49
Total			11.19
Total $\times 0.08$			0.90

It should be understood that adding the air concentrations from the emission sources depicted in Figure 2-5 does not necessarily represent actual dispersion conditions. This is because the concentration from each source is computed assuming the worst-case wind direction for that source, and this worst-case wind direction may not be the same for all sources; there cannot be three different simultaneous wind directions. Using the technique, however, is considered to be health protective and can be applied to screening-level situations where the estimated combined concentration at the receptor is used to rule-out the possibility of excessive risks or to demonstrate that a particular air pathway ARAR can not be exceeded. For risk evaluation purposes, the combined 1 h average air concentration must be converted to an annual average. This is done by multiplying the combined 1-h average air concentration by the annual conversion factor of 0.08 from Table 2-3. If, in addition, a State air toxics regulation specifies that an acceptable air concentration of benzene at the receptor must be based on a 24-h averaging time, compliance with the ARAR can be determined by multiplying the combined 1-h average air concentration by the 24-h conversion factor of 0.4 from Table 2-3.

Table 2-3. Averaging Time Conversion Factors.^a

Averaging Time	Multiplying Factor
3 hours	0.9 (± 0.1)
8 hours	0.7 (± 0.2)
24 hours	0.4 (± 0.2)
Annual	0.08 (± 0.2)

^a Source U.S. EPA, 1992a

In addition to the specified receptor location given in the example above, the SCREEN3 model can also automatically generate the location of and the associated air concentration at the point of maximum plume impact. For area sources, this location may be on or offsite. Further,

SCREEN3 can generate air concentrations based not only on user-specified distances, but also on an automated distance array between a user-specified minimum and maximum distance. For example, Figure 2-6 shows a sample SCREEN3 model output for a square area emission source with equal side lengths of 284.49 meters. In this case, the automated distance array generated air concentrations at 142 through 1,000 m. In addition, the model searched for the distance from the center of the square source to the point of maximum air concentration. For this example, the point of maximum concentration is at 202 m from the center of the source, and the concentration is 62.72 mg/m³.

Figure 2-6. Example of SCREEN3 Model Output File

*** SCREEN3 MODEL RUN ***
*** VERSION DATED 96043 ***

Small Typical Superfund Landfill

SIMPLE TERRAIN INPUTS:

SOURCE TYPE = AREA
EMISSION RATE (G/(S-M**2)) = .391800E-06
SOURCE HEIGHT (M) = .0000
LENGTH OF LARGER SIDE (M) = 284.4900
LENGTH OF SMALLER SIDE (M) = 284.4900
RECEPTOR HEIGHT (M) = .0000
URBAN/RURAL OPTION = RURAL

THE REGULATORY (DEFAULT) MIXING HEIGHT OPTION WAS SELECTED.

THE REGULATORY (DEFAULT) ANEMOMETER HEIGHT OF 10.0 METERS WAS ENTERED.

MODEL ESTIMATES DIRECTION TO MAX CONCENTRATION

BUOY. FLUX = .000 M**4/S**3; MOM. FLUX = .000 M**4/S**2.

*** FULL METEOROLOGY ***

*** SCREEN AUTOMATED DISTANCES ***

*** TERRAIN HEIGHT OF 0. M ABOVE STACK BASE USED FOR FOLLOWING DISTANCES ***

DIST (M)	CONC (UG/M**3)	STAB	U10M (M/S)	USTK (M/S)	MIX HT (M)	PLUME HT (M)	MAX DIR (DEG)
142.	60.22	6	1.0	1.0	10000.0	.00	45.
200.	62.64	6	1.0	1.0	10000.0	.00	45.
300.	24.65	6	1.0	1.0	10000.0	.00	45.
400.	18.05	6	1.0	1.0	10000.0	.00	45.
500.	14.54	6	1.0	1.0	10000.0	.00	45.
600.	12.27	6	1.0	1.0	10000.0	.00	45.
700.	10.68	6	1.0	1.0	10000.0	.00	45.
800.	9.505	6	1.0	1.0	10000.0	.00	45.
900.	8.608	6	1.0	1.0	10000.0	.00	45.
1000.	7.893	6	1.0	1.0	10000.0	.00	45.

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MAXIMUM 1-HR CONCENTRATION AT OR BEYOND 142. M:

202. 62.72 6 1.0 1.0 10000.0 .00 45.

*** SUMMARY OF SCREEN MODEL RESULTS ***

CALCULATION PROCEDURE	MAX CONC (UG/M**3)	DIST TO MAX (M)	TERRAIN HT (M)
SIMPLE TERRAIN	62.72	202.	0.

Dispersing Point Emission Sources and Flares

“Point” sources are those that emit pollutants through a stack or vent. Examples of point sources include passive LFG vents and gas treatment systems such as enclosed flares and leachate air strippers. Flares, on the other hand, emit pollutants directly to ambient air and not through a stack. The user should note that there are several differences in SCREEN3 input data requirements between point sources (e.g., enclosed flares) and flare sources (e.g., open flares). Input requirements include:

- (1) Point or flare source release height in meters.
- (2) Stack inside diameter in meters for point sources. For flare sources, an effective inside diameter is calculated by the program from other parameters.
- (3) For point sources, stack gas exit velocity in meters per second or stack flow rate in either cubic meters per second or cubic feet per minute. The program defaults to accepting a gas exit velocity, but a flow rate can be entered by preceding the value with either “VM=” (for cubic meters per second) or “VF=” (for cubic feet per minute). For flare sources, SCREEN3 assumes an effective gas exit velocity of 20 m/s.
- (4) Ambient temperature in Kelvin ($K = ^\circ C + 273$). If the ambient temperature is unknown, enter 293 K, which corresponds to 20 °C. No ambient temperature input is required for flare sources; the model assumes an ambient temperature of 293 K.
- (5) Total heat release in calories per second (cal/s) for flare sources. The heat release is calculated as shown in Equation 2-9. Total heat release is not a point source input.

$$HR = MF \times \frac{1}{31,536,000 \text{ s/yr}} \times \frac{8.57 \times 10^6 \text{ cal}}{m^3} \quad 2-9$$

where:

HR = Heat release rate in calories per second and

MF = CH_4 flow rate from LandGEM or source test in cubic meters per year.

Two input options (complex terrain and building downwash) are also provided in the SCREEN3 program for both point and flare sources but are not available for area sources. The complex terrain option is used to estimate impacts for cases where terrain elevations exceed stack height. The building downwash option accounts for the effect of structures near a source or upon which a point or flare source stands. In most cases, neither of these options will be needed for landfill dispersion modeling.

As with area sources, one SCREEN3 model run can be performed for each point source or

flare with a unity emission rate of 1 g/s to generate a series of dispersion coefficients at the receptors of interest. The actual 1-h average air concentration is calculated as the product of the dispersion coefficient and the actual stack emission rate determined by stack sampling. In the case of open flares, the combustion gases are not enclosed, thereby making stack sampling impossible. Controlled emissions of individual LFG constituents are typically estimated based on a theoretical destruction removal efficiency (e.g., 98%). Additional information on control efficiency can be found in AP-42 Table 2.4-3. For a more complete discussion of the input requirements to the SCREEN3 program or guidance on use of the options mentioned here, users should consult U.S. EPA, 1995a.

2.2.1.4.2 *Refined Atmospheric Dispersion Models*

A Tier II exposure assessment of landfill emissions may be desired if the results of a Tier I analysis have been used to characterize health risks that are found to exceed a level of concern such as the maximum predicted lifetime cancer risk or the maximum predicted chronic noncancer hazard index. A Tier II assessment involves the use of site-specific source and facility layouts as well as meteorological information. Tier II analysis of a landfill is performed to provide the most scientifically-refined indication of the impacts of emissions. Dispersion modeling for the Tier II analysis procedure is based on EPA's Industrial Source Complex, Version 3 (ISC3) model. The ISC3 model and user's guide can be found on the EPA SCRAM website.

The ISC3 model consists of two parts, a long-term version (ISCLT3) and a short-term version (ISCST3). The long-term version is used for annual concentration estimates, such as the dispersion coefficients required for risk characterization. The ISC3ST version can also be used for annual concentration estimates and is considered to be the ISC3 version-of-choice for most dispersion modelers. Unlike SCREEN3, which has worst-case meteorological data built-in, ISC3 requires the user to provide local-specific meteorological data. ISCLT3 uses annual meteorological data based on joint frequency distributions of wind speed, wind direction, and atmospheric stability category, known as STAR (Stability Array) summaries. The ISC3ST model uses sequential hourly meteorological data. Both types of meteorological data are available from the National Climatic Data Center in Asheville, North Carolina. Sequential hourly data that have been quality assured are available for many National Weather Service stations across the United States from the SCRAM website.

ISC3 Input Requirements

There are two basic types of inputs that are needed to run the ISC3 models. They are (1) the input run stream file, and (2) the meteorological data file. The run stream setup file contains the selected modeling options as well as source location and parameter data, receptor locations, meteorological data file specifications, and output options. As with Tier I exposure assessments, the emission rate can be the actual emission rate or a unity emission rate used to generate dispersion coefficients (normalized air concentrations).

Unlike SCREEN3, ISC3 can model multiple sources and source types simultaneously, allowing area and point sources (there is no flare option in ISC3) to be combined in the same model run. The allowance for multiple sources in the model provides for more realistic representations of non-rectangular landfills than does SCREEN3. By division into smaller

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rectangular parts, each of which appears as a separate source in the run stream file, a landfill that is not adequately represented by a simple rectangle can be more realistically modeled. The screening technique described in Section 2.2.1.4.1 of this document uses the SCREEN3 model to estimate combined air concentrations from more than one emission source. The combined air concentration, however, does not accurately represent actual dispersion conditions but, rather, represents a worst-case scenario. Use of the ISC3 model more accurately describes the combined-source type of source-receptor geometry. In addition, the screening technique estimates long-term (e.g., annual) averages based on a theoretical correction factor applied to a worst-case 1-h average concentration. The ISC3 model uses actual site-specific meteorological data to disperse contaminants over the user-specified averaging time.

Rather than using an assumed automated distance array as in SCREEN3, ISC3 provides several options for positioning receptors. Individual receptors can be located at discrete locations, or grids of receptors can be generated by the model in the user's choice of either rectangular or polar coordinates. Multiple discrete receptors and receptor grids can all be combined as desired by the user. Users should be aware that large numbers of receptors can lead to long model run times.

ISC3 Input Data

Input source parameters for area and point sources in the ISC3 run stream file are similar to those required by SCREEN3 but also include the physical location. Area source parameters are (U.S. EPA, 1995b)

- (1) Area emission rate in $\text{g/m}^2\text{-s}$; this can be calculated from a unit emission rate, such as 1 Mg/year divided by the area;
- (2) Release height above ground in meters; usually zero (0.0 m) is used to model ground-level releases from a landfill;
- (3) Area source geometry and orientation (see the ISC3 user's guide).

Input parameters required for point sources are

- (1) Point emission rate in g/s. This can be a unit emission rate such as 1 g/s;
- (2) Release height above ground in meters (i.e., the stack height);
- (3) Point source orientation (see the ISC3 user's guide);
- (4) Stack gas exit temperature in Kelvins;
- (5) Stack gas exit velocity in meters per second;
- (6) Stack inside diameter in meters;

Both the run stream and meteorological input files are described in detail in U.S. EPA, 1995b. All run stream file options and formats are fully described in the user's guide, which should be consulted before attempting to develop a run stream file to model a landfill.

A third type of input may also be used by the models when implementing the dry deposition and depletion algorithm feature. Use of this feature may be necessary if an analysis of multi-media risks or ecological impacts of landfill emissions is desired. A complete description of this option and its use is available in the user's guide.

ISC3 Output Data

Output from the ISC3 model is placed in a text file, the name of which is specified by the user on the command line when starting a modeling run. The output file contains a copy of the input run stream file, model setup messages (including any errors or warnings detected by the model), a summary of the inputs, the model results, and the model execution messages.

Model results can be presented as a tabular summary of the overall maximum modeled air concentrations (or dispersion coefficients for a unit emission rate input) as well as by receptor. The user can also choose from tables of results for individual sources, for groups of sources, and for the contribution of each source within a user-defined group. Selecting the optional source contribution table for inclusion in the output file is recommended for determining the exposure from each source in cases where there are multiple emission sources. As described in Section 2.2.1.4.1 and illustrated in Table 2-2, the contribution table for each area, or parcel, of the landfill can be generated using a unit emission rate of 1 g/m²-s for each parcel. The contribution table will give the dispersion coefficient for each parcel at the receptor of interest based on the unity emission rate. The actual air concentration at the receptor as contributed by each parcel is then the product of the actual emission rate and the dispersion coefficient. The total air concentration from all parcels is then the sum of the parcel-specific actual air concentrations.

In addition to the tabular result options that produce tables in the output file, there is an option to create a separate output file that can be used to plot the results. The resulting file contains the *x* and *y* coordinates for each receptor location as well as the long-term (usually annual) average dispersion coefficient value at each receptor. This file can be used with a graphics package (e.g., SURFER, GNUPLOT) to generate contour plots. Many such programs are available, although the file may need to be edited (e.g., removing the header information) in order to produce plots. These output options are also discussed more completely in the ISC3 user's guide.

2.2.2 Determining Ambient Air Impacts by Air Monitoring/Sampling

A major concern at SFL sites is the potential exposure via the air pathway of residents and workers in the areas surrounding the landfill. The degree of concern varies from site-to-site depending on the emissions of LFG COPCs. The exposure of offsite receptors typically is evaluated at several steps in the Superfund process, and both modeling and monitoring approaches may be employed as part of an exposure assessment.

2.2.2.1 Field Monitoring and Whole air Sampling

Within this section, the term “monitoring” refers to real- or near real-time assessment of air concentrations using portable instruments. The term “sampling” refers to whole air sampling techniques requiring laboratory analytical methods. This section deals exclusively with monitoring and sampling methods designed to estimate air concentrations for offsite receptors. Air monitoring for remedial site workers is covered under the site health and safety plan and is subject to the air standards of the Occupational Safety and Health Administration (OSHA). This type of air monitoring is not included in this document. Appendix A of this document contains detailed information on monitoring, sampling, and analytical methods for determining

the ambient air concentrations of target analytes including LFG COPCs.

The evaluation of inhalation exposure using a monitoring or sampling approach generally involves measuring the concentrations of target analytes at the point of exposure or facility boundary of the site for ground-level emission sources such as LFG emissions from the landfill cover or passive LFG vents. In the case of elevated emission sources (e.g., stacks), sampling is typically conducted at the areas of maximum expected impacts as determined by preliminary dispersion modeling. The screening-level dispersion modeling techniques given in Section 2.2.1.4.1 of this document can be used to first determine whether emissions of individual COPCs represent a possible threat to human health. If so, refined dispersion modeling described in Section 2.2.1.4.2 can assist in determining the locations of the areas of expected maximum air concentrations as an aide in placing air sampling stations.

For ground-level emission sources, a fixed network of samplers is typically located around the perimeter of the site. The number of sampling locations will depend on the size of the site, among other factors. For large sites surrounded by nearby residences or businesses, a 12-station network may be used to provide nearly complete coverage of the fence line (i.e., a station every 30 degrees as illustrated in Appendix A). In some cases, only samples from stations located directly upwind or downwind of the site for a given sampling period will be analyzed to save time and money; samples collected perpendicular to the emission plume are not analyzed. Alternatively, a smaller number of movable stations may be used that may be placed daily according to predicted wind patterns. If the predictions are wrong, however, the sampling stations may not be within the emission plume as needed.

In general, compliance with long-term action levels (ARARs and/or risk-based air concentrations) is based on daily samples collected at each location. In lieu of daily sampling, every sixth-day sampling is often employed. Broad-based collection methods such as specially treated canisters (EPA Method TO-15), or solid sorbent sampling (i.e., Carbotrap 300, charcoal, Tenax, etc.), are usually selected for VOCs so that all the target analytes can be measured using only one or two sampling and analysis approaches. Alternatively, dedicated gas chromatographs (GCs) or gas chromatographs/mass spectrometers (GC/MSs) can be used as point samplers, or open path monitors (OPMs) may be used in some cases to provide near real-time data and to minimize unit analytical costs. Fewer options exist for particulate matter, metals, and some semi-volatiles (SVOCs), although standard methods are available (see Appendix A).

2.2.2.2 Radial Plume Mapping

One of these alternative methods involves a technique developed through research funded by EPA's National Risk Management Research Laboratory (NRMRL), which uses ground-based optical remote sensing technology, known as radial plume mapping. The radial plume mapping technique is performed with an optical remote sensing sensor such as an open path Fourier transform infrared (OP-FTIR) spectrometer, open-path tunable diode laser absorption spectroscopy (OP-TDLAS), or ultraviolet differential optical absorption spectroscopy (UV-DOAS). The light energy is transmitted from an optical remote sensors (ORS) to a retroreflector (mirror) target, which is usually set up at a range of 100 to 500 meters. The returned light signal is received by the single telescope and directed to a detector. The light is

absorbed by the molecules in the beam path as the light propagates to the mirror and again as the light is reflected back to the analyzer.

A promising monitoring approach is the use of OP-FTIR. These monitors are spectrographic instruments configured to monitor the open air over extended paths of hundreds of meters or more. They rely on the interaction of light with matter to obtain data on the species present and their associated air concentrations. The potential advantages of OP-FTIR include near real-time air concentrations, no requirement for sample collection, no additional analytical costs (i.e., laboratory costs), and concentrations that are path-averaged values instead of concentrations at specific sampling points. Disadvantages include the lack of standard operating procedures (SOPs), spectral interferences (e.g., water vapor), the lack of reference spectra for some compounds of interest, and detection limits for some compounds that are higher than those of conventional sampling methods (EPA, 1993a). However, recent advances, including the development of standard operating procedures, facility manual, and EPA test methods for use of ORS, has resulted in wider usage and acceptance of this technology.

Recent innovations include the development of ORS method to obtain path-configured optical paths. The multipollutant concentration data along with wind vector information are processed using an integrating algorithm to yield a mass emission flux for the source. The acquisition of path integrated concentration data can be accomplished with several types of optical remote sensing instruments. The differences between instruments is the spectral range used, the type of detector, and the algorithm used to interpret the data. The OP-FTIR methodology is capable of identifying approximately 100 of 189 hazardous air pollutants regulated under the Clean Air Act.

The horizontal radial plume mapping (HRPM) approach provides spatial information to path-integrated measurements acquired in a horizontal plane by an ORS system. This technique yields information on the two-dimensional distribution of the concentrations in the form of chemical-concentration contour maps. This form of output readily identifies chemical “hot spots,” the location of high emissions. This method can be of great benefit for performing site surveys before, during, and after site remediation activities.

HRPM surveys are usually performed with the ORS beams located as close to the ground as is practical. This enhances the ability to detect minor constituents emitted from the ground, since the emitted plumes dilute significantly at higher elevations. The survey area is typically divided into a Cartesian grid of n times m rectangular cells. In some unique cases, the survey area may not be rectangular due to obstructions, and the shape of the cells may be slightly altered accordingly. A mirror is located in each of these cells, and the ORS sensor scans to each of these mirrors, dwelling on each for a set measurement time (usually 30 seconds). The system scans to the mirrors in the order of either increasing or decreasing azimuth angle. The path-integrated concentrations measured at each mirror are averaged over several scanning cycles to produce time-averaged concentration maps. Meteorological measurements are made concurrent to the scanning measurements.

The vertical radial plume mapping (VRPM) method maps the concentrations in the vertical plane by scanning the ORS system in a vertical plane downwind from an area source. One can

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obtain the plane-integrated concentration from the reconstructed concentration maps. The flux is calculated by multiplying the plane-integrated concentration by the wind speed component perpendicular to the vertical plane. Thus, the VRPM method leads to a direct measurement-based determination of the upwind source emission rate.

The ORS combined with the radial plume mapping method can be used for both fence-line monitoring applications, and real-time, on-site, remediation monitoring and source characterization. An infrared light beam, modulated by a Michelson interferometer is transmitted from a single telescope to a retroreflector (mirror) target, which is usually set up at a range of 100 to 500 meters. The returned light signal is received by the single telescope and directed to a detector. The light is absorbed by the molecules in the beam path as the light propagates to the retroreflector and again as the light is reflected back to the analyzer. Thus, the round-trip path of the light doubles the chemical absorption signal. One advantage of ORS monitoring is that the concentrations of a multitude of infrared absorbing gaseous chemicals can be detected and measured simultaneously with high temporal resolution.

The chemical vapor, emitted from an emission source, forms a plume that is carried by the wind across the multiple infrared beams. The ORS concentration measurements can be used with wind data to calculate the emission rate applying the RPM method for vertical planes. The beam measurements avoid the uncertainties that are inherent in the traditional point measurements. Meteorological and survey measurements are also made. A theodolite is used to make the survey measurement of the azimuth and elevation angles and the radial distances to the retroreflectors, relative to the ORS.

2.2.2.3 Analytical Detection Limits

One of the most important issues relative to ambient monitoring is analytical detection limits. As pointed out in U.S EPA 1992a, however, current measurement techniques, in some cases, do not achieve detection limits low enough to ensure that no significant health risks exist. For example, the following list provides ambient concentrations (at 25 °C) associated with a 1-in-1,000,000 cancer risk for several LFG constituents using EPA standard residential exposure assumptions and toxicity factors from Integrated Risk Information System (IRIS), National Center for Environmental Assessment (NCEA), or Health Effects Assessment Summary Tables (HEAST) as applicable.

<u>LFG Constituent</u>	<u>Concentration (ppbv) at 10⁻⁶ Risk</u>
Benzene	0.10
Carbon tetrachloride	0.03
Chloroform	0.02
Perchloroethylene	0.62
Trichloroethylene	0.27
Vinyl chloride	0.22
1,1-Dichloroethylene	0.01

Because modern analytical methods (e.g., TO-15) can achieve detection limits down to 2.0 to 0.5 ppbv, nearly all of the carcinogens listed above would not be detected at levels associated with a 1-in-1,000,000 cancer risk. Risk management decisions for compounds that may exist below the analytical detector limits are not discussed in this guidance.

In addition to the issue of analytical detection limits, methods used to collect samples can also provide a false sense of security. Careful attention is needed during the development of an ambient air monitoring or sampling plan to ensure proper placement of equipment (e.g., upwind and downwind sample collection) and appropriate timing of sample collection. U.S. EPA (1993a) provides guidance on many aspects of ambient air monitoring and sampling at Superfund sites.

As mentioned previously, the COPCs in LFG emissions are typically associated with chronic (long-term) exposure risks. Exceptions arise during active remediation (e.g., drum removal, contaminated soil excavation), when high short-term exposures can occur. In most cases, however, an ambient air sampling program should be designed to characterize long-term concentrations downwind of the site. The frequency of sample collection depends on (U.S. EPA, 1993a)

- The temporal variability in emission rates (for LFG emissions there can be significant temporal variability in emission rates of individual constituents),
- The variability of meteorological and other factors that affect pollutant dispersion,
- The level of confidence needed for determining mean or maximum downwind concentrations, and
- The level of available funding.

EPA Method TO-15 is the method most commonly employed to assess the presence and concentrations of toxic volatile constituents in LFG emissions. This method, along with a great deal of information on other ambient air sampling and analytical methods, can be found at <http://www.epa.gov/ttn/amtic/airtox.html> (accessed August 2005), which is EPA's Ambient Monitoring Technology Information Center Web site. Appendix A of this document provides information on ambient air monitoring, sampling, and analytical methods for site-specific conditions. Appendix B of this document includes a generic QAPP that may be used to develop the site-specific QAPP. Appendix C presents the Wilcoxon Statistical Procedures used to identify the number of near homogeneous areas within the study area.

3. Assessing Subsurface Vapor Migration

Subsurface vapor migration of LFG is a function of several site-specific factors including pressure and diffusion gradients, subsurface lithology and soil stratigraphy, and the presence or absence of high permanent groundwater that tends to block subsurface vapor flow. Offsite subsurface vapor migration is directly proportional to the pressure and diffusion gradients that exist between the waste perimeter and the location of interest. Vapor transport follows Darcy's law for vapor flow through a porous medium as a function of the pressure gradients. In addition, molecular diffusion through the air-filled soil pores must also be considered, especially for older landfills that have limited methane generation potentials. If LFG migration occurs, CH₄ and landfill gas COPCs can enter into buildings due to pressure-driven flow and diffusion.

Intrusion of subsurface vapors into indoor air can also occur from contaminated groundwater that has migrated offsite. In addition to the generation of leachate, LFG can contaminate the underlying aquifer by dissolution. Due to the multi-directional flow of LFG, groundwater up gradient of the landfill may be contaminated. If contaminated groundwater migrates offsite and under buildings, a combination of diffusion and convection can cause vapor-phase contaminants to enter buildings through cracks, gaps, and openings in the building foundation.

Subsurface geology is extremely important in assessing vapor migration. Soil strata that exhibit relatively high vapor permeability (e.g., sands) may act as advection conduits offering relatively low resistance to LFG flow. In addition, preferential vapor pathways such as karst lithology, subsurface utility conduits, and even subterranean animal burrows and vegetative root pathways offer very little resistance to vapor flow in the soil vadose (unsaturated) zone. At several sites, methane has been found at different depths below ground surface under offsite structures, suggesting that the LFG is moving laterally within several different soil strata. Once the vertical soil permeability is greater than the lateral permeability, the LFG may surface to ambient air or be drawn into buildings by a combination of diffusion and advection as a result of a pressure gradient between the soil column and an under pressurized building interior. Soil surface conditions also play an important role in subsurface vapor transport. Lateral vapor migration is often at a maximum when the soil surface is frozen or paved. Under such conditions, the lateral permeability of the soil is considerably higher than the vertical permeability at the soil surface.

Subsurface vapor migration of LFG may result in two outcomes that must be addressed: (1) high concentrations of methane pose safety hazards due to the possibility of explosions within offsite or on-site structures, and (2) elevated concentrations of the toxic constituents of the LFG

may constitute health hazards within structures.

Methane is combustible in air when enough oxygen is present to support combustion, and the CH₄ vapor concentration is between the LEL of approximately 5 percent by volume and the UEL of approximately 15 percent by volume. Subsurface vapor migration of LFG can result in these conditions within structures resulting in explosions. Even if the methane concentration within the building is not explosive, the COPCs within the LFG can be present at concentrations that exceed the target risk level and/or the target hazard index.

Figure 3-1 shows a general flow diagram for assessing the potential impacts from subsurface vapor migration of landfill gas. These procedures begin with a determination of whether subsurface CH₄ exists at the landfill property boundary. The presence of CH₄ acts as a predictor of whether other toxic LFG constituents may be present in offsite and onsite structures. If methane is detected in perimeter subsurface soils or in onsite buildings, regulatory requirements may be triggered pursuant to 40 CFR §258. In addition, indoor air sampling may be required to establish indoor concentrations of CH₄ and toxic COPCs. Soil gas sampling may also be used along with modeling to estimate the indoor concentrations of LFG COPCs. Appendix A contains sampling and analytical procedures for estimating indoor, outdoor, and soil gas concentrations.

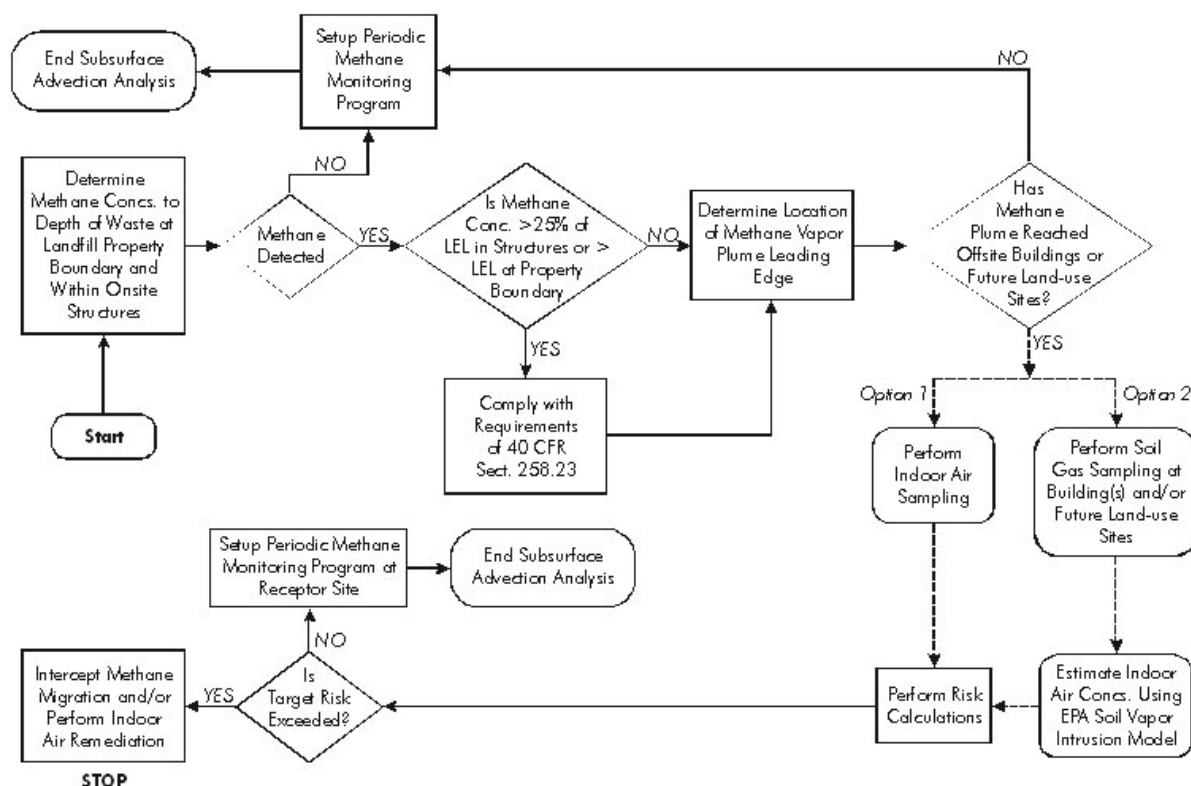


Figure 3-1. Flow Chart for Assessing Subsurface Vapor Migration by Convection.

3.1 Screening-Level Vapor Migration Modeling

Both screening-level and simulation models exist for estimating the subsurface vapor migration of LFG to offsite receptors. The simulation models, however, are academic algorithms with limited availability and require a great deal of input data. The screening-level model of Little et al. (1992) is a steady-state model for estimating the indoor air concentration of volatile species within a structure located a given distance from the perimeter of the landfill wastes. It should be noted that this model **does not** account for preferential vapor pathways but operates under the assumption of Darcian steady-state vapor flow through a porous medium (i.e., soils). The model also operates under the assumption that advective vapor transport occurs only in the lateral direction and that the soil surface acts as an impenetrable layer. This tends to overestimate the vapor concentration reaching the building of interest. Nonetheless, this model may be used to make an order-of-magnitude estimate of the indoor air concentration. The effects of possible preferential pathways **must** also be considered using monitoring techniques described in later sections of this document.

From Little et al. (1992), the attenuation coefficient (a) that expresses the ratio of the indoor air concentration to the vapor concentration at the landfill perimeter is calculated by

$$a = \left(\frac{k_v}{\mu_{lfg}} \right) \left(\frac{P_{source} - P_0}{L} \right) \left(\frac{A_B}{Q_{bldg}} \right) \quad 3-1$$

where:

- a = Attenuation coefficient (unitless);
- k_v = Soil vapor permeability in centimeters squared;
- μ_{lfg} = LFG dynamic viscosity in grams per centimeter-second (1.15×10^{-04});
- P_{source} = Subsurface LFG pressure at the boundary in grams per centimeter-second squared;
- P_0 = Subsurface pressure at the building in grams per centimeter-second squared (0);
- A_B = Area of building below grade in square centimeters;
- Q_{bldg} = Building ventilation rate in cubic centimeters per second; and
- L = Depth to contamination below building in centimeters.

The soil vapor permeability (k_v) can be estimated as the soil intrinsic permeability. The intrinsic permeability is a property of the soil alone that varies with the size and shape of connected soil pores; it does not consider the reduced permeability due to soil moisture. The soil vapor permeability or intrinsic permeability can be estimated by

$$k_v = \frac{K_S \mu_w}{\rho_w g} \quad 3-2$$

where:

- k_v = Soil vapor (intrinsic) permeability in centimeters squared;
- K_S = Soil saturated hydraulic conductivity in centimeters per second;
- μ_w = Dynamic viscosity of water (0.01307 g/cm-s at 10 °C);

ρ_w = Density of water in grams per cubic centimeter (0.999 g/cm³)
 g = Acceleration due to gravity (980.665 cm/s²).

The value of K_s can be measured for the soil between the landfill perimeter and the building using in situ techniques. The value of K_s can also be approximated from the class average values of the Soil Conservation Service (SCS) soil textural classifications shown in Table 3-1 from Schaap and Leij (1998). Please note that the units of the saturated hydraulic conductivities in Table 3-1 are cm/h.

Table 3-1. Class Average Values of Soil Saturated Hydraulic Conductivity.

Soil Textural Classification, USDA	Class Average Satu- rated Hydraulic Conductivity (cm/h)
Sand	26.78
Loamy sand	4.38
Sandy loam	1.60
Sandy clay loam	0.55
Sandy clay	0.47
Loam	0.50
Clay loam	0.34
Silt loam	0.76
Clay	0.61
Silty clay loam	0.46
Silt	1.82
Silty clay	0.40

The soil textural classifications in Table 3-1 can be determined from the SCS classification chart shown in Figure 3-2. The percent sand, silt, and clay can be estimated from site-specific boring logs or can be determined with more confidence using either the American Society for Testing and Materials (ASTM) *Standard Test Method for Particle-Size Analysis of Soils (D422-63)* or by using the analytical procedures found in the U.S. Natural Resources Conservation Service (NRCS) *Soil Survey Laboratory Methods Manual, Soil Survey Laboratory Investigations Report No. 42*. If Equation 3-1 is used to estimate indoor air concentrations, the soil vapor permeability (k_v) is a key parameter for convective vapor transport. Therefore, if the soil saturated hydraulic conductivity is estimated using the SCS soil textural classification, use of the correct classification is important. Multiple soil borings should be taken between the landfill property boundary and the building of interest to establish the soil classifications for each stratum from the soil surface to the depth of the landfill.

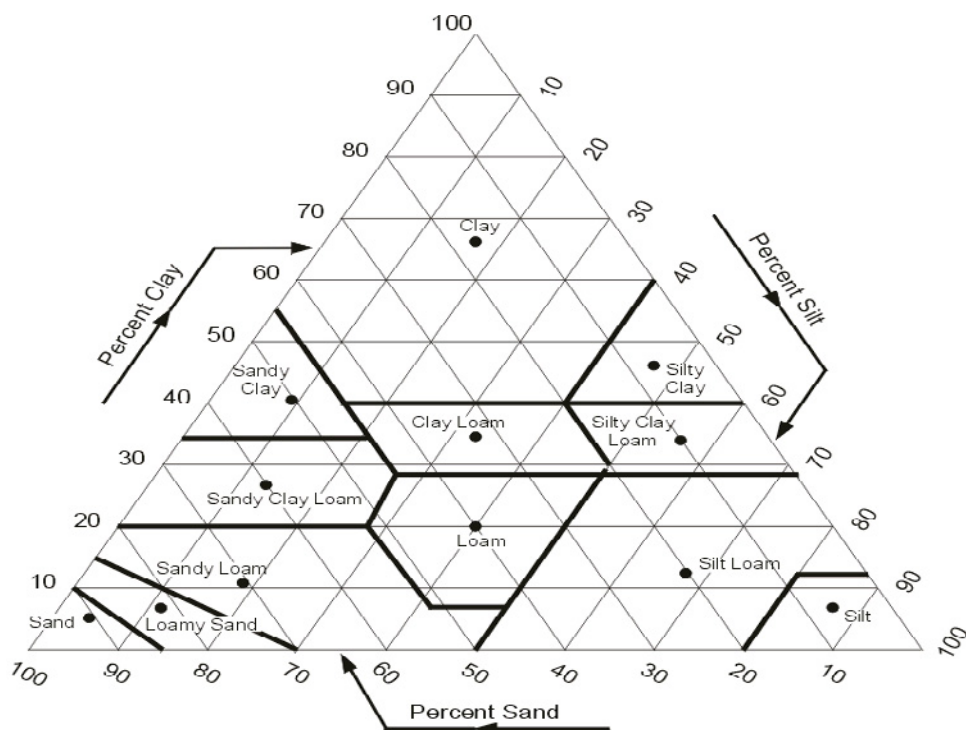


Figure 3-2. U.S. Soil Conservation Service Classification Chart Showing Composition Centroids (solid circles).

For buildings with basements, the value of A_B includes the floor area and wall area below grade. For residential structures with basements, the default value of A_B is 1,000,000 cm² from EQ (2004). This value can be used or site-specific values can be substituted. From EQ (2004), the average building ventilation rate (Q_{bldg}) for a single-family detached residence in the United States is 56,335 cm³/s. The average building ventilation rate for commercial or industrial buildings is typically higher than that of residential structures. The building ventilation rate is the product of the building volume and the air exchange rate. For commercial/industrial buildings, the air exchange rate may range from approximately 0.25 to 2.0 exchanges per hour. ASTM E 1739-95 indicates that commercial/industrial enclosed-space air exchange rate of 0.00023 s⁻¹ (0.929 hr⁻¹) is typical. A default value of 1.0 air exchange rate per hour is the value listed in the California Environmental Protection Agency's "Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air" for commercial buildings.

The value of the subsurface landfill gas pressure at the landfill boundary (P_{source}) should be measured at the property boundary in native soils to avoid the possibility of penetrating drummed wastes with the probe. This is usually accomplished using a cluster well of soil vapor probes at different depths (see Figure 3-3). These wells are normally used for subsurface methane monitoring. Each probe should be positioned in a different subsurface soil stratum. Special attention should be given to pressures measured in high permeability strata such as sands. Installation specifications for pressure probes can be found in EPA Reference Method 2E in Appendix A of 40 CFR 60.

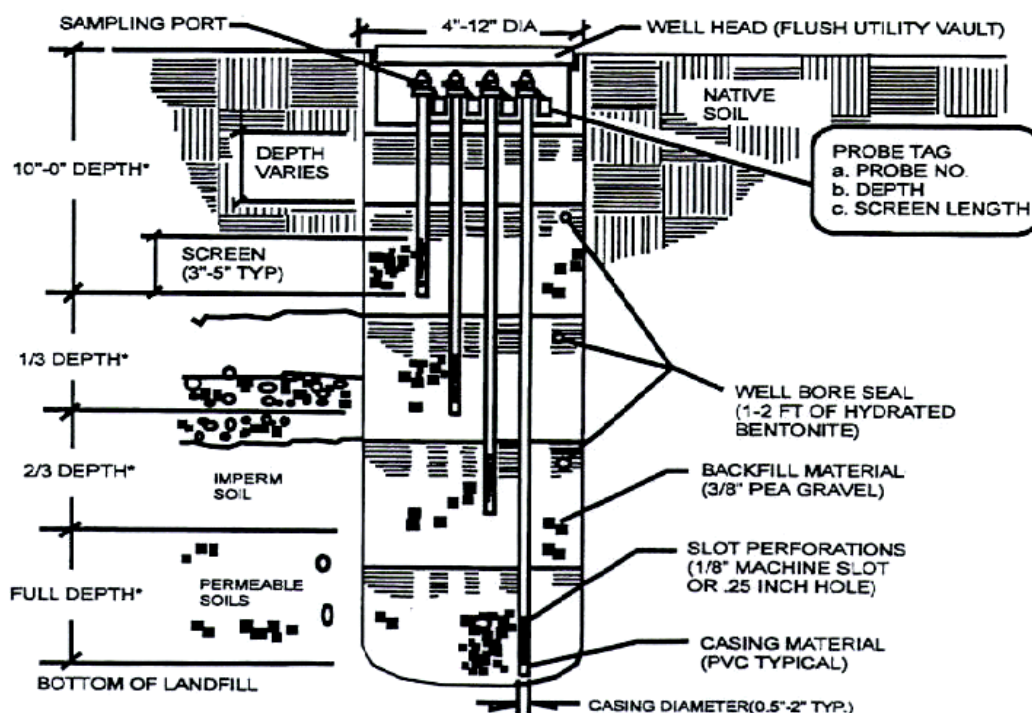


Figure 3-3. Example of a Multi-Depth Cluster Well.

With an estimate of the attenuation coefficient (a), the indoor air concentration at the building of interest is calculated by

$$C_{bldg} = a \times C_{source} \quad 3-3$$

where:

- C_{bldg} = Steady-state indoor air concentration in micrograms per cubic meter,
- a = Attenuation coefficient (unitless)
- C_{source} = Vapor concentration measured at landfill boundary in micrograms per cubic meter.

It should be stressed that use of the Little et al. (1992) model does not account for preferential vapor pathways and that the model operates under the assumptions that the LFG vapor front has reached the building and that steady-state conditions have been achieved. Preferential vapor pathways can be assessed by performing methane sampling using portable detectors under or within structures and within any suspected vapor transport conduits (e.g., underground utilities, sewers, etc.). However, direct measurements indoors and under the slab may be preferred.

3.2 Determining the Extent of Methane Migration

RCRA Subpart C of Part 258 requires monitoring of subsurface CH₄ concentrations at the landfill property boundary and within onsite structures. If CH₄ concentrations are greater than 25 percent of the LEL (1.25% by volume) within onsite buildings, or subsurface concentrations are greater than the LEL (5 percent by volume) at the property boundaries, installation of a gas migration control system is required.

Perimeter subsurface monitoring wells are the most commonly used method for monitoring subsurface CH₄ concentrations. Although the number of wells is not specified in the Part 258 rules, the number of wells and well spacing is determined on a site-specific basis. Please note that State or local rules may specify a minimum number of wells and well spacing. Probes should be placed at the landfill property line within native soils and should be placed between and not immediately opposite any LFG extraction wells. LFG monitoring systems should be designed by professional engineers and certified geologists. Migration monitoring probes may be of single or multi-depth design. Single depth probes can be used with prior knowledge of the depth at which methane is migrating. Without such knowledge, multi-depth probes are used and typically grouped together in a cluster well design. Figure 3-3 shows a typical cluster well. Gas samples can be taken from each sampling port at the top of each probe to provide methane as well as NMOC and COPC concentrations at depth. If whole air samples are taken for COPC concentrations, extreme care must be taken to avoid sample dilution from ambient air infiltration. This includes use of a leak-tight seal at the sampling port and leak-tight fittings in the sampling equipment.

The deepest multi-depth sampling probes are typically installed to the depth of the refuse around the perimeter of the landfill. A separate probe should be installed to the center of each permeable geologic layer. CH₄ concentrations can be determined using portable instruments such as a flame ionization detector (FID) as discussed in Appendix A. Although the FID will ionize and detect most NMOCs as well as CH₄, the relatively small NMOC concentration can be included in the CH₄ concentration without unacceptable errors (i.e., CH₄ concentrations are in the percent range while NMOC concentrations are in the parts-per-million range). A photo ionization detector (PID) can not be used to measure CH₄ concentrations because the detector is insensitive to CH₄.

If the CH₄ concentrations are greater than the LEL within any onsite structure or if the subsurface methane concentrations at any depth are greater than 25 percent of the LEL at the property boundary, the mitigation requirements of 40 CFR Part 258 are applicable. If subsurface CH₄ is detected at the property boundary, further analysis is required regardless of the concentration. Once CH₄ is discovered in native soils at the landfill property line, an analysis should be performed to discover the location of the subsurface CH₄ vapor front. This can be performed by drilling additional vapor monitoring wells between the landfill property line and any offsite structures (including any hypothetical future land use sites). In addition, monitoring for CH₄ can be performed using portable instruments for any suspected preferential vapor pathways. These might include sewers, utility conduits (e.g., water lines and meters), or any other subterranean pathways. If CH₄ is discovered near or beneath any offsite buildings, the two options discussed below are available for estimating possible indoor air concentrations.

3.2.1 Indoor Air Sampling

Indoor air sampling within a structure can be performed for both CH₄ and COPCs. Great care must be exercised whenever entry to a confined space is needed to complete the subslab or indoor air sampling exercise. Unfortunately, ventilation to reduce gas concentrations to levels below the LEL contradict the effort to determine the indoor and subslab concentrations. CH₄ sampling can be performed using portable instruments. If CH₄ is discovered in indoor air, sampling for COPCs should be considered even if the CH₄ concentrations are below the LEL. Indoor air sampling for COPCs may be performed using several methods including whole air sampling (e.g., specially treated canisters) and passive sampling using solid sorbents. The reader is referred to U.S. EPA, 1992b) for a more detailed discussion of indoor air sampling. In addition, Appendix A of this document discusses the various sampling and analytical techniques used for indoor air sampling.

Special Note:

The objective of indoor air sampling is to determine the incremental risks only from LFG contaminants caused by subsurface vapor intrusion. This can be complicated by interferences from contaminated or ambient air, and from offgassing of household chemicals and building products. For example, plywood can offgas formaldehyde and carpets can offgas a series of chemicals. The objective of indoor sampling is to determine only the incremental risks from the LFG contaminants. Indoor air sampling can be combined with outdoor air sampling and limited soil gas sampling to reduce the uncertainty in the indoor sampling results. For example, if a particular contaminant is found in indoor air, in soil gas beneath the building, but not in outdoor air, more confidence can be placed in an assumption that all or part of the indoor concentration is due to vapor intrusion. When performing indoor air sampling, a well formulated sampling plan is critical. Finally, 10⁻⁶ risk-based indoor air concentrations for some COPCs are in the low parts-per-billion range. These concentrations can approach the analytical method detection limits for some compounds such as vinyl chloride, and 1,1-dichloroethylene. Analytical results for these types of contaminants may be flagged by the laboratory as estimated values. The analyst must therefore keep in mind the inherent uncertainty in these values.

3.2.2 Soil Gas Sampling Under Buildings

The second option for determining indoor air concentrations of LFG COPCs is to perform soil gas sampling beneath buildings. Once an average soil gas concentration of each COPC has been determined, the subsurface vapor intrusion model of Johnson and Ettinger (1991) may be used to estimate indoor air concentrations. This technique has the advantage of avoiding the complicating factors inherent in indoor air sampling but exhibits a higher degree of uncertainty in the results.

Soil gas sampling can be performed using either whole air sampling techniques or solid sorbent sampling. Whole air sampling typically involves collecting the soil gas sample in specially treated canisters for subsequent analysis of volatile species by EPA Method TO-15. Passive sorbent sampling involves the burial of sorbent cartridges at a known depth below grade for an extended time period (typically 72 to 120 hours). Once the sorbent cartridges are retrieved, they are sent to the laboratory for thermal desorption and analysis (e.g., a modified TO-1 analysis for volatiles).

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Whole air sampling typically employs the use of an evacuated specially treated canister connected to a flow controller and subsequently connected to the sampling probe. The sampling probe is first purged of at least two volumes of air using a special fitting and a purge pump. Flow is then stopped to allow the soil pore air to re-equilibrate over a given time period. This allows time for the vapor concentration in the soil pores to re-establish equilibrium conditions. Actual sampling then begins at a sampling rate low enough to prevent ambient air from infiltrating the sample. For shallow soil gas sampling, air may flow down the annulus of the probe if the sampling rate is too high and the seal at the ground surface is not air-tight. An airtight seal may be achieved if one uses modeling clay or expansive alcohol laced foam. Air infiltration will act to dilute the sample. Once a sufficient sample volume has been extracted, the canister is shipped to the laboratory for analysis. It should be stressed that soil gas concentrations may vary considerably over relatively small distances given the heterogeneity of the soil. If sampling is used to estimate soil gas concentrations beneath a building floor, the sampling probes should be inserted through holes drilled in the basement slab. Alternatively, angle borings can be made to insert the probe under the building from outside the footprint of the building floor in contact with the soil.

Passive sampling using solid sorbents can also be used to estimate average soil gas concentrations. The concentration term is normally a calculated value based on the cross-sectional area of the sorbent cartridge, the molecular diffusion rate of the contaminant in air, the total mass of each contaminant collected, the sampling duration, and an empirical adsorption rate constant for the sorbent. Recent EPA technology verification reports produced by the EPA National Exposure Research Laboratory (U.S. EPA 1998a, 1998b) concluded, at least for one proprietary sorbent cartridge, that the comparability of the reported vapor-phase concentrations between whole air sampling techniques and solid sorbent sampling is not linear. That is to say that comparability was favorable at low parts per billion by volume ranges, but solid sorbent cartridge concentrations increased by only marginal amounts as the whole air sampling concentrations increased by up to two orders-of-magnitude. Nonetheless, the use of passive solid sorbent sampling offers a relatively uncomplicated method for detecting at least which contaminants are present in soil gas.

Whether the average soil gas concentration directly beneath the building floor in contact with the soil is determined by whole air or solid sorbent sampling, a rough approximation of the steady-state indoor air concentration in the building (C_{bldg}) can be estimated by

$$C_{bldg} = \frac{C_{source}}{1000} \quad 3-4$$

where C_{source} is the soil gas concentration measured directly below the building floor and 1,000 is the attenuation coefficient for a source adjacent to the building (API, 1998). A more rigorous estimate of the indoor air concentration can also be made from the procedures of Johnson and Ettinger (EQ, 2004) by

$$C_{bldg} = C_{source} \left(\frac{Q_{soil}}{Q_{bldg}} \right) \quad 3-5$$

where:

- C_{bldg} = Steady-state indoor air concentration in micrograms per cubic meter,
- C_{source} = Soil gas concentration measured directly beneath the building floor in contact with the soil in micrograms per cubic meter,
- Q_{soil} = Volumetric flow rate of soil gas entering the building in cubic centimeters per second,
- Q_{bldg} = Building ventilation rate in cubic centimeters per second,

and

$$Q_{soil} = \frac{2\pi\Delta P k_v X_{crack}}{\mu \ln(2Z_{crack}/r_{crack})} \quad 3-6$$

where:

- ΔP = Pressure differential between soil surface and the enclosed space in grams per centimeter-second squared,
- X_{crack} = Floor-wall seam perimeter in centimeters,
- μ = Viscosity of air in grams per centimeter-second,
- Z_{crack} = Crack depth below grade in centimeters, and
- r_{crack} = Equivalent crack radius in centimeters.

For single-family detached residences, the default value of ΔP is 40 g/cm-s² from EQ (2004). The value of k_v is calculated from Equation 3-2. The value of X_{crack} is calculated as two times the floor length plus two times the width of the floor in contact with the soil. The default value of X_{crack} for residential construction is 3,844 cm from EQ (2004). The value of μ is 1.75×10⁻⁰⁴ g/cm-s, and the value of Z_{crack} is the depth below grade to the top of the floor in contact with the soil. The default value of Z_{crack} for basement construction is 200 cm from EQ (2000). The value of the equivalent crack radius (r_{crack}) is calculated by

$$r_{crack} = \eta(A_B/X_{crack}) \quad 3-7$$

where:

- r_{crack} = Equivalent crack radius (cm)
- η = A_{crack}/A_B , ($0 \leq \eta \leq 1$)
- A_B = Area of floor and walls below grade (cm²)
- X_{crack} = Floor-wall seam perimeter (cm).

The term A_{crack} is the total area of a 0.1cm crack that runs the perimeter of the basement floor, and A_B is the area of the floor and walls below grade. The default values of A_{crack} and A_B for a single-family detached residence with a basement are 384 cm² and 1,692,321 cm², respectively from EQ (2004).

3.3 Mitigation Strategies for Subsurface Vapor Migration

Whether an indoor air concentration of each LFG COPC is determined by indoor air sampling or by a combination of soil gas sampling and modeling, a risk evaluation is performed

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to determine the aggregate cancer risk and the hazard index for chronic exposure to non-carcinogens. If the target cancer risk or the target hazard index is exceeded, mitigation of the LFG vapor migration should be undertaken. Methods for managing subsurface migration involve collecting the LFG to an extent that minimizes the lateral pressures driving the gas through the subsurface. Section 5.1 discusses both passive and active collection systems.

Two objectives exist for reducing LFG migration: (1) minimizing safety hazards associated with high methane concentrations, and (2) reducing health hazards associated with LFG toxics. Different approaches to collecting LFG can be taken depending on whether one or both of these objectives is to be met. If reducing CH_4 concentrations in offsite soils is the only objective, either passive or active collection systems have merit. Passive systems such as horizontal trenches or a series of vertical wells have been employed at many sites to reduce offsite soil CH_4 concentrations to acceptable levels (e.g., less than 25 percent of the LEL).

If the objective is to reduce concentrations of LFG toxics, active collection systems are recommended using the design criteria specified in the CAA NSPS/EG. During the research for this guidance, several instances were found where passive systems were used to prevent subsurface migration and had failed to reduce toxics concentrations to below levels of concern. Active systems were subsequently used to reduce the concentrations of toxics in the offsite soils.

The LEL for CH_4 is 5 percent by volume, and the UEL is 15 percent by volume. This means that within the 5 to 15 percent range, potential exists for landfill fires or explosions. Whether or not a fire or explosion will occur depends on the availability of oxygen and an ignition source. Figure 3-4 is a graph showing the relationship between CH_4 and O_2 where flammable mixtures can occur.

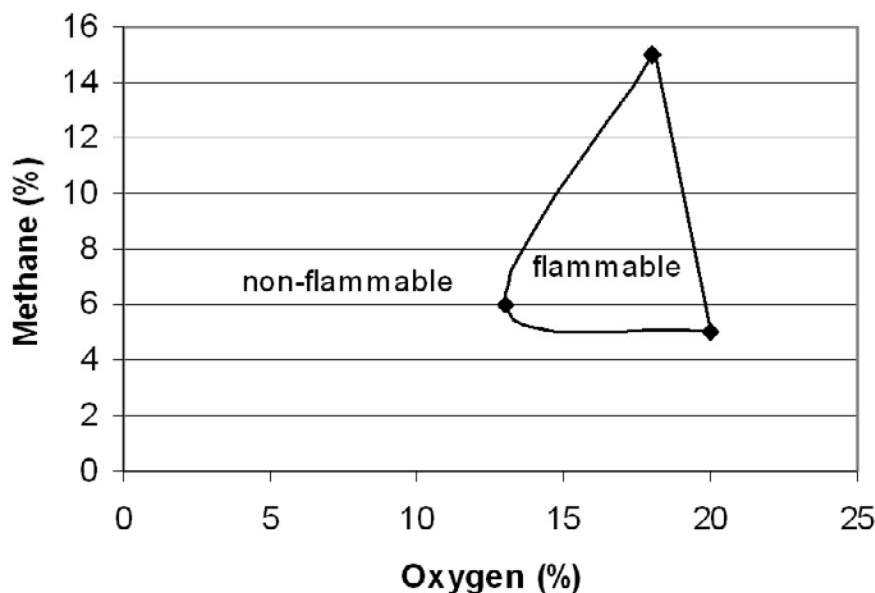


Figure 3-4. Flammability of Methane/Oxygen Mixtures (adapted from U.S. EPA, 1999b, Appendix E).

As shown in Figure 3-4, flammable mixtures of CH₄ and O₂ exist when methane is within its explosive limits (5 to 15 percent) and O₂ is at approximately 12 to 13 percent or more. There is also the potential for an explosion when CH₄ builds up above its LEL in confined spaces. At landfills, these confined spaces can be buildings, well head vaults, or other structures.

Underground landfill fires generally occur when ambient air is drawn into the landfill. Air can infiltrate the landfill by two mechanisms: advection and diffusion. Some of the ways advection can cause air infiltration include excessive vacuum at active gas collection wells, separations at cover seams caused by deterioration or settlement, gas well and trench lateral separations, well seal failures, earthen cover cracks due to dessication and general cover permeation, and by atmospheric (barometric) pressure cycling, which can pump air into the upper portions of the landfill during low atmospheric pressure events. Most of these infiltration mechanisms can be overcome with proper operation and maintenance. Excessive vacuum at active gas collection wells, however, may be more difficult to correct. Gas control systems such as an enclosed flare operate most effectively when the methane concentration is greater than 25 percent. Aggressive collection minimizes emissions to ambient air but may encourage air infiltration, especially at active gas collection system well seals, and thus dilute the LFG methane concentration. Typical well seals are made of hydrated bentonite, but dessication of the bentonite from prolonged periods of little or no precipitation can cause seal failures such that ambient air is drawn into the upper most regions of the landfill wastes. Prolonged seal failures can result in oxygen contents increasing within deep sections of the landfill. In addition, general diffusion of ambient air through permeable cover materials can introduce oxygen into the wastes, especially for older landfills with minimal methane generation potentials. Diffusion through the cover material may be most apparent for arid regions of the country where the air-filled porosity of the cover is higher.

Oxygen content of a landfill increases as air enters it, inhibiting anaerobic decomposition. This can result in an aerobic decomposition zone that is usually near the landfill surface. This aerobic zone promotes composting that can generate a considerable amount of heat. This heat, in combination with enough O₂ to support combustion and a local dilution of the CH₄ concentration below the UEL, can cause spontaneous combustion and a resulting CH₄ explosion or fire.

Where subsurface migration is found to be a problem, horizontal barrier trenches or vertical extraction wells should be installed at the site perimeter. Horizontal barrier trenches are often installed to intercept LFG migrating offsite in the subsurface. These are typically constructed by excavating a perimeter trench to at least the depth of the waste (deepest waste within a certain distance from the trench). A barrier material (e.g., heavy thickness plastic sheeting) is placed on the outer wall of the trench. A horizontal collector pipe is laid between gas conducting materials within the trench (e.g., 1 to 7 cm gravel). Vertical risers are installed at various lengths of the horizontal collector pipe to convey the gas to vents at the surface or to a control device. Collection may be passive or supplemented by gas moving equipment.

These trench barrier systems have generally been reliable at reducing CH₄ migration (e.g., to levels below 25 percent of the LEL). Their record, however, in reducing the migration of LFG toxics to below the levels of concern is spotty. Instances have been noted where toxics

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(e.g., vinyl chloride) have continued to migrate at significant levels following installation of barrier trenches. Presumably, the migration pathway was either under or around the trench. Hence, a soil gas monitoring program should be used to verify the performance of the barrier trench (or perimeter wells, if these were the selected approach).

Figure 3-5 is a photograph of an abandoned horizontal trench system. The vertical risers are connected to a horizontal pipe that, at one time, directed the gas to a vent at the top of the landfill. Figure 3-6 shows an alternative migration barrier system. In this system, a series of vertical wells are connected and routed to a series of carbon drums and an elevated vent stack. It should be noted that activated carbon is not effective in removing many of the important toxic LFG constituents such as vinyl chloride (see Section 5.3).



Figure 3-5. Abandoned Horizontal Barrier Trench System.



Figure 3-6. Alternative Migration Barrier System.

Air infiltration is caused when too much vacuum is applied to the system or when wells are poorly sealed, causing ambient air to be pulled into the landfill and potentially explosive or flammable conditions. The operational standards for the NSPS/EG call for maintaining a LFG temperature less than 55 °C (130 °F) and either a N₂ level less than 20 percent by volume or an O₂ level less than 5 percent by volume. The owner or operator may establish a higher temperature, N₂, or O₂ value at a particular well; however, there must be data demonstrating that the elevated parameter(s) does not cause fires or significantly inhibit anaerobic decomposition of the waste (40 CFR §60.753).

The collection system must be operated to maintain surface concentrations below 500 ppmv methane. The NSPS/EG do not specify how to measure compliance with the requirement to minimize subsurface migration. The upper limit for CH₄ concentration in offsite soils is generally set at less than 25 percent of the LEL (1.25 percent by volume). For safety reasons, the CH₄ content in onsite soils should be kept below the LEL (5% by volume).

For collection systems constructed to achieve compliance with the NSPS/EG, the collection and control system must be operated until the following conditions have been met (§60.752):

- The landfill is no longer accepting wastes, is permanently closed as per the requirements of §258.60, and has submitted a closure report as required in §60.757(d);
- The collection and control system has been operated for a minimum of 15 years;
- As specified in §60.754(b), the calculated NMOC emission rate is less than 50 Mg/yr on three successive test dates (test dates no less than 90 days and no more than 180 days apart).

Alternatively, an active collection and control system may be installed to achieve compliance with another ARAR (e.g., ambient air limits or health risk standards). Similar criteria can be applied for removal of the equipment as specified in the NSPS/EG. After at least 15 years of operation, a risk evaluation and an evaluation of compliance with ARARs can be performed with LFG test data to determine compliance with the ARAR and to determine that the target cancer risk and/or hazard index is not exceeded.

If CH₄ migration interception methods are not successful, a supplemental strategy of indoor air remediation can be implemented to reduce CH₄ and COPC concentrations within affected buildings. Site experience has shown that the building remediation techniques typically used for radon intrusion can be successfully applied to landfill gas intrusion. The EPA document titled *Options for Developing and Evaluating Mitigation Strategies for Indoor Air Impacts at CERCLA Sites* (U.S. EPA, 1993b) contains a complete review of indoor air mitigation techniques. Additionally, several excellent documents on this subject are available from the U.S. Department of Energy Lawrence Berkeley National Laboratory (LBL). These documents may be downloaded to a PC from the Indoor Environment Department of the LBL at <http://eetd.lbl.gov/ied/ied.html> (accessed August 2005). The Indoor Air Quality Division of the EPA Office of Air and Radiation also publishes documents concerning indoor air remediation. In particular, EPA 1993c, titled *Radon Mitigation Standards* (EPA-402/R-93/078, revised April 1994), is available at <http://www.epa.gov/iaq/radon/pubs/mitstds.html> (accessed August 2005).

3.4 Indoor Vapor Intrusion from Contaminated Groundwater

As mentioned at the beginning of this chapter, the production of leachate and the migration of LFG can contaminate the underlying aquifer. If contaminated groundwater migrates offsite, vapor volatilizing from the top of the water table can migrate up and into buildings. In this situation, vapor transport is a function of both diffusion and advection. Figure 3-7 shows a flow chart for assessment of human exposure to this pathway. The assessment begins with a determination as to whether contaminated groundwater has migrated underneath offsite buildings. If so, modeling is first performed to estimate the indoor air concentrations originating from each groundwater contaminant. The estimated indoor air concentrations are then used in a risk evaluation to determine whether the aggregate target cancer risk or the target hazard index is exceeded. If this first-tier analysis indicates unacceptable risks, either soil gas measurements and modeling, or indoor air sampling is undertaken to refine the indoor air concentration estimates.

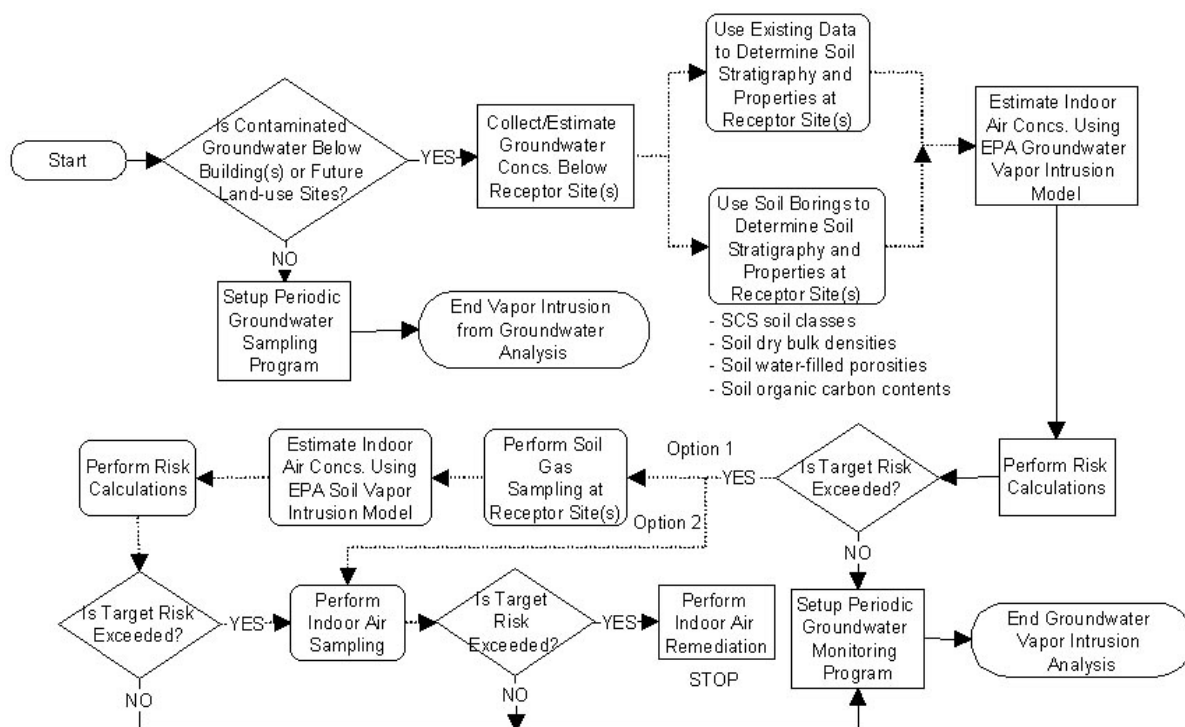


Figure 3-7. Flow Chart for Assessing Vapor Intrusion from Contaminated Groundwater.

At the first soil air-groundwater interface, aqueous-phase contaminants below the top of the water table will volatilize according to Henry's law such that

$$C_{source} = H'_{TS} C_w \quad 3-8$$

where:

- C_{source} = Vapor concentration at the air-water interface in micrograms per cubic meter,
 H'_{TS} = Henry's law constant at the groundwater temperature (dimensionless), and
 C_w = concentration of the VOC of interest in groundwater in micrograms per cubic meter.

These vapors will then diffuse upward toward the soil surface until they enter into a pressure field created within the soil column surrounding the building. This pressure field is created by a pressure gradient between the atmospheric pressure and the under-pressurized building interior. The under-pressurization is caused by wind effects on the building and by stack effects from building heating and mechanical ventilation. Under most circumstances, the pressure field extends perhaps one to two meters below the building floor in contact with the soil depending on the interior dynamic pressure and the soil vapor permeability. Once the diffusing vapors reach the subsurface pressure field, they are drawn into the building by advection through cracks or openings in the building foundation. Figure 3-8 illustrates the diffusion and advection processes that result in indoor vapor intrusion from contaminated groundwater.

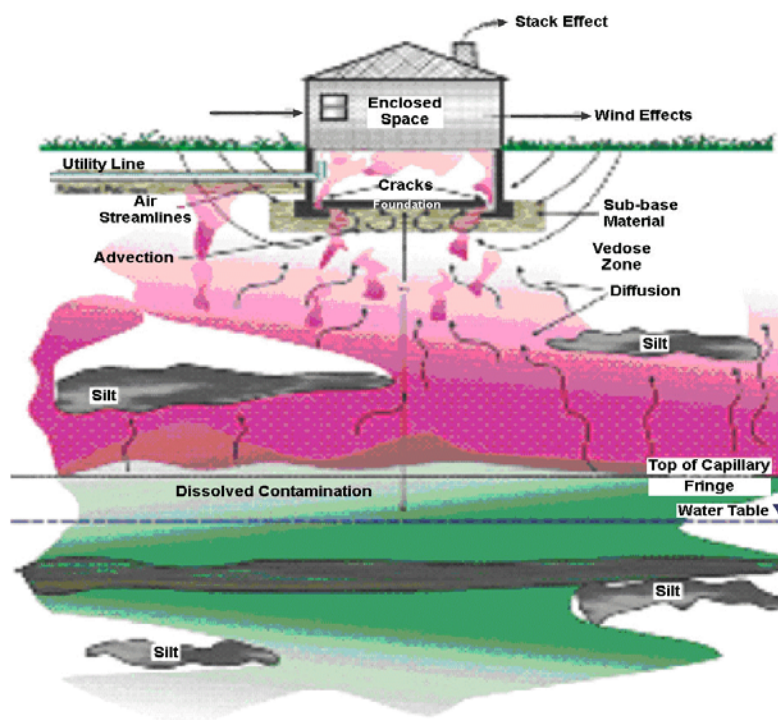


Figure 3-8. Indoor Vapor Intrusion from Groundwater.

Recent experience at a site in Denver, Colorado, has shown that this pathway of inhalation exposure is credible and can account for incremental cancer risks as high as approximately 1 in 10,000 even when the depth to the water table is significant (10 to 15 feet). In addition, the

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2001 Supplemental Guidance of Superfund Soil Screening Levels includes this exposure pathway when estimating risk-based soil screening levels (SSLs).

Johnson and Ettinger (1991) developed a screening-level model for estimating the indoor air concentrations of vapor-phase contaminants emanating from contamination in underlying soils or below the top of the water table. The EPA Superfund program has developed a series of spreadsheet models based on the work of Johnson and Ettinger. These spreadsheets and an accompanying user's guide are available from the Superfund risk assessment web site at http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm (accessed August 2005).

Two of these spreadsheet models deal directly with vapor intrusion from contaminated groundwater. Both models theoretically partition the groundwater contaminants into aqueous and vapor-phases based on Henry's law. That is to say that the models assume that the groundwater concentration is less than the solubility limit in water—i.e., Nonaqueous Phase Liquids (NAPL) is not considered. The GW-SCREEN model provides a first-tier estimate of indoor air concentrations and risks based on steady-state conditions. Within this model, only the most sensitive model parameters can be user-defined, all other input parameters are set to default values for detached single-family residences. The GW-ADV model provides a more refined estimate of the indoor air concentration and associated risks based on user-specified data for all input parameters. The user's guide to these models should be consulted for specific model features, assumptions, and limitations.

In addition, the SG-SCREEN and SG-ADV models are also available for estimating indoor air concentrations and associated risks from measured soil gas concentrations below or adjacent to buildings.

In the case of groundwater contamination due to NAPL, the GW-SCREEN or GW-ADV models can be used by assuming that the groundwater concentrations at the first air-groundwater interface are at the aqueous solubility limit. This approach will produce source vapor concentration values (C_{source}) approaching the single component saturated vapor concentration based on Raoult's law for residual-phase contaminants (NAPL). If sampling data are available for component concentrations of light nonaqueous-phase liquids (LNAPL) that tend to float on the top of the water table, the mole fraction of each component can be determined. In such cases, a better estimate of the source vapor concentration can be made by multiplying the calculated mole fraction of each component by its aqueous solubility limit and using the resulting product as the initial groundwater concentration in either of the groundwater vapor intrusion models.

The models referred to above require soil properties data from the soil surface to the depth of the water table or to the soil gas sampling depth, as appropriate. These properties include soil dry bulk densities, soil moisture contents, and the SCS soil textural classifications. With these data, the models will estimate the steady-state indoor air concentration directly above the contaminated groundwater as well as the associated incremental risks.

If this first-tier evaluation results in an exceedence of the target risk level, two options are

available for making a more refined estimate of the indoor air concentrations. As described in Sections 3.2.1 and 3.2.2, indoor air sampling or a combination of soil gas sampling beneath the building(s) of interest and modeling can be used to estimate indoor air concentrations for a second-tier estimate of the associated risks. If the second-tier evaluation results in unacceptable risks from indoor inhalation of vapor-phase groundwater contaminants, indoor remediation techniques referred to in the previous section of this document should be considered.

4. Air Pathway ARARs

Under CERCLA Section 121, remedies selected at Superfund sites must protect human health and the environment and must comply with ARARs. Remedial actions taken under CERCLA Sections 104, 106, or 122 that are conducted entirely on site do not require Federal, State, or local permits, whether conducted by EPA, another Federal agency, a State, or a responsible party. On-site remedies must comply with substantive requirements of ARARs but need not comply with the administrative and procedural requirements. On-site remedial activities covered by the permit exemption include any activity occurring on site prior to the response action itself (e.g., activities during the remedial investigation/feasibility study). “On-site” is defined as the areal extent of contamination and all suitable areas in close proximity to the contamination necessary for implementation of the response action. Although CERCLA Section 121(e) exempts facility owners/operators from having to obtain permits for on-site remedial activities, the substantive requirements and conditions that would otherwise be included in the permit must be met. The reason for the permit exemption is to preserve flexibility and avoid lengthy, time-consuming procedures when developing and implementing remedial alternatives (U.S. EPA, 1989).

Air pollution problems at Superfund co-disposal landfills are usually the result of emissions of gas or particulate matter (e.g., dusts). Such emissions may be released through a stack, vent, or some other functionally equivalent opening. Emissions that could not reasonably pass through such openings are considered to be “fugitive” emissions. Gaseous emissions may be due to the venting of LFG, vaporization of liquids, thermal destruction of LFG, or chemical and biological reactions with solid and liquid wastes. Emissions of particulate matter are likely to be caused by construction, maintenance and inspection traffic, and wind blown surface materials.

The following activities and events, commonly performed during CERCLA remediation of SFLs, may be sources of air emissions:

- LFG emissions through permeable cover materials,
- LFG emissions through passive vents,
- Emissions from LFG control systems (e.g., flares, internal combustion engines, and turbines),
- Leachate processing equipment (e.g., air strippers and evaporators),
- Waste excavation and handling,
- Construction activities and traffic on unpaved roads, and
- Wind erosion of soils.

4.1 CAA ARARs

Except for extraordinary circumstances, Federal air pathway ARARs under the CAA for SFLs are limited to the EG for municipal solid waste landfills. In specific cases where the SFL is part of an active MSW landfill, the NSPS and other Federal air pathway requirements may constitute ARARs. In such cases, the RPM/OSC should work closely with the EPA Regional Air Programs Office to determine which additional Federal requirements may be ARARs.

The NSPS and EG promulgated under Section 111(b) of the CAA are in place to control emissions of NMOCs from MSW landfills (see the text box to the right for the definition of an MSW landfill under the NSPS/EG). Under the NSPS and EG, NMOC is used as a surrogate measure of VOCs, a tropospheric ozone precursor. Promulgated EG under Part 60 are not enforceable; the EG only stipulate the requirements for an approvable state implementation plan under Section 111(d) of the CAA. To be enforceable, the EG requirements must be contained in either a Federal or approved State plan codified under 40 CFR Part 62. For States without an EPA approved 111(d) landfill plan, the promulgated November 8, 1999 Federal plan (64 FR 60689), 40 CFR Part 62, Subpart GGG, is applicable and stipulates enforceable requirements for affected landfills. The reader should consult the Federal Register for the latest versions of the NSPS (40 CFR Part 60 Subpart WWW) and the EG (40 CFR Part 60, Subpart Cc) and the Code of Federal Regulation, 40 CFR Part 62.

Definition of an MSW Landfill under the NSPS and EG - an entire disposal facility in a contiguous geographical space where household waste is placed in or on land. An MSW landfill may also receive other types of RCRA Subtitle D wastes such as commercial solid waste, nonhazardous sludge, conditionally exempt small quantity generator waste, and industrial solid waste. Portions of an MSW landfill may be separated by access roads. An MSW landfill may be publicly or privately owned. An MSW landfill may be a new MSW landfill, an existing MSW landfill, or a lateral expansion (40CFR §60.30c).

For most new landfills, the EPA has delegated the NSPS regulatory authority to the States. For existing landfills, the States are required to implement the EG requirements through a State Section 111(d) plan approved by EPA. As an alternative, States may request and receive delegation of the Federal plan. Approved State Section 111(d) landfill plans, including EPA Federal plan delegations, are listed in 40 CFR Part 62. An exception could be a State or Federal plan that was promulgated after the last July 1 publication date of the Code of Federal Regulations.

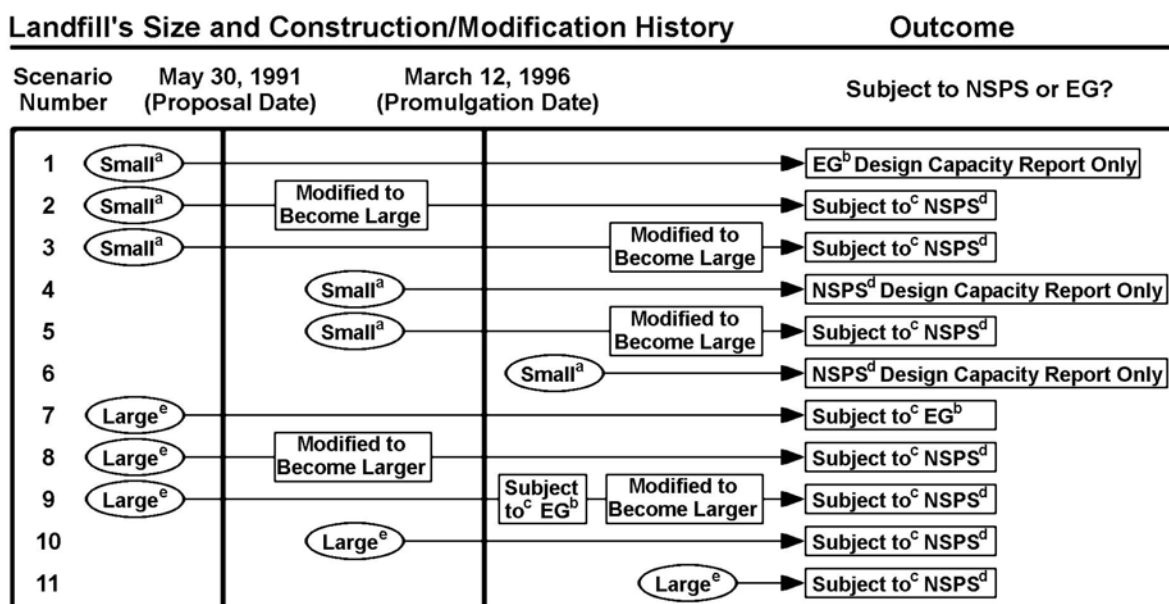
As shown in the definition, SFLs are potentially subject to the NSPS/EG because they often contain household wastes. Whether the NSPS or EG apply to an MSW landfill is determined by two factors: age and size of the landfill. The NSPS apply to new landfill sites, while the EG apply to existing landfills. “New” landfills are considered to be those sites that began construction, modification, or reconstruction on or after May 30, 1991. “Existing” landfills are those that accepted waste on or after November 8, 1987, but have not been constructed, modified, or reconstructed since May 30, 1991.

Landfills that are new or have been modified or reconstructed must comply with the NSPS. A modified landfill is one that is permitted to increase volumetric capacity typically by

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horizontal expansion. Remedial actions such as those performed under CERCLA, RCRA, or State actions are not considered to be construction, modification, or reconstruction and do not, in and of themselves, subject a landfill to the NSPS (EPA, 1999b). Hence, for SFLs, EG applicability is more likely to be the issue requiring assessment. However, if a portion of the site is a SFL and there is also a newer and active portion of the site that is subject to the NSPS, the whole landfill including the SFL is subject to the NSPS.

The NSPS and EG include provisions for a size exemption. Landfills with a design capacity under 2.5 million Mg or 2.5 million m³ are exempt from the rules. The landfill capacity must be measured in megagrams or cubic meters, but the owner may request a change in measurement. The landfill design capacity can be taken from the most recent Federal, State, local, or other official permit used to license the facility, or it can be calculated. The owner has a choice of how to report the design capacity. Landfills with a maximum NMOC emission rate under 50 Mg/yr are also exempt from many parts of the rules. Figure 4-1 is a diagram that outlines applicability issues as they relate to landfill size and construction/ modification history.



^a Small means design capacity less than 2.5 million Mg or 2.5 million m³.

^b Landfills that began construction, modification, or reconstruction before May 30, 1991, are subject to the EG.

^c "Subject to" means the landfill must submit annual emission reports and must install controls if emissions are equal to or greater than 50 Mg/yr.

^d Landfills that began construction, modification, or reconstruction on or after May 30, 1991, are subject to the NSPS.

^e Large means a design capacity equal to or greater than 2.5 million Mg or 2.5 million m³.

Figure 4-1. NSPS Landfill Applicability.

Due to the age of SFLs, they are not likely to be subject to the NSPS (i.e., constructed, modified, or reconstructed after May 30, 1991). Some sites may be subject to the EG if wastes were accepted on or after November 8, 1987. Still, most SFLs operated only until the early to mid-1980's. Regardless of when the site last received wastes, EPA considers the EG to be a relevant and appropriate requirement if the design capacity cutoff and the NMOC emissions cutoff have been exceeded. Therefore, the remainder of this discussion will focus on the Section

111(d) plan and requirements for those sites meeting or exceeding the size and NMOC emissions thresholds described above.

4.1.1 Requirements for the CAA Section 111(d) Plans and NESHAPS

If the landfill exceeds the size thresholds (greater than 2.5 million Mg or 2.5 million m³), the owner must quantify NMOC emissions to determine if there is a need to install emission control equipment. NMOC emissions are calculated using a theoretical first-order CH₄ generation model. This model and methods to estimate emissions are described in detail in Chapter 2. A computerized version of the LFG emissions model (LandGEM) is also available (see Chapter 2). To a large degree, the LandGEM model is dependent on three variables: a CH₄ generation rate constant (k); the refuse CH₄ generation potential (L_0); and the NMOC concentration in the LFG (C_{NMOC}).

A flow chart is presented as Figure 4-2 that summarizes the steps to be taken under the NSPS or EG to determine the need for LFG collection and control (along with the CFR citations, where appropriate). There are three method tiers for estimating NMOC emissions using the LFG model (40 CFR §60.754). These methods must be used to determine whether a landfill is subject to the collection and control requirements of the EG. If a SFL is not subject to the EG based on its closure date (prior to November 8, 1987), the collection and control requirements are still considered to be relevant and appropriate, if the site meets or exceeds the NMOC emissions threshold of 50 Mg/yr and the design capacity threshold of 2.5 million Mg or 2.5 million m³.

Determining design capacity at Superfund landfills - Records, such as waste receipts and solid waste permits needed to estimate design capacity are often not available for SFLs. Surveys can provide information on waste depth and lateral extent to estimate waste volume. For typical SFLs (i.e., those having closed prior to the mid-1980's which will have waste that has undergone settling and degradation), a reasonable waste density to assume is 1,800 pounds per cubic yard (NSWMA, 1985). Densities achieved in landfills actively accepting MSW are reported to vary between 700 and 1,600 pounds per cubic yard (EPA, 1998c). If at all possible, a design capacity (waste in place) estimate should be confirmed if any waste acceptance records are available.

Tier I methods rely on the use of default values for all three variables. The NSPS Tier I default value for k is 0.05 for all parts of the country but can vary depending on annual average precipitation. Hence a Tier II or III procedure may be beneficial for any facility that triggers applicability as a result of the default value in the Tier I analysis. Facilities located in dry areas (average annual rainfall less than or equal to 25 inches) use a rate of 0.02. Facilities located in wetter areas (average annual rainfall greater than 25 inches) use a value of 0.04. Those facilities that are predicted by the model to emit 50 Mg/yr of NMOC or more are required to install emission control equipment (within 30 months of determining the emission rate for the site) or to recalculate the NMOC emission rate using Tier II or Tier III procedures. If emission rates are below 50 Mg/yr, the facility is required to periodically recalculate NMOC emissions until such time that the estimated NMOC emission rate meets or exceeds 50 Mg/yr (EPA, 1999b).

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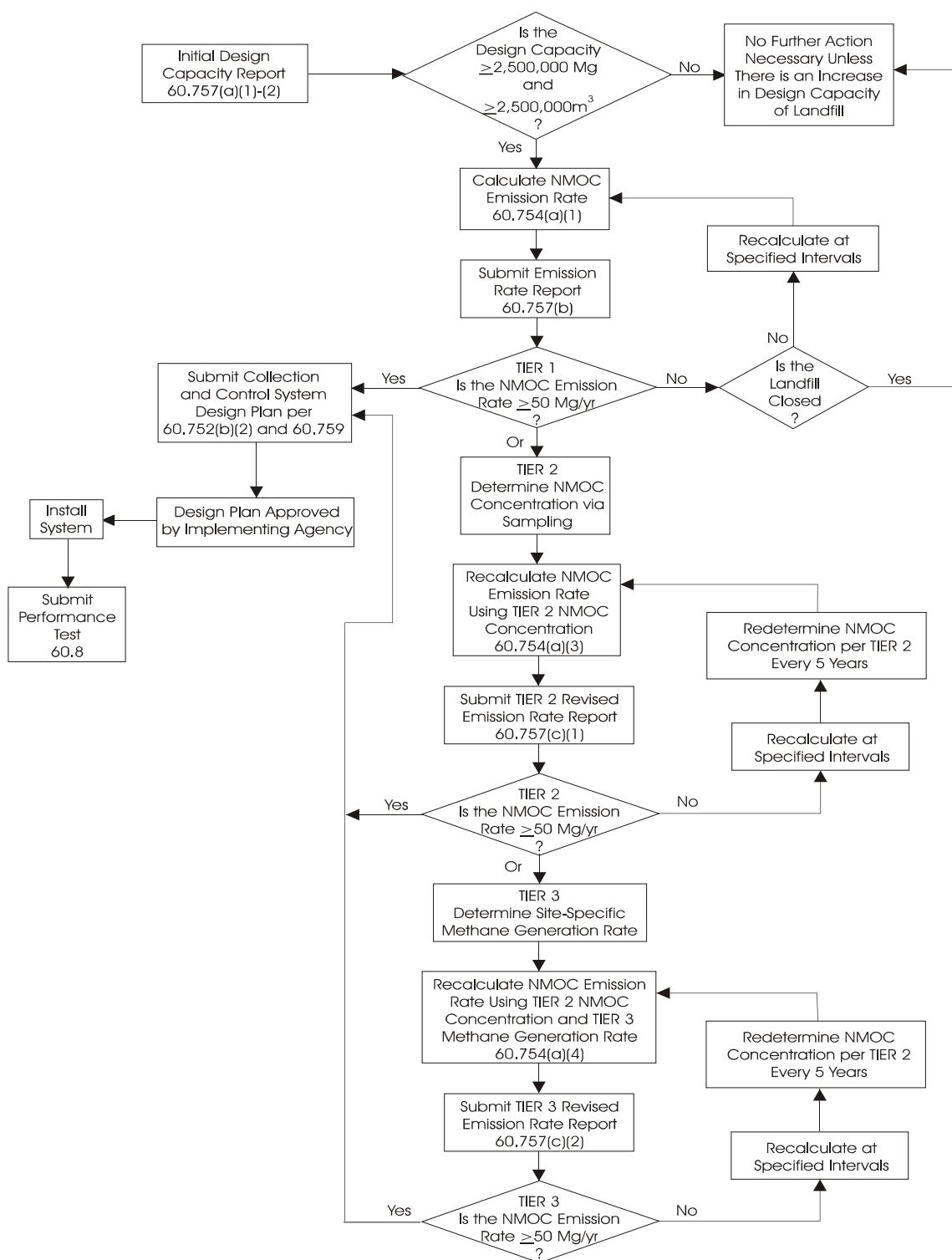


Figure 4-2. Flow Chart for Determining Control Requirements.

MSW landfill owners have a second option if NMOC emission rates are greater than or equal to 50 Mg/yr after using Tier I calculations. The EG provide for a Tier II assessment that is more accurate and based upon site-specific information using EPA Reference Methods 25C or 18 to establish the LFG NMOC concentration. These data are then used in the LFG emission model to calculate the annual NMOC emission rate.

If Tier II procedures show NMOC emissions still greater than or equal to 50 Mg/yr, the owner may opt for Tier III testing. Using EPA Reference Method 2E (40 CFR 60, Appendix A), a site-specific CH₄ generation rate constant is determined to yield more accurate results. If Tier III results are greater than or equal to 50 Mg/yr, the owner must install control equipment. Tier III testing is expensive and, to date, few MSW landfill owners have opted to use this testing procedure to avoid control requirements.

MSW landfill owners must install equipment that is the best demonstrated technology (BDT). A passive or active LFG collection system can be used. For compliance with the EG, a Collection and Control System Design Plan must be prepared and submitted to the responsible agency for review. The Collection and Control Design Plan must show that: (1) the control equipment will collect LFG at a maximum flow rate for the life of the equipment; (2) LFG must be collected from all areas of the landfill that have had waste in them for more than 2 years and the area is closed or for more than 5 years if the area is open and still active; (3) the control equipment can collect gas (for active systems only) at a rate sufficient to keep wellheads at a negative pressure; and (4) the system must be able to contain subsurface gas migration. The control equipment (e.g., flare) must achieve an NMOC emission rate of 20 ppmv dry as hexane at 3 percent O₂ or reduce NMOC emissions by 98 percent by weight (U.S. EPA, 1999b). For open flares, the control device must comply with the design and operating requirements of 40 CFR 60, §60.18.

In order to remove control equipment, the owner must demonstrate compliance with three conditions: (1) the landfill must be permanently closed as defined under 40 CFR §258.60; (2) the controls must have been in operation for at least 15 years; and (3) the annual NMOC emissions rate must be less than the emission rate cutoff taken on three successive dates between 90 and 180 days apart (U.S. EPA, 1999b).

The requirements for monitoring collection systems include monitoring the landfill surface to verify that CH₄ concentrations are being kept below 500 ppmv. Figure 4-3 is a flow chart of the surface monitoring requirements under the EG (U.S. EPA, 1999b).

Under Section 112(d) of the CAA, EPA was required to regulate major sources of 188 HAP listed in Section 112(b) of the CAA. On July 16, 1992 (57 FR 31576), EPA published a list of industrial source categories, which included MSW landfills, that emit one or more of these HAP.

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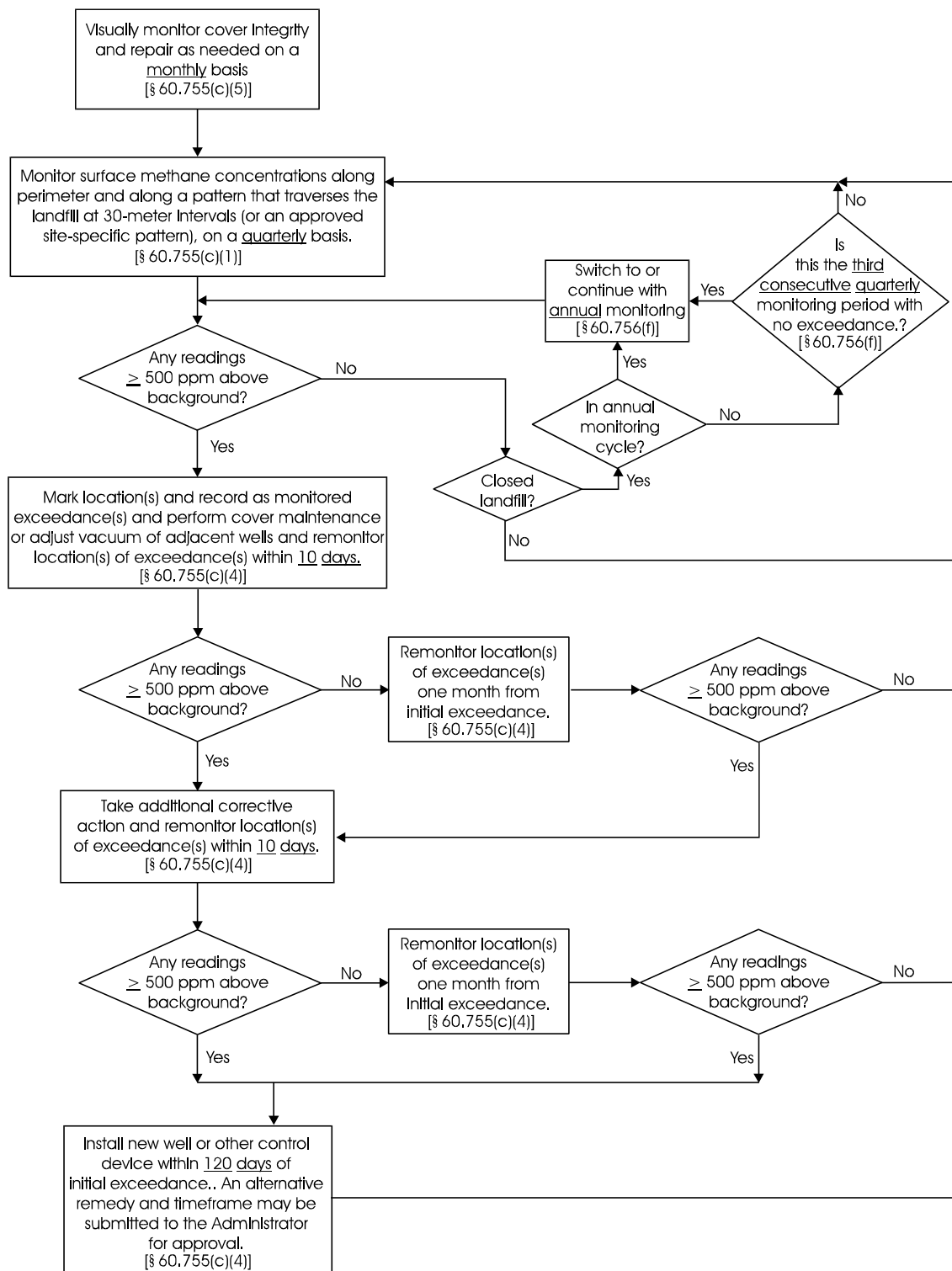


Figure 4-3. Flow Chart of Surface Monitoring Requirements.

Under Section 112(k) of the CAA, EPA developed a strategy to control emissions of HAPs from area sources in urban areas, identifying 33 HAPs that present the greatest threat to public health in the largest number of urban areas as the result of emissions from area sources. Municipal solid waste landfills were listed on July 19, 1999, as an area source category to be regulated pursuant to Section 112(k) because 13 of the listed HAPs are emitted from MSW landfills (64 FR 38706).

On January 16, 2003 EPA published the National Emission Standards for Hazardous Air Pollutants (NESHAP) for MSW landfills (40 CFR Part 63 Subpart AAAA). The final rule is applicable to both major and area sources and contains the same requirements as the EG and NSPS. The final rule adds startup, shutdown, and malfunction (SSM) requirements; adds operating condition deviations for out-of-bounds monitoring parameters; requires timely control of bioreactor landfills; and changes the reporting frequency for one type of report.

The final NESHAP rule contains the same requirements as the EG/NSPS (40 CFR Part 60, Subparts Cc and WWW), plus SSM definition and reporting of deviations for out-of-range monitoring parameters. Also, the final rule requires compliance reporting every 6 months whereas the EG/NSPS requires annual reporting. For bioreactors at large landfills, the NESHAP rule also requires timely installation of controls, and allows timely removal of controls. The final NESHAP rule applies to area source landfills if they have a design capacity equal to or greater than 2.5 million Mg or 2.5 million m³ and have estimated uncontrolled emissions of 50 Mg/yr NMOC or more or if they are operated as a bioreactor. The final rule does not apply to area source landfills (including bioreactors) with a design capacity less than 2.5 million Mg or 2.5 million m³. It also does not apply to conventional area source landfills that have estimated uncontrolled emissions of less than 50 Mg/yr NMOC. The EG/NSPS require landfills that meet the design capacity criteria to periodically calculate uncontrolled annual NMOC emissions. If an area source landfill that currently has estimated uncontrolled emissions less than 50 Mg/yr increases to 50 Mg/yr in the future, it will become subject to the NESHAP at that time.

4.2 RCRA Subtitle C Air Pathway ARARs

The RCRA rules that apply to air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs) may be ARARs for certain remedial activities. These rules may be ARARs for circumstances where a liquid hazardous waste stream generated at the point of origin (such as landfill leachate and LFG condensate) are treated or combusted on-site.

Under the RCRA rules, 40 CFR §261.2(b) states that “Materials are solid waste if they are abandoned by being: (1) disposed of; or (2) burned or incinerated; or (3) accumulated, stored, or treated (but not recycled) before or in lieu of being abandoned by being disposed of, burned or incinerated”. Further, a solid waste is defined as a hazardous waste pursuant to §261.4(b) if it meets the criteria of a “characteristic hazardous waste” described in Subpart C of §261, or a “listed hazardous waste” described in Subpart D of §261. The EPA Hazardous Waste Number F039 (listed hazardous waste) is defined as follows:

Leachate (liquids that have percolated through land disposal wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of

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this part. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other Hazardous Wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F026, F027, and/or F028).

Therefore, if historical records at a specific landfill indicate that more than one EPA listed hazardous waste was deposited in the landfill, the leachate is considered a listed hazardous waste under EPA Hazardous Waste Number F039. If it cannot be determined that listed hazardous wastes were ever deposited in the landfill, a determination must still be made as to whether the leachate is a “characteristic hazardous waste” as defined in Subpart C of §261. In addition, it must also be determined whether any landfill gas condensate retrieved from a gas collection system, although not leachate, is also a characteristic waste under Subpart C of §261.

Subpart C of §261 specifies four tests to be conducted on a solid waste (leachate or condensate) to determine whether it is a characteristic hazardous waste. These tests are for: (1) ignitability, (2) corrosivity, (3) reactivity, and (4) toxicity. The corrosivity and toxicity criteria are the two most likely tests that would decide whether the leachate or condensate is a characteristic hazardous waste. The test for the toxicity criteria uses the TCLP referenced in §261.24. Associated with this test is a list of chemical constituents and their associated threshold maximum concentrations. If an aliquot of the leachate or condensate exhibits one constituent concentration greater than its associated threshold value, the leachate or condensate is considered to be a characteristic hazardous waste.

Assuming that the leachate, condensate, or both are characteristic hazardous wastes, treatment of the wastes would be subject to the RCRA air pathway rules. For example, if the LFG condensate is burned in an enclosed flare, controlled flame combustion of the condensate would mean that the enclosed flare constitutes an “incinerator” by definition (§260.10). This would then require that the enclosed flare meet all of the requirements for an incinerator found in 40 CFR Part 264 Subpart O. In addition, this would trigger the requirement to perform an indirect risk assessment for combustor emissions pursuant to the Omnibus Authority granted under the Hazardous and Solid Waste Act (HSWA) of 1986.

Pretreatment of landfill leachate considered to be hazardous waste before delivery to any publicly owned treatment works (POTW) using air strippers or leachate evaporators would be considered initiation of a new hazardous waste treatment facility. If the treatment units consisted of air strippers and/or evaporators, as well as storage tanks and associated plumbing, this would subject the emissions of the system to the requirements of 40 CFR Part 264 Subpart X for miscellaneous units, Subpart AA for air emission standards for process vents, Subpart BB for air emission standards for equipment leaks, and Subpart CC for air emission standards for tanks, surface impoundments, and containers.

If the leachate or condensate is determined to be a characteristic hazardous waste only because of failing the TCLP, a separate pretreatment system could be installed (e.g., liquid-phase activated carbon adsorption) to reduce the constituent concentrations below the TCLP threshold values. If the leachate or condensate then passes the TCLP, further treatment (e.g., burning in an enclosed flare) would not be subject to the RCRA air emission or treatment rules. The pretreatment system, however, would still be subject to the applicable TSD treatment

standards.

4.3 RCRA Subtitle D Air Pathway ARARs

Pursuant to the requirements of Subpart C of 40 CFR Part 258 (§258.23), owners or operators of all new and existing municipal solid waste landfills (MSWLFs) must monitor and control for the possible explosive buildup of CH₄ gas within buildings. This is accomplished by ensuring the following:

- (1) The concentration of CH₄ gas generated by the facility does not exceed 25 percent of the lower explosive limit for CH₄ in facility structures (excluding gas control or recovery system components); and
- (2) The concentration of CH₄ gas does not exceed the LEL for CH₄ at the facility property boundary.

The owners or operators of all MSWLF units must also implement a routine CH₄ monitoring program to ensure that the standards set above are met. The frequency and type of CH₄ monitoring system must be based on site-specific soil conditions, hydrogeologic conditions, and the location of facility structures and the property boundaries.

If CH₄ is detected exceeding the levels stated above, immediate action is required to ensure protection of human health. In addition, the State Director must be notified. Within seven days of a detection exceeding either of these levels, a record of the CH₄ levels detected and a description of the steps taken to protect human health are to be placed in the landfill operating records. Within 60 days of such a detection, a remediation plan must be implemented and placed in the operating records. Further, the State Director must be notified that the plan has been implemented. The remediation plan must describe the nature and extent of the problem and the proposed remedy.

The requirements of §258.23 are considered ARARs for all Superfund co-disposal landfills. Compliance with these ARARs constitutes the impetus behind establishing a methane monitoring program regardless of whether the Clean Air Act NSPS or EG are also ARARs.

4.4 State Air Pathway ARARs

In order for a State requirement to be considered an ARAR, they must:

- Be promulgated (be legally enforceable and of general applicability),
- Be identified to EPA in a timely manner,
- Not result in an in-state ban on land disposal of hazardous waste,
- Be more stringent than Federal requirements.

Even if the State standard meets these conditions, it may be waived if it is found not to have been applied uniformly and consistently throughout the State.

State or local program requirements may apply as ARARs for LFG emissions. These requirements are generally of four types:

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- Landfill emissions control,
- Ambient air quality standards,
- Acceptable health risk levels, and
- Nuisance rules.

Landfill surface emissions control programs are designed to monitor and reduce emissions of methane from the landfill surface. These programs were originally designed to reduce the safety hazards associated with high methane concentrations near the landfill surface. Later, these programs were often designed or revised to limit emissions of NMOCs or toxic LFG constituents.

These control programs typically involve routine sampling for methane over the surface of the landfill. Where these local rules exist to reduce methane hazards, a typical trigger level for excess methane is typically 500 ppmv. In areas where the rule is designed to reduce emissions of NMOCs or toxics, a lower threshold is specified (often approximately 50 ppmv).

It should be noted that the CAA NSPS and EG also have requirements for surface monitoring of emissions to verify adequate operation of a required collection and control system (40 CFR §60.753). The surface monitoring program requires monitoring over the entire surface of the landfill at 30 meter intervals and at discrete locations where high methane concentrations may exist (e.g., surface cracks, stressed vegetation).

Another common type of State or local regulatory program that might be considered an ARAR for LFG is an ambient air quality standard. These standards may exist for one or more of the substances listed in Table 1-1 and are usually expressed as a concentration at the facility fence line. For example, the States of California, New Hampshire, Michigan, New Jersey, Ohio, Virginia, North Carolina, South Carolina, and others have ambient standards for many hazardous or toxic compounds that are common LFG constituents.

Other States have lists of toxics with a threshold ambient air concentration for each (typically derived from acute and chronic acceptable exposure levels). Multiple standards may exist for varying averaging times (e.g., maximum one hour, 24-hour, or annual average). The methods for estimating LFG emissions and exposures in Chapter 2 can assist in the determination of compliance with ARARs of this type.

Health risk standards are the last type of State or local ARAR relative to LFG. Some States have programs in place to limit health risks from air pollution sources below a certain level of significance (e.g., a 1-in-1,000,000 carcinogenic risk). Generally, these standards are associated with permitting new or modified sources. If collection and control of LFG is required, however, the control equipment may be considered a new source and is often subject to permitting requirements. In these instances, the permit applicant is often required to show that the risk posed by the new equipment is below a specified threshold.

Many State or local air quality agencies may also have one or more nuisance rules aimed at controlling air emissions from any source construed as a public nuisance. These rules were generally developed to cover odor and visibility issues; however, they may also cover emissions

of toxic substances.

5. Landfill Gas Collection and Control Systems

Control of co-disposal landfill air emissions requires both effective collection of the LFG and effective destruction of organics in the collected gas. Due to the variability of site-specific factors that affect LFG generation and collection, a wide variety of collection systems are possible. These systems may include active collection wells (both vertical and horizontal), passive collection wells, and gas interception trenches. Control systems typically used include open flares and enclosed flares. Other control systems such as internal combustion engines (ICEs) and gas turbines are used for energy recovery in the production of electric power for resale. These types of energy recovery control systems are typically used at active MSW landfills where a portion of the landfill is subject to a CERCLA remedial action. This chapter covers the general concepts of collection and control systems used at the majority of closed or abandoned landfill sites.

5.1 Landfill Gas Collection Systems

The following discussion from U.S. EPA (1991) provides an overview of gas collection techniques. In addition, Appendix E of U.S. EPA (1999b) provides a summary of the design plan requirements for all collection systems subject to the CAA NSPS or EG.

Landfill collection systems can be categorized into two basic types: active systems and passive systems. Active collection systems employ mechanical blowers or compressors to provide a pressure gradient in order to extract the LFG. Passive collection systems rely on the natural pressure gradient (i.e., internal landfill pressure created due to LFG generation) or concentration gradients to convey the LFG to the atmosphere or to a control system.

An active landfill gas collection system consists of vertically or horizontally installed landfill gas collection wells. The well is designed and constructed so as to prevent air infiltration into the well intake screen area to minimize surface atmospheric air infiltration into the landfill. At the wellhead, each well is connected to the next wellhead by a well header pipe and so on until all headers gathering pipe has been connected to all wells. If there is more than one header pipe they are finally connected to a one main large diameter pipe. This one large diameter main pipe is then connected to a knock out receiver (pot) that removes liquid water condensate. The pipe coming out of the knock out receiver is then connected to the intake pipe of the landfill gas blower or compressor. The out going pipe from the blower is then finally connected to the flare stack or candle stick burner intake.

If the collected gas is to be released directly to the atmosphere without combustion, then vertical pipes with gooseneck top are normally installed at regular intervals along each header pipe to vent landfill gas to the atmosphere. This type of landfill gas collection is known as a passive gas collection system.

Based on theoretical evaluations, well-designed active collection systems are considered the most effective means of gas collection. Generally, passive collection systems have much lower collection efficiency since they rely on natural pressure or concentration gradients as a driving force for gas flow rather than a stronger, mechanically-induced pressure gradient. A passive system, however, can be nearly equivalent in collection efficiency to an active system if the landfill design includes synthetic liners on the top, bottom, and sides of the landfill.

Active collection systems can be further categorized into two types: vertical well systems and horizontal trench systems. Both types of systems are discussed in Section 5.1.1. Passive systems are discussed in Section 5.1.2. The type of collection system employed often depends on the landfill characteristics and landfill operating practices. For example, if a landfill employs a layer-by-layer landfilling method (as compared to cell-by-cell methods), an active horizontal trench collection system may be preferred over an active vertical well collection system due to the ease of collection system installation.

5.1.1 Active Collection Systems

Active collection systems employ mechanical blowers or compressors to create a pressure gradient and extract the LFG. Active collection systems consist of two major components:

- Gas extraction wells and/or trenches and
- Gas moving equipment (e.g., piping and blowers).

Gas extraction wells may be installed in the landfill refuse or along the landfill perimeter. For a landfill that is actively accepting waste, wells are generally installed in the capped sections. Additional wells are installed as more refuse is accumulated.

The wells consist of a drilled excavation 12 to 36 in. in diameter. A 2 to 6 in. diameter pipe—polyvinyl chloride (PVC), high-density polyethylene (HDPE), stainless steel, or galvanized iron—is placed in the well, and the well is filled with 1-in. diameter or larger, crushed stone. The pipe is perforated in the area where gas is to be collected but solid near the surface to prevent air infiltration. A typical extraction well is shown in Figure 5-1.

In unlined landfills, gas extraction wells are usually drilled to the depth of the groundwater table or to the base of the landfill, whichever is less. In lined landfills, wells are typically drilled to only 75 percent of the landfill depth to avoid damaging the liner system. Typical well depths range from 20 to 50 feet but may exceed 100 feet. The spacing between gas extraction wells depends on the landfill characteristics (e.g., type of waste, degree of waste compaction, LFG generation rate, etc.) and the magnitude of pressure gradient applied by the blower or compressor. Typical well spacing ranges from 50 to 300 feet.

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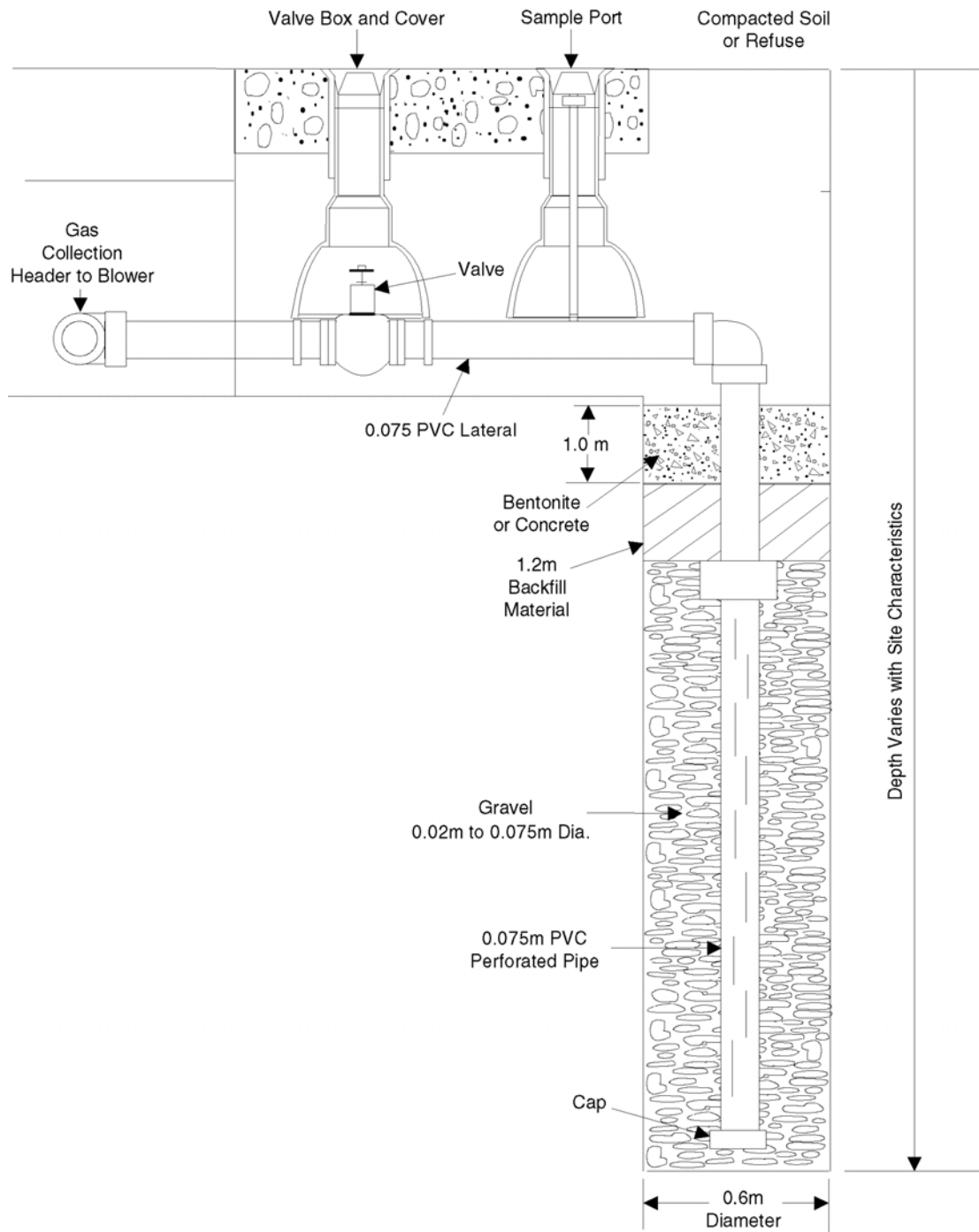


Figure 5-1. Gas Extraction Well Head Assembly.

Trenches may be installed instead of or in combination with wells to collect the LFG. The trenches can be vertical or horizontal at or near the base of the landfill. A vertical trench is illustrated in Figure 5-2. A vertical trench is constructed in much the same manner as a vertical well, except that it extends to the surface along one dimension of the landfill. Horizontal trenches are installed within a landfill cell as each layer of waste is applied. This allows for gas collection as soon as possible after gas generation begins and avoids the need for above-ground piping which can interfere with landfill maintenance equipment. A horizontal trench is illustrated in Figure 5-3.

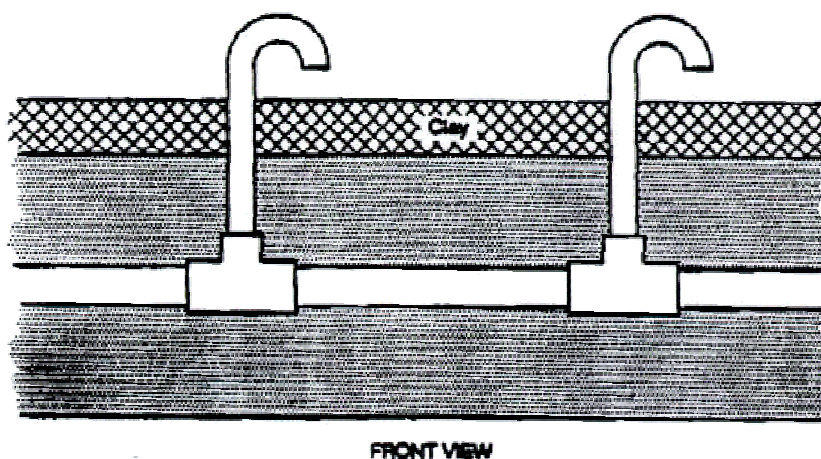


Figure 5-2. Vertical Trench for Active Collection System.

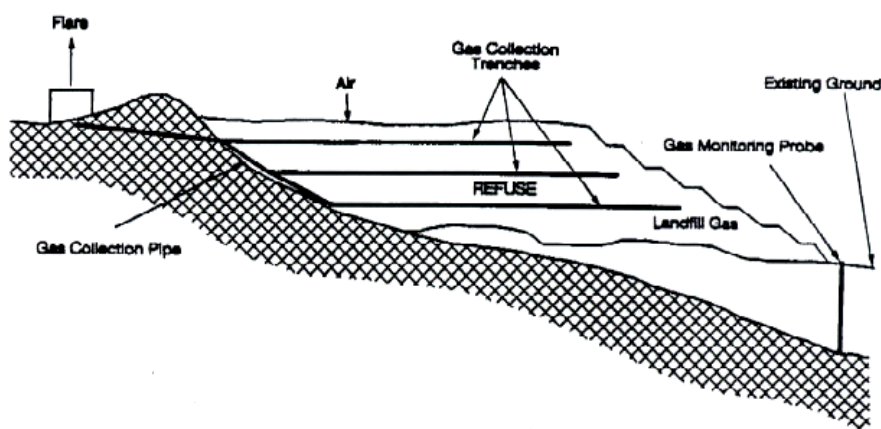


Figure 5-3. Horizontal Trench Collection System.

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A gas collection header system conveys the flow of collected LFG from the well or trench to the facility housing the blower or compressor. A typical header pipe is made of PVC or polyethylene and is 6 to 24 inches in diameter.

At SFL sites, the collected LFG is conveyed through the header system by a blower. The size and type of blower depends on total gas flow rate, total system pressure drop, and vacuum requirements. For systems requiring only a small vacuum (up to 40 inches of water), sites often use centrifugal blowers, which offer the advantage of easy throttling throughout their operating range. These blowers can accommodate total system pressure drops of up to 50 inches of water and can transport high flow rates (100 to 100,000 cfm). For lower flow rates and higher pressures, regenerative (combination of axial and centrifugal) blowers are often used.

5.1.2 Passive Collection Systems

As indicated above, passive collection systems rely solely on natural pressure or concentration gradients in the landfill to capture LFG. Like active systems, passive collection systems use extraction wells to collect LFG. The construction of passive collection wells is similar to that of active wells which is illustrated in Figure 5-1.

The well construction for passive systems is much less critical than for active systems primarily because the collection well is under positive pressure and air infiltration is not a concern. Additionally, elaborate well head assemblies are not required because monitoring and adjustment is not necessary. However, it is important that a good seal be provided around the passive well when synthetic cover liners are used. Either a boot type seal, flange type seal, concrete mooring, or other sealing technique is typically used at each well location to maintain the integrity of the synthetic liner.

5.1.3 Effectiveness of Landfill Gas Collection

The effectiveness of an active landfill gas collection system depends greatly on the design and operation of the system. From the perspective of air emission control, an effective active collection system design would include the following attributes:

- Gas moving equipment capable of handling the maximum landfill gas generation rate,
- Collection wells and trenches configured such that landfill gas is effectively collected from all areas of the landfill, and
- Design provisions for monitoring and adjusting the operation of individual extraction wells and trenches.

An effective passive landfill gas collection system would also include a collection well or trench configuration that effectively collects LFG from all areas of the landfill. The efficiency of a passive collection system would also greatly depend on good containment of the LFG. An example of good containment would be synthetic liners on the top, sides, and bottom of the landfill.

The first criteria that should be satisfied for an active system is gas moving equipment capable of handling the maximum LFG generation rate; blowers and header pipes need to be

sized to handle the maximum LFG generation rate. In addition, collection header pipes should also be sized to minimize pressure drop.

Each extraction well or trench has a zone of influence within which LFG can be effectively collected. The zone of influence of an extraction well or trench is defined as the distance from the well center to a point in the landfill where the pressure gradient applied by the blower approaches zero. The zone of influence determines the spacing between extraction wells or location of trenches since an effective collection system covers the entire area of the landfill. The zones (or radii) of influence for gas extraction wells are illustrated in Figure 5-4.

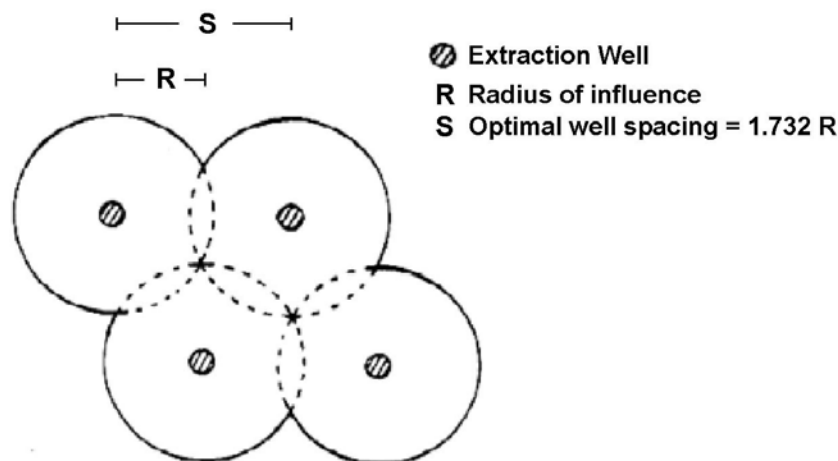


Figure 5-4. Zones of Influence for Gas Extraction Wells.

The spacing between extraction wells depends on the depth of the landfill, the magnitude of the pressure gradient applied by the blower, type of waste, degree of compaction of waste, and moisture content of gas. For perimeter extraction wells, additional variables such as the outside soil type, permeability of the soil, moisture content of the soil, and stratigraphy should be considered.

The desired method for determining effective well spacing at a specific landfill is the use of field measurement data. EPA Reference Method 2E can be used to determine the average stabilized radius of influence for both perimeter wells and interior wells, and this measured radius of influence can then be used to site wells. A good practice is to place wells along the perimeter of the landfill (but still in the refuse) no more than the perimeter radius of influence from the perimeter, and no more than two times the perimeter radius of influence apart. As shown in Figure 5-5, a helpful technique is to site the location of each well and draw a circle with radius equal to the radius of influence (perimeter radius of influence for perimeter wells and interior radius of influence for interior wells). Once the perimeter wells are sited on the landfill plot plan, the interior wells are sited at no more than two times the interior radius of influence in an orientation such that essentially all areas of the landfill are covered by the radii of influence.

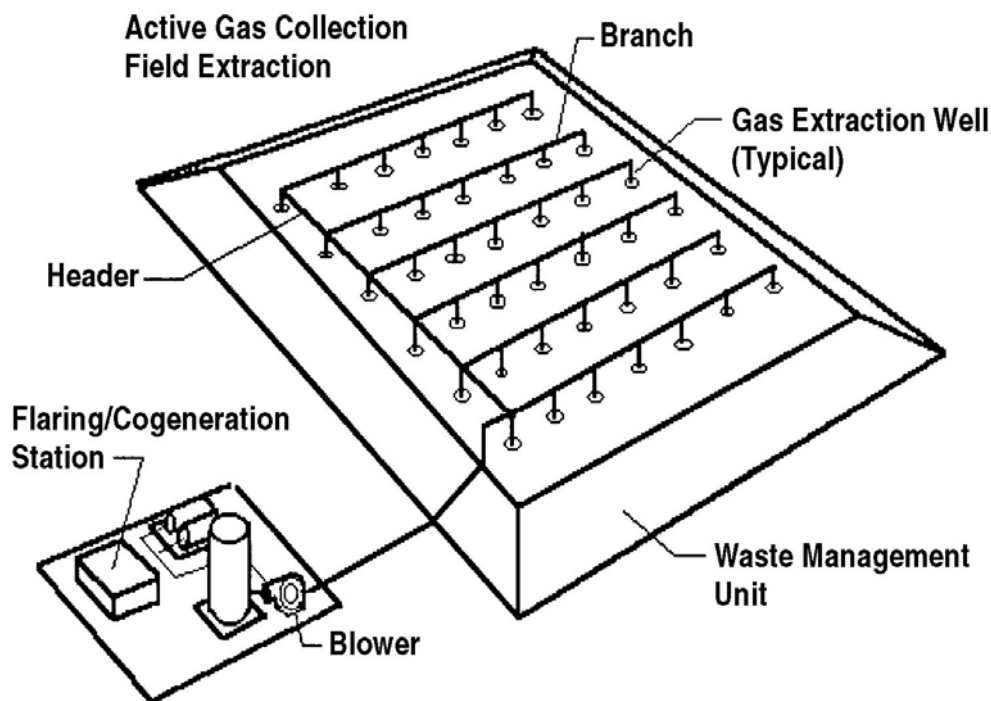


Figure 5-5. Typical Gas Control System.

In situations where field testing is not performed, the well spacing can be determined based on theoretical concepts. Understanding the behavior of LFG through the municipal landfill refuse and cover material is important in order to design the LFG collection system properly. The flow of LFG can be described by Darcy's Law, which correlates the flow of gas through porous media as a function of the gas properties (e.g., density and viscosity), the properties of the porous media (e.g., permeability of refuse and cover), and pressure gradient.

When active collection systems (both vertical and horizontal) are designed, it is also important to understand the relationship between the magnitude of vacuum applied and the degree of air infiltration into the landfill. Excessive air infiltration can kill the methanogens, which produce LFG from the municipal refuse. If excessive air infiltration continues, decomposition becomes aerobic and the internal landfill temperature can increase and possibly lead to a landfill fire. If the landfill conditions are such that air infiltration is significant (e.g., highly permeable cover and/or shallow landfill), the magnitude of vacuum applied may need to be reduced to minimize the amount of air infiltration. A direct consequence of the reduced vacuum is an increased number of wells or trenches required to achieve the same collection efficiency. Therefore, consideration of air infiltration is required in designing the active collection systems for shallow landfills. The problem of air infiltration does not exist for passive systems since passive systems rely on the natural pressure gradient (i.e., difference between atmospheric pressure and internal landfill pressure) rather than applying vacuum.

Appendix G of U.S. EPA (1991) contains detailed information useful in designing active or passive gas collection systems. U.S. EPA (1999b) provides an overview of the design plan requirements for landfills subject to the NSPS or EG. All of the EPA documents concerning MSW landfill regulatory requirements and design criteria are available for download from the EPA website at <http://www.epa.gov/ttn/atw/landfill/landflpg.html> (accessed August 2005).

5.1.4 LFG to Energy Considerations

Although it may not be required by rule or by hazard and risk assessment, decision makers may want to consider the technical and economic feasibility of using the LFG as an energy source. Using LFG as an energy source helps to reduce odors and other hazards associated with LFG emissions, and it helps prevent methane from migrating into the atmosphere and contributing to local smog and global climate change. MSW landfills are one of the largest sources of human-related CH₄ emissions. At the same time, CH₄ emissions from landfills may represent a lost opportunity to capture and use it as a significant energy resource. The LFG to energy projects are economically driven and are sensitive to customer needs, the volume of gas, and the rate at which it is generated. Once the gas is collected, it may be simply burned or flared (wasted); or be used as an alternative fuel supply for vehicles; or be used to generate electricity; or replace fossil fuels in industrial and manufacturing operations such as cement manufacturing, steel making, and greenhouse operations; or be upgraded to pipeline quality gas. The EPA's Landfill Methane Outreach Program (LMOP) is a voluntary assistance and partnership program that promotes the use of landfill gas as a renewable, green energy source. LMOP helps businesses, States, energy providers, and communities protect the environment and build a sustainable future by preventing emissions of methane through the development of landfill gas energy projects. The Web page for this program is <http://www.epa.gov/lmop/> (accessed August 2005).

5.2 Evaluating Existing Gas Collection Systems

In some cases, an active or passive gas collection system will already be in-place at a facility at the time of site discovery. For these types of situations, the existing system should be analyzed to determine if it is adequate for the purposes of collecting the majority of landfill gas and whether an active system is operated in such a way as to minimize the infiltration of ambient air and thus reduce the possibility of landfill fires. The following sections present theoretical procedures that can be used to make a screening-level determination of the adequacy of existing collection systems.

5.2.1 Assessment of Existing Active Gas Collection Systems

To determine if the operating practices for an existing active gas collection system are adequate for reducing air infiltration at the well head, the actual measured vacuum at each well can be compared with a theoretical maximum value that minimizes air infiltration. The following equations from Appendix G of U.S. EPA (1991) can be used to calculate the theoretical maximum vacuum pressure at each well. The theoretical vacuum pressure is then compared with the measured vacuum pressure. If the actual vacuum pressure for a specific well

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is greater than the theoretical value, consideration should be given to reducing the actual draft at affected wells by re-balancing the active collection system. The theoretical maximum vacuum pressure that minimizes air infiltration (P_v) is calculated by

$$P_v = P_{atm} - \left[(0.25L)(k_{cover}) + (k_{refuse})(D_{cover}) \right] \left(\frac{Q_{gen}}{A} \right) \left(\frac{0.0244}{k_{cover}} \right) \left(\frac{\mu_{air}}{k_{refuse}} \right) \quad 5-1$$

where:

- P_v = Theoretical vacuum pressure in Newtons per square meter or pascals,
- P_{atm} = Atmospheric pressure (101,325 N/m²),
- 0.25 = Assumes well depth is 75% of landfill depth,
- L = Landfill depth in meters,
- k_{cover} = Intrinsic cover permeability in square meters,
- k_{refuse} = Intrinsic refuse permeability in square meters,
- D_{cover} = Cover thickness in meters,
- Q_{gen} = Peak landfill gas generation rate in cubic meters per second,
- A = Landfill area in square meters,
- 0.0244 = Fraction of air in landfill gas assuming an allowable O₂ of 0.5%, and
- μ_{air} = Viscosity of air in Newton-seconds per square meter.

The value of P_v can be converted to units of inches water gauge (w. g.) at 60 °F by dividing P_v by 248.84. The value of the peak landfill gas generation rate (Q_{gen}) is normally determined using the LandGEM model (see Chapter 2). A typical value for the intrinsic refuse permeability (k_{refuse}) is 3.7×10^{-3} m²; and the viscosity of air (μ_{air}) is 1.8×10^{-5} N-s/m². Table 5-1 provides typical values for the permeability (k_{cover}) and thickness (D_{cover}) of three cover materials from U.S. EPA (1991).

Table 5-1. Typical Cover Permeability and Thicknesses.

Cover type	Permeability (m ²)	Thickness (m)
Synthetic	1.0×10^{-18}	7.6×10^{-4}
Clay	5.0×10^{-15}	0.61
Soil	1.0×10^{-14}	0.61

The area of the landfill (A) in Equation 5-1 can be estimated from the design capacity by

$$A = \frac{DC}{\rho_{refuse}^i L} \quad 5-2$$

where:

- A = Area of landfill in square meters,
- DC = Landfill design capacity in kilograms,
- ρ_{refuse}^i = In situ refuse bulk density in kilograms per cubic meters,

L = Landfill depth in meters.

Once the theoretical vacuum pressure is calculated using Equation 5-1 for each well, the radius of influence (R_a) of the well can be estimated from U.S. EPA (1991) by

$$\frac{P_l^2 - P_v^2}{P_v^2} = \frac{R_a^2 \ln(R_a/r) \mu_{lfg} \rho_{refuse} Q_{gen}}{DC k_{refuse} (WD/L)} \quad 5-3$$

where:

- P_l = Internal landfill pressure in Newtons per square meter,
- P_v = Well head vacuum pressure in Newtons per square meter,
- R_a = Radius of influence of well in meters,
- r = Radius of outer well (casing) in meters,
- μ_{lfg} = Landfill gas viscosity in Newton-seconds per square meter,
- ρ_{refuse} = Refuse density in kilograms per cubic meters,
- Q_{gen} = Peak landfill gas generation rate in cubic meters per second,
- DC = Landfill design capacity in kilograms,
- k_{refuse} = Intrinsic refuse permeability in square meters,
- WD = Well depth in meters,
- L = Landfill depth in meters.

The internal landfill pressure (P_l) should be measured at or near the well of interest. The value of the well vacuum pressure (P_v) is calculated by Equation 5-1. The landfill gas viscosity (μ_{lfg}) is 1.15×10^{-5} N-s/m², and a typical value for the refuse density (ρ_{refuse}) is 625 kg/m³.

Equation 5-3 can be solved interactively for the radius of influence (R_a) using an optimization algorithm such as Goal Seek found in the Microsoft Excel spreadsheet program. This is done by entering the equations for the left and right sides of Equation 5-1 within separate cells of the spreadsheet. The Goal Seek algorithm is then invoked such that the value of R_a is changed until both sides of Equation 5-1 are equal.

With a value of the radius of influence for each well, a circle representing the zone of influence of each well can be drawn to scale on a site plot plan. With these data, dead areas between zones of influence can be detected. Dead areas are treated by installing new collection wells. This may be especially important for landfills without side and bottom liners where the surrounding native soils offer relatively low resistance to pressure-driven subsurface vapor flow.

The same type of analysis as that performed above can also be done for horizontal active collection systems as well as for passive collection systems. The reader is referred to Appendix G of U.S. EPA (1991) for the appropriate equations.

The screening-level procedures detailed above are designed to provide a rough estimate of the maximum well head vacuum pressure that minimizes air infiltration and the adequacy of the existing system with regards to LFG collection. It should be noted that the value of the well vacuum pressure calculated using Equation 5-1 assumes that the depth of the well pipe is 75

percent of the depth of the landfill. This assumption is based on a depth at which any possible damage to a landfill bottom liner (if applicable) is avoided. In addition, Equation 5-1 operates under the assumption that 0.5 percent O_2 in the LFG, based on an air concentration of 2.44 percent, is the optimal value. A higher O_2 content may be acceptable (i.e., greater air infiltration) if aerobic decomposition in the upper reaches of the landfill is kept to a minimum and the increased infiltration does not dilute the CH_4 concentration below the UEL of 15 percent by volume. Excessive aerobic conditions are usually detected by an increase in the gas temperature at the well head. Gas temperatures greater than approximately 130 °F indicate that composting is occurring, which increases the possibility of landfill fires.

5.3 Landfill Gas Control Systems

There are two types of LFG control options for SFLs. The first involves destruction of the LFG constituents by combustion, and the second involves energy recovery from the combustion of the gas for the purposes of generating electricity for resale. Energy recovery techniques are used at active MSW landfills and include the use of ICEs, gas turbines, or boiler-to-steam turbine systems. Because SFLs are closed landfills in most cases, information on energy recovery systems is not included in this document.

5.3.1 Open Flares

LFG combustion devices that destroy the gas include open flares and enclosed flares. Open flares can be located at ground level or can be elevated. Although some of these flares operate without external assist (to prevent smoking), most are air-assisted or use the velocity of the gas itself to mix the gas and combustion air. Flares shall be designed for and operated with no visible emissions except for periods not to exceed a total of 5 minutes during any 2 consecutive hours. Flares shall be operated with a flame present at all times and an owner/operator has the choice of adhering to either: (A) meet the heat content specifications (greater than 300 Btu/scf if steam assisted, greater than 200 Btu/scf if unassisted) and meet the maximum tip velocity specifications (less than 60 ft/sec or up to 400 ft/sec if the LFG heat content is greater than 1,000 Btu/scf) or (B) the flare must have a diameter of 3 inches or greater, be operated without assistance, the LFG must have a hydrogen content of 8.0 percent (by volume) or greater, and the flare must not have an exit velocity less than 37.2 m/sec (122 ft/sec). 40 CFR Part 60.18 provides the control device requirements specific to the NSPS applicable to landfill owners using open flares to meet the regulatory requirements.

LFG is conveyed to the open flare through the collection header and transfer lines by one or more blowers. A knock-out drum is normally used to remove gas condensate. The LFG is usually passed through a water seal before going to the flare. This prevents possible flame flashbacks, caused when the gas flow rate to the flare is too low and the flame front pulls down into the stack. Purge gas (N_2 , CO_2 , or natural gas) also helps to prevent flashback in the flare stack caused by low gas flow rates. The total volumetric flow rate to the flame must be carefully controlled to prevent low flow flashback problems and to avoid flame instability. Figure 5-6 shows a small skid-mounted open flare next to a blower station.



Figure 5-6. Skid-Mounted Open Flare and Blower Station.

5.3.2 Enclosed Flares

Enclosed flares are located at ground level and are enclosed with fire resistant walls (shell) which extend above the top of the flame. Air is admitted in a controlled manner at the bottom of the shell. The temperature above the flame can be monitored and the offgas sampled. This type of flare is in general use at many SFLs because the inlet and combustion gases can be sampled for a determination of the percent NMOC reduction achieved. Figure 5-7 shows an enclosed ground flare and blower station, while Figure 5-8 shows a skid-mounted enclosed ground flare.



Figure 5-7. Enclosed Ground Flare and Blower Station.



Figure 5-8. Small Skid-Mounted Enclosed Ground Flare.

LFG is conveyed to the flare station through the collection header and transfer lines by one or more blowers. Purge gas is usually needed only for initial purging of the system upon start-up or during a restart after a flameout. LFG condensate is removed by a knockout drum. In some cases, LFG condensate is burned in the flare as a liquid stream injected above the burners (see Section 4.2). A water seal or flame barrier is located between the knockout drum and the flare to prevent flashbacks. The number of burner heads and their arrangement into groups for staged operation depends on the LFG flow rate and composition.

To ensure reliable ignition, pilot burners with igniter are provided. The burner heads are enclosed in an internally insulated shell that can be of several shapes, such as cylindrical, hexagonal, or rectangular. The height of the flare must be adequate for creating enough draft to supply sufficient air for smokeless combustion and for dispersion of the thermal plume. Some enclosed flares are equipped with automatic damper controls. The damper controls adjust the intake of air by opening and closing the damper near the base of the stack depending on the combustion temperature. A thermocouple located about 3 feet below the stack outlet is typically used to monitor combustion temperature. Stable combustion and efficient operation can be obtained with landfill gases that have heat contents as low as 100 to 120 Btu/scf. It should be noted that the NSPS standards prohibit the use of flares if the heat content is below 200 Btu/scf; hence supplemental fuel must be provided for flares subject to these regulations.

5.4 Carbon Adsorption Systems

Activated carbon systems are sometimes used to control NMOC emissions from ancillary treatment systems such as leachate air strippers. Activated carbon acts to adsorb the NMOC constituents on the surface area of the carbon granules; for the most part, methane passes through the carbon bed and is not adsorbed. Carbon is activated by a process that greatly

increases the surface area of the granules, thus increasing the number of adsorption sites.

Two problems exist with the use of activated carbon. First, water vapor acts as an interferent to adsorption by competing for adsorption sites. Second, the adsorption of certain organic species on activated carbon is minimal. Compounds with one or more of the following physical/chemical properties do not readily adsorb or remain adsorbed to activated carbon, especially at low vapor concentrations and high relative humidities:

- Molecular weight less than 50 g/gmol (approximate),
- Boiling point less than 20 °C,
- Index of refraction at 20 °C less than 1.40.

In addition, other compounds in the gas stream with a higher affinity for carbon adsorption will often dislodge (desorb) these compounds. These factors in combination may result in these types of compounds passing through the carbon bed quickly and, consequently, in unacceptable inhalation risks.

The following equation developed by the activated carbon manufacturer Calgon Corporation, and presented by Yaws et al. (1995), can be used to estimate the activated carbon adsorption capacity of individual organic species:

$$\log_{10} Q_i = A + B \mu_i + C \mu_i^2 + D \mu_i^3 + E \mu_i^4 + F \mu_i^5 \quad 5-4$$

where:

- Q_i = Adsorption capacity of compound i at equilibrium in cubic centimeters of liquid per 100 g of carbon,
 μ_i = Adsorption potential of i (unitless),
 A = 1.71
 B = -1.46×10^{-2}
 C = -1.65×10^{-3}
 D = -4.11×10^{-4}
 E = 3.14×10^{-5}
 F = -6.75×10^{-7}

and

$$\mu_i = \frac{T}{(V_i \Gamma_i) \log_{10}(P_i^{sat} / p_i)} \quad 5-5$$

where:

- μ_i = Adsorption potential of compound i (unitless),
 T = Temperature in Kelvins,
 V_i = Liquid molar volume of i in cubic meters per gram-mol, (= 1/density $\times$ molecular weight),
 Γ_i = Relative polarizability of compound i (unitless),
 P_i^{sat} = Vapor pressure of compound i in atmospheres,
 p_i = Partial pressure of compound i in atmospheres,

and,

$$\Gamma_i = \frac{[(n^2 - 1)(n^2 + 1)]_i}{[(n^2 - 1)(n^2 + 1)]_{n\text{-hep tan } e}} \quad 5-6$$

where:

Γ_i = Relative polarizability of compound i (unitless), and
 n = Index of refraction (unitless).

The index of refraction of the compound of interest can be found in the literature. The following sources list refractive indexes for a wide variety of substances:

- The CRC Handbook of Chemistry and Physics,
- Lange's Handbook of Chemistry,
- The Merck Index,
- Chemical catalogs (e.g., the one from Aldrich Chemical Co.), and
- MSDS datasheets (many are available on the web).

The index of refraction of n-heptane is 1.3876.

The partial pressure of a given constituent (p_i) in Equation 5-5 can be determined from its vapor concentration and the ideal gas law by

$$p_i = \frac{C_{v,i} \times R \times T}{MW_i} \quad 5-7$$

where:

$C_{v,i}$ = Vapor concentration of compound i in grams per cubic centimeter,
 R = Ideal gas constant (82.05 atm-cm³/mol-K),
 T = Temperature in Kelvins, and
 MW_i = Molecular weight of compound i in grams per mol.

An example of using the above procedures is the determination of the adsorption capacity of vinyl chloride on activated carbon at a temperature of 25 °C and an inlet concentration of 100 ppmv. Under these conditions, the adsorption capacity is calculated to be approximately 2.3 grams of vinyl chloride liquid adsorbed for every 100 grams of carbon. As can be seen, the carbon adsorption capacity of vinyl chloride is very small. For this reason, a subsequent risk evaluation would be done assuming that the vinyl chloride emissions are essentially uncontrolled.

In addition to the procedures cited above for estimating the adsorption capacity, adsorption isotherms relating the adsorption capacity as a function of the partial pressure and temperature can often be acquired from the manufacturer of the activated carbon. These isotherms and the equations given above assume a single contaminant in the vapor stream. Actual adsorption of individual contaminants in a multi-component vapor stream will be somewhat less.

5.5 Stack Sampling

Methods for assessing combustion equipment emissions (e.g., enclosed flares, boilers, ICEs, etc.) are given in Table 5-2. These include methods for such pollutants as NO_x, SO₂, CO, and NMOCs and for toxic LFG COPCs. Table 5-2 contains a column for EPA Reference Test Methods found in 40 CFR Part 60, Appendix A and a column for RCRA SW-846 Test Methods. SW-846 is a compendium of RCRA test methods titled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* and is available from the EPA Office of Solid Waste website at: <http://www.epa.gov/sw-846/> (accessed August 2005).

Table 5-2. Stack Sampling Methods for LFG Combustion Equipment.

Pollutant	EPA Reference Methods	EPA SW-846 Methods
Oxides of nitrogen (NO _x)	7 or 7E	NA ^a
Sulfur dioxide (SO ₂)	6	NA
Carbon monoxide (CO)	10 or 3C	NA
Nonmethane organic compounds (NMOCs)	25/25A/25B or 18	NA
Volatile organic compounds (VOCs)	18	0030 or 0031
Chlorinated dioxins/furans	23	0023A
Hydrogen chloride (HCl)	26	0050 or 0051
Mercury (Hg)	101A	0060

^a NA = Not applicable.

In some respects, the SW-846 test methods may be more suitable for high temperature combustion sources such as enclosed flares. EPA Reference Methods 25 or 18, however, must be used to determine compliance with the 98 percent by weight NMOC reduction requirements or the 20 ppmv NMOC concentration requirements of the NSPS or EG.

Mercury-bearing material has been placed in municipal landfills from a wide array of sources including fluorescent lights, batteries, electrical switches, thermometers, and general waste. Despite its known volatility, persistence, and toxicity in the environment, the fate of mercury (Hg) in landfills has not been widely studied. Landfills are designed to reduce waste through generation of methane by anaerobic bacteria. This suggests the possibility that these degradation systems might also serve as bioreactors capable of generating methylated Hg compounds. The toxicity of these Hg compounds indicates the need to determine if they are emitted in municipal landfill gas (LFG).

Mercury is a highly toxic heavy metal that exists primarily in three forms: elemental Hg, inorganic Hg compounds (e.g., mercuric chloride), and organic Hg compounds (e.g., methyl and dimethyl mercury). People are most likely to be exposed to Hg through the consumption of fish or seafood. Mercury is most likely to be present in fish tissue as methyl mercury, which happens to be the most toxic form of Hg to humans. However, concern over air emissions is not limited to methyl mercury because other forms of Hg can be converted to methyl mercury in the

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environment through methylation.

In the initial development of emissions factors for constituents of LFG, the U.S. EPA published a default total Hg concentration in AP-42 equivalent to 292 parts per trillion (ppt), with no data on individual Hg species. At this concentration, Hg emissions from landfills are extremely low, if not negligible. However, in the late 1990s, a study conducted by Lindberg et al. at a landfill in Florida suggested that levels of total Hg in LFG might be several times higher than EPA default values, though still much lower than other common landfill trace constituents. This study was also perhaps the first to positively identify the more toxic organic mercury compounds methyl and dimethyl mercury in LFG.

EPA researchers measured Hg inside the landfill gas vents at concentrations ranging from a few hundred to several thousand nanograms per cubic meter. Although the higher end is equivalent to levels emitted by a coal-fired utility plant, the volume of gas emitted at a landfill is considerably lower. Consequently, the overall contribution of Hg to the atmosphere from municipal landfill gas is small in comparison to coal-fired power plants. However, there may be important contributions of Hg to the atmosphere in the immediate local area near the landfill.

During the NESHAP rule making, EPA found insufficient data to adequately characterize the concentrations of Hg in landfill gas or determine their significance. Based on the available information, it was concluded that the Maximum Achievable Control Technology (MACT) floor for Hg is no emissions reductions because there are no alternatives above that floor. The NESHAP standard does not require a reduction in Hg emissions. Although the NESHAP does not require Hg emissions reductions, the risks and hazards associated with mercury continues to be a sensitive subject with the ecological community.

6. Illustrative Case Studies

The procedures and methodologies described within this guidance were implemented at three separate sites, and a summary of each case study is presented herein. These case studies were not intended to provide a comprehensive site analysis or complete risk assessment. Case studies were developed for:

- Somersworth Sanitary Landfill Superfund Site, City of Somersworth in Strafford County, New Hampshire. EPA-600/R-05/142.
- Rose Hill Regional Landfill Superfund Site is located within the town of South Kingstown, Rhode Island in the Village of Peace Dale. EPA-600/R-05/141.
- Bush Valley Landfill Superfund Site is located in Harford County, Maryland, one mile from the town of Abingdon. EPA-600/R-05/143.

The parameters of the three case studies are summarized in Table 6-1.

Table 6-1. Comparisons of the Case Studies.

Parameter	Somersworth	Rosehill	Bush Valley
Capacity, Mg	300,000	199,692	303,128
Size, acres	26	28	16
Year open	1958	1967	1974
Size of grid, m ²	900	900	900
Number of grids	179	190	108
Number of COPCs	11	10	9
Number of parcel per Wilcoxon analysis	1	2	4
COPC with highest LFG concentration	Toluene	Toluene	Vinyl chloride
COPC with largest facility boundary ambient air concentration	Xylene	Xylene	Xylene
COPC exceeding $R=10^6$, HI = 1	None	None	Trichloroethylene

The example case studies are published as standalone documents for reference by the practitioner. They are available for viewing or downloading from EPA's Hazardous Waste Cleanup Information (CLU-IN) web site at <http://clu.in.org> (accessed August 2005). Hard copies are available from:

National Technical Information Service
5285 Port Royal Road

Springfield, VA 22161

Telephone: (703) 605-6000, (800) 553-6847 (U.S. only)

6.1 Summary of the Somersworth Sanitary Landfill Superfund Site

Two independent studies were conducted to characterize the landfill emissions being generated by the Somersworth Sanitary landfill.

The two studies used inherently different methods for determining LFG emissions. Study 1 utilized both above and below grade LFG analyses, whereas, Study 2 exclusively used above grade ambient analyses. Study 1 utilized whole air broad spectrum ambient sampling and below grade LFG sampling (i.e., Summa sampling). The below grade sample locations were chosen after an extensive surface survey, using field instrumentation, was completed. In comparison, Study 2 used ground-based optical remote sensing to quantify the LFG emissions and to calculate emission fluxes. Radial plume mapping was used to detect potential hot spots. Vertical scans were conducted to determine mass flux emissions for speciated organic compounds using OP-FTIR. Study 1 relied on fate and transport models for derivation of the LFG emission fluxes. Study 2 used an algorithm that integrated the measured COPC concentrations using real time wind speed to estimate the gas emission fluxes.

The Somersworth Sanitary Landfill Superfund Site (the “Site”) is located 1 mi southwest of the center of the City of Somersworth in Strafford County, New Hampshire. The Site includes an approximately 26 acre waste disposal area. The City owns the entire landfill area and much of the adjacent wetlands northwest of the former landfill. The landfill was operated by the City from the mid 1930's until 1981 when the City began taking wastes to a regional incinerator. With the cessation of land fill operations, the City installed four ground water monitoring wells near the Site's northern and western boundaries. Samples taken from these wells indicated the presence of VOC contamination. As a result of this and subsequent investigations, the landfill was placed on the NPL on September 8, 1983. Approximately ten acres of the eastern portion of the landfill have been reclaimed by the City for recreational facilities; tennis and basketball courts, ball fields, and a playground. Numerous soil gas monitoring wells have been installed and are routinely monitored around the extent of the landfill. The majority of these wells are located along the borders immediately adjacent to residential development. From previous studies there is an indication that the groundwater flows northwesterly towards the Peter's Marsh Brook, and it surfaces to the brook and adjacent wetlands.

Based upon the results of the Remedial Investigation and the alternatives presented in the feasibility study, EPA issued a Record of Decision (ROD) on June 24, 1991 documenting the selection of an innovative technology to remediate groundwater at the site. This technology uses elemental iron in a permeable reactive “wall” which treats contaminated groundwater as it flows through it. A key element of this remedy is the use of a permeable landfill cover to allow precipitation to flush contamination through the waste. The contaminants are treated as the groundwater passes through the wall. Existing records indicated that LFG was being generated, so it was decided to use this site to illustrate this document.

6.1.1 Somersworth - Study One

Field activities for the Somersworth site were conducted in July 2002. Site activities included debriefing interested parties and stake holders, screening landfill surface, reducing screening data, determining “hot spots” and homogeneity, sampling landfill soil gas, sampling passive vent gas, sampling perimeter well gas, and sampling ambient air.

To assist with the field activities a 30 m by 30 m sampling grid was developed across the extent of the landfill area prior to the field activities. This sampling grid was developed to include the entire landfill boundary area and to extend 30 m beyond that boundary area. Each node (the intersection of the grid lines shown in Figure 6-1) of this grid was then numbered, forming a serpentine sampling pathway across the grid, and 179 monitoring and potential sampling locations were identified. The grid was superimposed on an aerial photograph (see Figure 6-1) in order to visualize the node locations and to establish where the monitoring and sampling efforts would begin.

The screening analysis procedures included taking measurements for NMOCs using a PID and for CH₄ using a FID. The PID and FID were calibrated to using certifiable zero air and 5 and 20 ppm gases. Both detectors were held no more than one inch above the ground while measurements were being made. Readings were taken for approximately one minute and the average value, excluding the extreme highs and lows, was recorded. In conducting the serpentine walk across the site, an effort was made to identify areas containing cracks and gaps in the landfill cover; and, to the extent possible, measurements were also made at these locations. Ninety seven percent of the targeted data was collected and validated. All predetermined sampling locations were not accessible due to a variety of reasons, ranging from being located on private property to being inaccessible because of extreme overgrowth or being in a waterway or roadway.

The screening data were used for two analyses. The first was for a hot spot analysis. This was done by importing the measured NMOC and CH₄ screening data set into a graphical contouring software package (Surfer) to produce concentration contours, which were layered over an aerial photograph of the site. This allowed for a visual determination of where the higher concentrations were recorded during the screening analysis. This method also allowed data to be divided into two data sets based on the contours derived from these data. This population division was used as part of the homogeneity determinations, which was the second analysis. This was done through statistical means by using the Wilcoxon Rank Sum statistical method. This method determines whether two data sets are statistically similar (i.e., homogeneous). If the two sets are determined to be similar, then the two populations are determined to be one nearly homogeneous area. If the two data sets are determined not to be statistically similar, then the two sets are said to be two non-homogeneous areas.

Based on the data analysis conducted, it was determined that the site is one nearly homogeneous area. It was determined that six LFG samples would be collected for demonstration purposes. The LFG samples were collected at the locations that had the highest recorded readings for CH₄ gas. It should be noted that due to the absence of detectable NMOC concentrations during the screening analysis it was determined that CH₄ gas concentrations would be used to determine further sampling strategies.

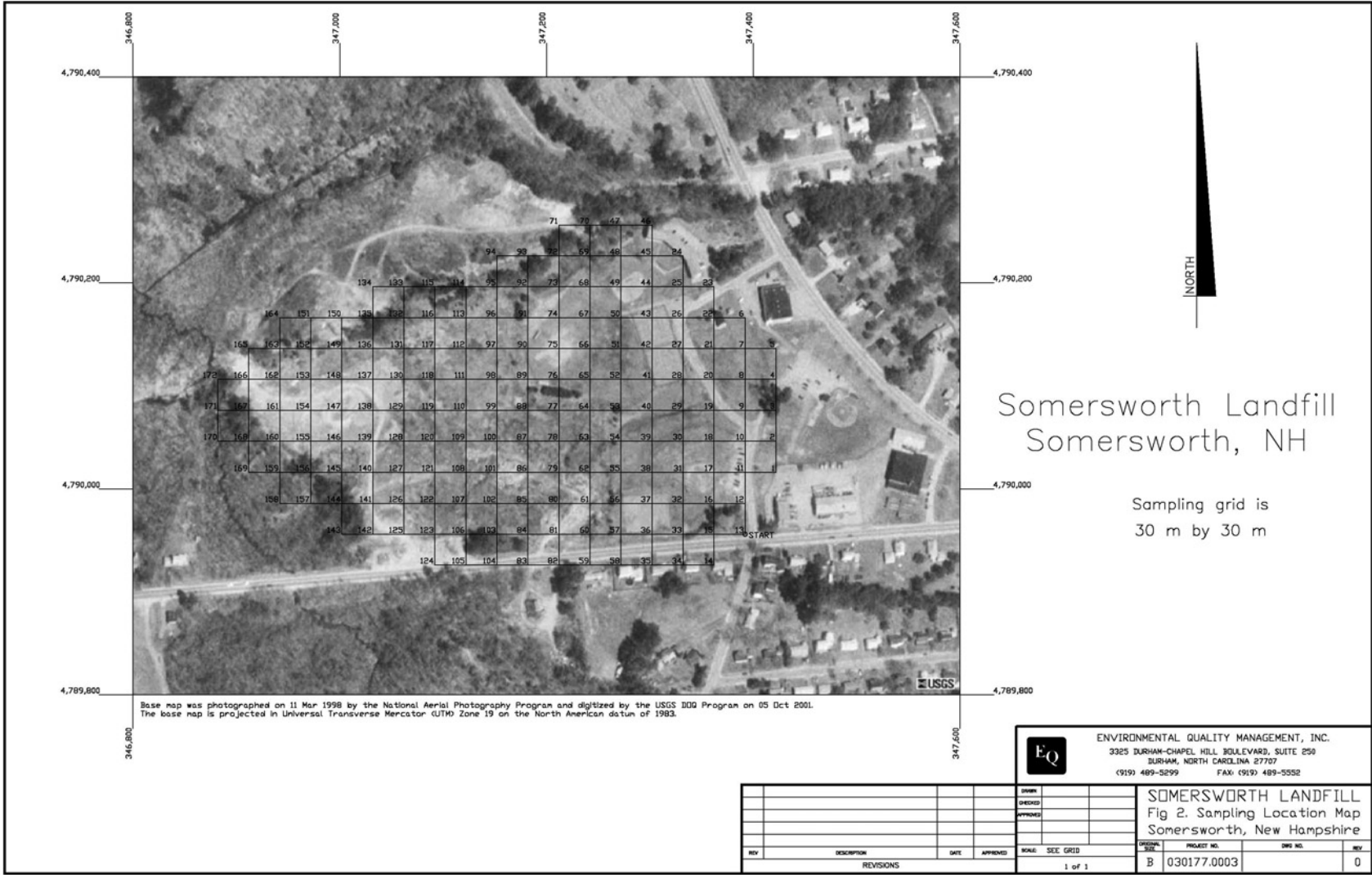


Figure 6-1. Somersworth Sampling Grid.

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Sampling was conducted using a slam-bar to drive a sampling hole through the landfill cover to approximately 5 feet below grade. A sampling probe was inserted into the landfill area, and the hole was sealed around the probe to minimize ambient air in-leakage. Additional field instrumentation was used to measure fixed gases (CO₂, N₂, and O₂) at each of the designated sampling locations. The fixed gas concentration values were used to verify that LFG was being collected. As part of this demonstration, LFG samples were collected for the COPC via evacuated Summa Canister, which were sent to an off-site commercial laboratory for analysis using EPA Method TO-15. The concentration results were validated, and the 90th percentile concentrations were determined for 11 COPCs. Table 6-2 presents the COPCs that were quantified.

Table 6-2. Somersworth COPCs that were Quantified.

COPCs	Landfill Gas Concentration 90 th Percentile	
	(ppmv)	(µg/m ³)
NMOC	2380	1.19×10 ⁶
1,1-Dichloroethene	0.00152	6.07
Benzene	0.244	7.93×10 ²
Chlorobenzene	0.0208	9.78×10 ²
Chloroethane	0.408	1.09×10 ³
1,4-Dichlorobenzene	0.4288	2.62×10 ³
Methylene Chloride	0.236	8.33×10 ²
Toluene	1.348	5.16×10 ²
Trichloroethene	0.01428	77.8
Vinyl Chloride	1.22	3.17×10 ³
m, p-Xylene	2.14	9.44×10 ³
o-Xylene	0.72	3.17×10 ³

LFG emission rates for each COPC were estimated using the LandGEM model. Figure 6-2 shows an example output file for NMOC emissions from the LandGEM model. Figure 6-3 shows the emission rate data for NMOC versus time. Table 6-3 provides the emission rates estimated for each COPC.

The next step in characterizing the emissions of LFG was to evaluate the ambient impact of each of the COPs. For this analysis, it is necessary to use an atmospheric dispersion model. For demonstration purposes SCREEN3 was used to provide a screening level assessment, and the model was configured as if the landfill was a rectangular area source. The landfill was modeled by using a unit emission rate of 1 g/s to provide a maximum 1-h concentration. Because the landfill was modeled on a unity basis, the emission rates generated from the LandGEM model were multiplied by the unity-derived concentration factor to determine the 1-h maximum concentrations for each COPC. To convert these maximum hourly concentra-

Model Parameters			
Lo : 170.00 m ³ / Mg ***** User Mode Selection *****			
k : 0.0500 1/yr ***** User Mode Selection *****			
NMOC : 2380.00 ppmv ***** User Mode Selection *****			
Methane : 58.0000 % volume			
Carbon Dioxide : 42.0000 % volume			
Landfill Parameters			
Landfill type : Co-Disposal			
Year Opened : 1958 Current Year : 2003 Closure Year: 2003			
Capacity : 300000 Mg			
Average Acceptance Rate Required from			
Current Year to Closure Year : 0.00 Mg/year			
Model Results			
Year	Refuse In Place (Mg)	NMOC Emission Rate	
		(Mg/yr)	(Cubic m/yr)
1959	1.304E+04	1.631E+00	4.549E+02
1960	2.609E+04	3.182E+00	8.877E+02
1961	3.913E+04	4.658E+00	1.299E+03
1962	5.217E+04	6.061E+00	1.691E+03
1963	6.522E+04	7.396E+00	2.063E+03
1964	7.826E+04	8.666E+00	2.418E+03
1965	9.130E+04	9.874E+00	2.755E+03
1966	1.043E+05	1.102E+01	3.075E+03
1967	1.174E+05	1.212E+01	3.380E+03
1968	1.304E+05	1.316E+01	3.670E+03
1969	1.435E+05	1.415E+01	3.946E+03
1970	1.565E+05	1.509E+01	4.209E+03
1971	1.696E+05	1.598E+01	4.459E+03
1972	1.826E+05	1.683E+01	4.696E+03
1973	1.957E+05	1.764E+01	4.922E+03
1974	2.087E+05	1.841E+01	5.137E+03
1975	2.217E+05	1.915E+01	5.341E+03
1976	2.348E+05	1.984E+01	5.536E+03
1977	2.478E+05	2.051E+01	5.721E+03
1978	2.609E+05	2.114E+01	5.897E+03
1979	2.739E+05	2.174E+01	6.064E+03
1980	2.870E+05	2.231E+01	6.223E+03
1981	3.000E+05	2.285E+01	6.375E+03
1982	3.000E+05	2.174E+01	6.064E+03
1983	3.000E+05	2.068E+01	5.768E+03
.	.	.	.
.	.	.	.
.	.	.	.
2001	3.000E+05	8.406E+00	2.345E+03
2002	3.000E+05	7.996E+00	2.231E+03
2003	3.000E+05	7.606E+00	2.122E+03
.	.	.	.
.	.	.	.
.	.	.	.
2200	3.000E+05	4.012E-04	1.119E-01
2201	3.000E+05	3.816E-04	1.065E-01
2202	3.000E+05	3.630E-04	1.013E-01

Figure 6-2. Somersworth - Example LandGEM Model Run Output.

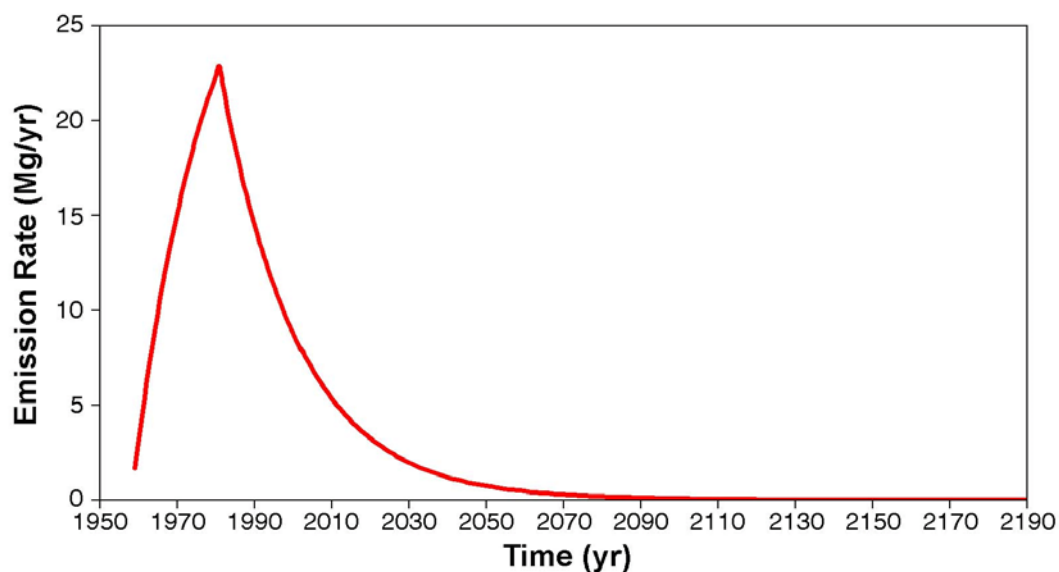


Figure 6-3. Somersworth NMOC Emission Rates versus Time.

Table 6-3. Somersworth - Emission Rates for COPCs.

COPCs	2002 Emission Rates (Mg/yr)
NMOC	7.996
1,1-Dichloroethene	5.744×10^{-6}
Benzene	7.431×10^{-4}
Chlorobenzene	9.127×10^{-5}
Chloroethane	1.026×10^{-3}
1,4-Dichlorobenzene	2.457×10^{-3}
Methylene Chloride	7.814×10^{-4}
Toluene	4.842×10^{-3}
Trichloroethene	7.314×10^{-5}
Vinyl Chloride	2.973×10^{-3}
m, p -Xylene	8.857×10^{-3}
o-Xylene	2.980×10^{-3}

tions to a representative annual concentration all derived 1-h concentrations were multiplied by the appropriate correction factor of 0.08. Table 6-4 provides the maximum annual concentrations for each COPC.

Table 6-4. Somersworth - Maximum Annual Concentrations of COPCs.

COPC	Maximum Annual Fence Line Concentration	
	(ppmv)	($\mu\text{g}/\text{m}^3$)
NMOC	4.14×10^{-2}	20.69
1,1-Dichloroethene	3.72×10^{-2}	1.486×10^{-5}
Benzene	5.92×10^{-7}	1.922×10^{-3}
Chlorobenzene	5.02×10^{-8}	2.361×10^{-4}
Chloroethane	9.89×10^{-7}	2.654×10^{-3}
1,4-Dichlorobenzene	1.04×10^{-6}	6.356×10^{-3}
Methylene Chloride	5.72×10^{-7}	2.021×10^{-3}
Toluene	3.27×10^{-6}	1.253×10^{-2}
Trichloroethene	3.47×10^{-8}	1.892×10^{-4}
Vinyl Chloride	2.96×10^{-6}	7.691×10^{-3}
m, p -Xylene	5.20×10^{-6}	2.291×10^{-2}
o-Xylene	1.75×10^{-6}	7.709×10^{-3}

These predicted ambient air concentrations were then compared to the target concentrations presented in Table 6-5, which also identifies target media concentrations corresponding to risk/hazard based concentrations for ambient air in residential settings. The target concentrations were derived using Equation 2-8 and the appropriate toxicity factors. The New Hampshire ambient air toxic standards are also displayed for comparative purposes. Only air concentrations that satisfy the prescribed cancer risk level and the target hazard index are included in Table 6-5. It would appear that the emissions from this site are below those that would be considered a health hazard.

6.1.2 Somersworth Study Two

The second study (Study 2) was conducted in September and October 2002 in which the emissions from the landfill were measured using an OP-FTIR spectrometer (U.S. EPA, 2004). This study involved a technique which uses ORS radial plume mapping techniques to evaluate emissions. The focus of this study was to characterize the emissions of CH_4 and hazardous air pollutants. Concentrations were measured for each compound and fluxes were calculated for each compound detected.

In reviewing the two studies it appears that the relative concentration contours generated via the field survey in Study 1 and OP-FTIR in Study 2, produce very similar concentration gradients and relative CH_4 hot spot locations. Table 6-6 shows a comparison of the hot spot locations identified from each study and gives their relative range of values within these areas. The measurement techniques do not differentiate between background levels and those emitted by the landfill. The CH_4 is presumed to be emitted by the landfill. The studies were completed independently and meteorological conditions are known to have been different. Study 1 was

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more windy than Study 2. Rainfall occurred two days prior to Study 1 and six days prior to Study 2. The significance of the differences is unknown.

Table 6-5. Somersworth Risk Analysis.

CAS No.	Chemical	Basis of Target Concentration	Target Ambient Air Concentration to Satisfy Both the Prescribed Risk Level and the Target Hazard Index ($R=10^{-6}$, $HI=1$) C_{target} ($\mu\text{g}/\text{m}^3$)		NH Regulated Toxic Air Pollutant Annual Ambient Limits ($\mu\text{g}/\text{m}^3$)	Total Ambient Air Concentrations ($\mu\text{g}/\text{m}^3$)
			Cancer	Noncancer		
75354	1,1-Dichloroethylene	NC ^a		$2.1 \times 10^{+2}$	67	1.5×10^{-5}
71432	Benzene	C ^b	0.25	0.31	3.80	1.9×10^{-3}
108907	Chlorobenzene	NC		62.	154	2.4×10^{-4}
75003	Chloroethane (ethyl chloride)	C	2.3	$1.0 \times 10^{+4}$	10,000	2.7×10^{-3}
106467	1,4-Dichlorobenzene	C	31.	$8.4 \times 10^{+2}$	800	6.4×10^{-3}
75092	Methylene chloride	C	4.1	$3.1 \times 10^{+3}$	414	2.0×10^{-3}
108883	Toluene	NC		$4.0 \times 10^{+2}$	400	1.3×10^{-2}
79016	Trichloroethylene	C	1.7×10^{-2}	37.	640	1.9×10^{-4}
75014	Vinyl chloride (chloroethene)	C	0.11	$1.0 \times 10^{+2}$	100	7.7×10^{-3}
108383	m, p-Xylene	NC		$1.1 \times 10^{+2}$	1033	2.3×10^{-2}
95476	o-Xylene	NC		$1.1 \times 10^{+2}$	1033	7.7×10^{-3}

^a NC = noncancer risk.

^b C=cancer risk.

Table 6-6. Somersworth - Comparison of CH₄ Concentrations by Study Method.

Location	Field Instrument ppmv	OP-FTIR ppmv
Southeast Corner Baseball Field	0.5 to 1.5	0.5 to 6.5
Tennis Court Area	0.5 to 8.0	1.0 to 1.5
Open Field North of Infiltration Gallery	0.5 to 3.0	0.5 to 2.5
Passive Vents (Light Pole Borings)	84 to 515	NA

No NMOC was detected by the FTIR unit at or above instrument detection limits, and Study 1 confirmed this finding via several methods. Study 1 found no detectable concentrations of NMOC above the landfill cover during the grid survey. Additionally, the ambient whole air samples collected at or near the CH₄ hot spots were below the analytical detection limits for all compounds except acetone and methylene chloride (two common laboratory contaminants). Lastly, Study 1 collected LFG data from below the landfill cover as part of the study technique, and the analysis of these data and subsequent modeling runs with LandGEM and SCREEN3 produced emission results that were well below the allowable detection of the OP-FTIR method and PID instrumentation.

6.2 Summary of the Rose Hill Regional Landfill Superfund Site

The Rose Hill Regional Landfill (Regional Landfill) is located within the town of South Kingstown, Rhode Island in the village of Peace Dale. The facility is composed of three separate, inactive, disposal areas, including the solid waste landfill, a bulky waste disposal area, and a sewage sludge landfill. These areas have been covered with soil and graded, and currently support vegetative cover. An active transfer station is located on site where municipal refuse is unloaded from the refuse collection trucks and transferred to trucks that haul the refuse offsite to a separate landfill facility owned and operated by the State of Rhode Island. Residential development has occurred along Broad Rock Road, 1200 feet east of the site. There has also been considerable development along Rose Hill Road to the north of the site. A golf course and clubhouse have been constructed on the west side of Rose Hill Road, immediately opposite the facility and to the north of an active sand and gravel operation.

The Rose Hill Regional Landfill, which began operation in 1967, is located in an abandoned gravel quarry. The Regional Landfill operated as a municipal disposal facility for the towns of South Kingstown and Narragansett. Industrial waste, however, was also accepted at the facility during its years of operation. In October 1983, the Regional Landfill reached its State permitted maximum capacity and ceased active land filling operations. The solid waste landfill located in the western portion of the site covers approximately 28 acres, and it operated from 1967 until 1982. The depth of the solid waste landfill varied, but it reportedly extended to bedrock in some places. Refuse was reportedly deposited in areas at, above, and below the water table. From 1977 to 1982, between 10 and 14 feet of solid waste was deposited. Boring logs indicate that bedrock was encountered at 31.3 feet on the west side of the site along Rose Hill Road. From a seismic survey it appears that the depth to bedrock along the south of the solid waste landfill is between 29 to 32 feet below ground surface. Upon closure, the solid waste landfill was covered with 0.5 to 2 feet of sandy soil and subsoil and seeded.

On-site groundwater monitoring wells contain several VOCs including dichloroethane, chloroethane, vinyl chloride, benzene, and xylenes, as well as some heavy metals. Visual observations indicate that Mitchell Brook, an unnamed brook, and the Saugatucket River are impacted by contaminated run-off from the site. Early investigations determined that landfill gases were migrating laterally off-site in the vicinity of some residential properties. Three private wells adjacent to the site are contaminated with low levels of organic compounds, as are on-site soils. The site is not completely fenced, making it possible for people to come into direct contact with the landfill materials on-site. EPA investigations during the winter and spring of

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1993 indicated gas migration from the landfill to nearby residences. In response to this information, the Town of South Kingstown installed gas alarms in the residences and relocated one residence.

The first operable unit remedy consists of the following components: (1) consolidate the bulky waste area landfill onto the solid waste area landfill; (2) collect and manage leachate and waters collected from run-off and de-watering operations during the excavation and consolidation of the bulky waste area; (3) apply a protective cover (hazardous waste cap) to the solid waste area landfill; (4) assess, collect and treat landfill gases via an enclosed flare; (5) inspect and monitor the integrity and performance of the cap over time; (6) monitor groundwater, surface water, leachate emergence, and LFG emissions over the duration of the remedial action; (7) implement deed restrictions (in the form of easements and covenants) on groundwater and land use to prevent access onto portions of the site where remediation activities warrant this restriction; (8) provide data to assess the need for taking any further response actions after the cap is in place and functional; (9) perform appropriate operation and maintenance of the remedy; and (10) plan for and conduct statutory 5-year reviews to ensure protectiveness. The State, with assistance from EPA and the two towns, will prepare and expect to release the bid package(s) and associated contract document(s) during the winter of 2004-2005. Actual construction of the remedy is planned to start during the early summer of 2005 and may take upwards of two years to complete.

6.2.1 Rose Hill - Using the Procedure of Screening with Probes Placed Just Below the Cover

For the reasons described above, it was determined that this site could be used to illustrate the screening and just-below-the-cover methods and procedures described earlier in this document. Field activities were conducted at the Landfill from July 22, 2002, through July 25, 2002. Field activities included landfill surface screening analysis, screening data reduction, hot spot and homogeneity determinations, landfill soil gas sampling, passive vent gas sampling, perimeter well gas sampling, and ambient air sampling.

Prior to arrival at the site, the U.S. EPA RPM notified the immediate surrounding residences and businesses that an assessment was to be conducted on and around the landfill area. This was performed as part of a public relation effort to notify the public and address any concerns prior to the activities taking place.

To assist with the field activities, a 30 m by 30 m sampling grid was developed across the extent of the landfill area prior to the field activities. This sampling grid was developed to include the entire extent of the landfill boundary area and to extend 30 m beyond it. The nodes of this grid were then numbered, forming a serpentine sampling pathway across the grid. Thus, a total of 190 predetermined sampling nodes comprised the sampling grid layout developed for this site. A reference point was identified using an identifiable landmark on the site to locate the starting point. Figure 6-4 shows the grid and pathway used for the screening analysis.



Figure 6-4. Rose Hill - Screening Sampling Grid.

6.2.2 Landfill Surface Screening Analysis

Once on site, the reference point was visually located, and using a handheld global positioning system (GPS), the starting point (node No. 1) was located to begin the screening analysis. The screening analysis included measurements for NMOCs, using a PID and for CH₄ using a FID. Both detectors were held no more than 1 in. above the ground while measurements were being made. It should be noted that the field instrumentation was very sensitive and drifted quite significantly due to gusts of wind across the landfill cover. Readings were taken for approximately 1 min, and the average values, excluding the extreme highs and lows, were recorded.

While conducting the serpentine walk across the site, an effort was made to identify areas containing cracks and gaps in the landfill cover, and measurements were made at these locations to the extent possible. All predetermined sampling nodes were not accessible due to a variety of reasons, ranging from being located on private property to inaccessible because of extreme overgrowth or being in a roadway or streambed. An attempt was made to collect a reading at each node, with measurements being collected not more than 10 m from it. If access within an acceptable range was not possible, a replicate reading was made at the next accessible node. These replicate readings were intended to provide additional information for Quality Assurance and Quality Control (QA/QC) purposes and were not intended to back fill missing data due to inaccessible areas. Duplicate readings were also taken at predefined locations as part of QA/QC efforts. These predetermined locations were selected based on a random number generator. All screening data were recorded on field log data collection forms along with any field notes relevant to this specific location. There was 89 percent data collection efficiency. Table 6-7 illustrates the screening sample results for the first 29 grid locations.

The screening data collected were used for two analyses. The first was for a hot spot analysis. This was accomplished by importing the screening data set into a graphical contouring software package (Surfer) to produce concentration contours, which were layered over an aerial photograph of the site. This allowed a visual determination of where the higher concentrations were recorded during the screening analysis. This also allowed the data to be divided into two sets based on the contours derived from these data. This population division was used as part of the homogeneity determinations. Figures 6-5 and 6-6 show the concentration contours for both NMOC and CH₄, respectively.

The second analysis provided a determination of the homogeneity of the site, which was done using the Wilcoxon Rank Sum statistical method. This method determines whether two data sets are statistically similar (i.e., homogeneous). If the two sets are determined to be similar, then the two populations are determined to be one nearly homogeneous area. If the two data sets are determined not to be statistically similar, then the two sets are said to be two non-homogeneous areas. To accomplish this task, the hot spot analysis was used to determine if there appeared to be two distinct population sets. For this site it was shown that there existed two nearly homogeneous areas.

Sampling activities included sampling landfill soil gas, passive vent gas, perimeter well gas, and ambient air. Each of these sampling methods will be discussed further in the following sections.

Table 6-7. Rose Hill Screening Sample Results (Partial)

Node No.	Sample ID No.	Actual UTM Coordinates		NMOC Conc. (ppm)	CH ₄ Conc. (ppm)
		Easting	Northing		
1	LFSG-02-072202- R- 001	291648	4593806	0.20	ND ^a
2	LFSG-02-072202- R- 002	291659	4593806	0.43	ND
3	LFSG-02-072202- R- 003	291686	4593802	0.20	ND
4	LFSG-02-072202- R- 004	291719	4593807	0.20	ND
5	LFSG-02-072202- R- 005	291742	4593813	0.20	ND
6	LFSG-02-072202- R- 006	291773	4593838	ND	ND
7	LFSG-02-072202- R- 007	291744	4593836	0.20	ND
8	LFSG-02-072202- R- 008	291714	4593835	0.20	1.00
9	LFSG-02-072202- R- 009	291683	4593833	1.80	ND
10	LFSG-02-072202- R- 010	291656	4593829	0.40	ND
11	LFSG-02-072202- R- 011	291645	4593834	ND	ND
12	LFSG-02-072202- D- 001	NA ^b	NA	NA	NA
13	LFSG-02-072202- D- 002	NA	NA	NA	NA
14	LFSG-02-072202- R- 012	291634	4593867	ND	ND
15	LFSG-02-072202- R- 013	291657	4593862	0.30	25.00
16	LFSG-02-072202- R- 014	291684	4593866	0.60	ND
17	LFSG-02-072202- R- 015	291712	4593865	ND	ND
18	LFSG-02-072202- R- 016	291745	4593865	ND	300.00
19	LFSG-02-072202- R- 017	291778	4593862	0.26	350.00
20	LFSG-02-072202- R- 018	291803	4593861	ND	ND
21	LFSG-02-072202- R- 019	291808	4593862	ND	ND
22	LFSG-02-072202- R- 020	291782	4593896	ND	ND
23	LFSG-02-072202- R- 021	291742	4593902	ND	ND
24	LFSG-02-072202- R- 022	291710	4593903	ND	ND
25	LFSG-02-072202- R- 023	291681	4593899	0.20	ND
26	LFSG-02-072202- R- 024	291654	4593897	ND	2.10
27	LFSG-02-072202- R- 025	291628	4593896	ND	ND
28	LFSG-02-072202- D- 003	NA	NA	NA	NA
29	LFSG-02-072202- D- 004	NA	NA	NA	NA

^a ND = not detected.^b NA = not available.

As part of this demonstration, landfill soil gas samples were collected for COPC analysis by two methods. The first set of samples was collected using a Summa canister and sent to an off-site commercial laboratory for analysis. The second set of samples was collected with Tedlar bags and analyzed at the on-site laboratory provided by EPA's Environmental Response Team Center (ERTC). Field instrumentation was used to measure fixed gases (CO_2 , N_2 , and O_2) at each of the designated sampling locations to verify that LFG was being collected. Sampling was conducted using a slam-bar to drive a sampling hole through the landfill cover; a sampling probe was inserted into the landfill area; and the hole was sealed around the probe to minimize ambient air in-leakage.

Three Tedlar bag and three Summa canister samples were collected at grid locations with the highest NMOC concentrations in each homogeneous area, yielding a total of six matched pair samples. While conducting the field measurements for fixed gases at grid No. 2, it was observed that the O_2 content was greater than 18 percent and the N_2 concentration was greater than 20 percent, indicating the absence of LFG in the sample. It was determined that high NMOC instrument reading at grid No. 2 could have been attributed to vehicle exhaust and not to LFG due to the close proximity of this location to the roadside. It was, therefore, determined that this sampling location should be abandoned to prevent sampling interference. The sampling location was moved to the node with the next highest screening concentration.

During the screening analysis of the site, it was observed that gas monitoring wells were installed within the interior of the landfill boundary area. These wells were not properly capped or sealed and were, therefore, assumed to be acting as passive vents through the landfill cover. Sampling was conducted using a slam-bar to drive a sampling hole through the landfill cover near these passive vents. A sampling probe was then inserted into the landfill, and the hole was sealed around the probe to minimize ambient air in-leakage. Summa canister samples were collected for COPC and fixed gas analysis, and Tedlar bag samples were collected for COPC analysis. Fixed gases were also analyzed at these locations using field instrumentation. These passive vents and sampling locations were identified at grid Nos. 80, 131, and 140.

This guidance recommends that sampling be conducted along the perimeter at wells located nearest to the hot spots and the closest off-site receptor. For this site demonstration, sampling was conducted at three of the perimeter wells, which were all located in close proximity to off-site receptors (i.e., residential houses). At each of these locations, Summa canisters and Tedlar bags were used to collect the samples analyzed for COPC and fixed gases. The Summa canister sampling rate was set to approximately 0.1 L/min in order to minimize the potential for ambient air leakage. The Tedlar bag sample was collected at approximately 1.0 L/min.

This guidance recommends that ambient air sampling be conducted at the locations where the highest NMOC concentrations are measured for each nearly homogenous area. For the purpose of this demonstration, two samples were collected at nodes 9 and 137 using a Summa canister. It should be noted that the sample taken at node 9 was located directly next to a storm drain that appeared from field observations to be acting as a passive vent. An ambient air sample was also collected at the perimeter well that was determined to be closest to the highest concentration observed on-site during the screening analysis.

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The laboratory did not detect any of the analytes in any sample blanks. The minimum and maximum percent recovery for the entire set of laboratory control samples was greater than 70 and less than 122, indicating that the laboratory was capable of accurately quantifying the results. The 4-bromofluorobenzene surrogate spike recovery was outside of the upper range for 10 out of 20 field samples; the maximum recovery was 363 percent. The high surrogate recovery for 4-bromofluorobenzene is indicative of matrix interference, and the results may be biased on the high side. All other spike surrogate recovery values were within the target range of 70 to 130 percent.

The analytical results between matrix spike and matrix spike duplicate (MS/MSD) analyses for each COPC have been assessed. Except for methylene chloride and acetone in the duplicate ambient air samples, the relative percent difference (RPD) for each of the matched sample pairs ranged from 2.15 to -13.33. The laboratory reported concentrations of methylene chloride and acetone in one of the duplicate ambient air samples but not the other. The RPD for methylene chloride and acetone in the ambient air samples was calculated to be 40 and -129.67, respectively. The RPD for the blind reference standard ranged from 0 to 148. The laboratory reported concentrations for methylene chloride, acetone, and toluene in the blind reference standard though they were not expected to be there. The reported values for the blind reference standard are less than five times the method detection limit (MDL) for each of the contaminants. The RPD for the laboratory control samples (LCS) ranged from 0 to 18. Except for 1,2,4-trichlorobenzene and hexachlorobutadiene, the calculated RPD for each LCS analyte was less than 5. Although neither methylene chloride nor acetone was found in the associated laboratory blanks, both of these contaminants are considered to be common laboratory contaminants. This narrow range indicates that the laboratory was capable of reproducing the analytical results.

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected under normal conditions. The sampling and analytical goal for completeness for all samples tested was 80 percent or more. Ninety-three percent of the targeted data was collected and validated. Figure 6-7 shows the concentration isopleth for the NMOC that was quantified by the laboratory. Figures for all ten of the COPCs that were detected by the laboratory were generated as part of the site report. These figures provided a visual presentation of the laboratory results and were used to help understand the dynamics of this landfill and to further quantify the division of this landfill into two distinct parcels. The data for individual COPCs were analyzed, and the 90th percentile concentrations of each, shown in Table 6-8, were determined for the northern and southern homogeneous parcels. Table 6-9 provides the analytical results for individual COPCs from the northern and southern landfill homogeneous parcels.

The 90th percentile concentration values were used as input parameters for the LandGEM model to estimate the emission rates for each of the COPCs. Because there were two distinct parcels, it was necessary to model each parcel individually for NMOC emissions. With all values input for each nearly homogeneous area, LFG emission rates for each COPC were estimated using the LandGEM model. Figure 6-8 shows an example output file for NMOC emissions from the LandGEM model, and Figure 6-9 shows the emission rate data for NMOC as a function of time. Table 6-10 provides the emission rates estimated for each COPC within each parcel of the landfill.

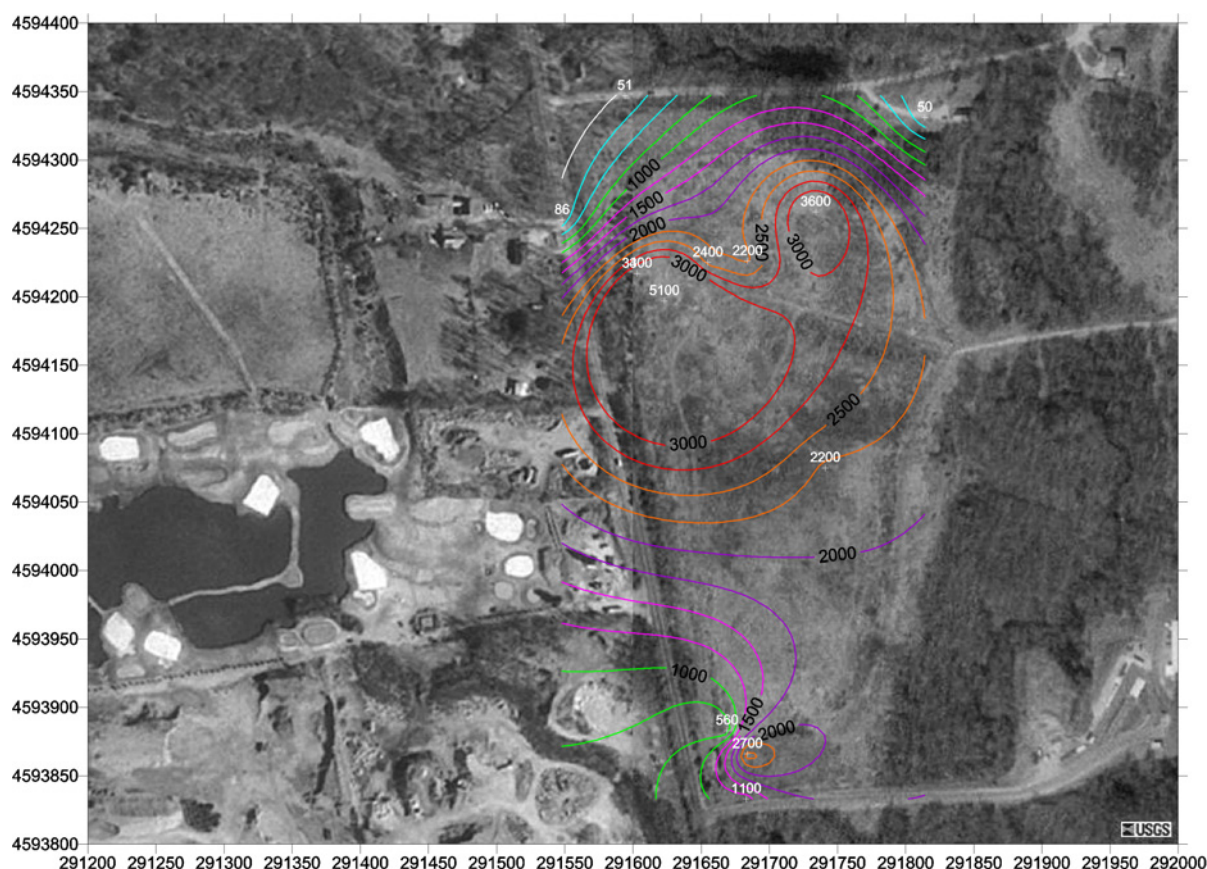


Figure 6-7. Rose Hill - NMOC Concentration (ppmv) Isopleths from Summa Sampling.

Table 6-8. Rose Hill - 90th Percentile Concentrations for Individual COPCs from the Northern and Southern Homogeneous Parcels.

COPCs	Northern Parcel		Southern Parcel	
	$\mu\text{g}/\text{m}^3$	ppmv	$\mu\text{g}/\text{m}^3$	ppmv
NMOC	$2.25 \times 10^{+6}$	4500	$1.27 \times 10^{+6}$	2550
1,1,1-Trichloroethane	$3.21 \times 10^{+3}$	0.58		
Benzene	$5.33 \times 10^{+3}$	1.64	$7.86 \times 10^{+2}$	0.242
Chlorobenzene	$1.04 \times 10^{+3}$	0.222	$3.38 \times 10^{+3}$	0.719
Chloroethane	$7.94 \times 10^{+3}$	2.96	$8.59 \times 10^{+2}$	0.3202
1,4-Dichlorobenzene	$6.16 \times 10^{+2}$	0.1008	$1.14 \times 10^{+3}$	0.1864
Toluene	$4.28 \times 10^{+3}$	1.118	$9.76 \times 10^{+3}$	2.5473
Trichloroethene	$3.41 \times 10^{+2}$	0.0625	$1.49 \times 10^{+2}$	0.02741
Vinyl Chloride	$1.61 \times 10^{+3}$	0.62	$7.78 \times 10^{+2}$	0.2992
m, p -Xylene	$2.97 \times 10^{+4}$	6.73	$1.65 \times 10^{+4}$	3.75
o-Xylene	$4.85 \times 10^{+3}$	1.1	$608 \times 10^{+3}$	1.542

Table 6-9. Rose Hill - Analytical Results for Individual COPCs.

Parcel	Node ID	Oxygen	Nitrogen	Methane	Carbon Dioxide	NMOC	1,1,1- Trichloroethane	Benzene	Chlorobenzene	Chloroethane	1,4-Dichlorobenzene	Toluene	Trichloroethane	Vinyl Chloride	m, p - Xylene	o - Xylene
	No.	(%)	(%)	(%)	(%)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)
Northern	137	0.19	1.2	56	42	3300	ND ^a	1.40	0.23	0.47	0.06	0.06	ND	ND	7.90	0.46
	148	4.1	67	7.8	21	3600	ND	0.19	0.04	4.00	ND	ND	ND	0.80	ND	0.09
	139	ND	0.31	56	43	2400	ND	1.80	0.19	0.87	0.03	1.40	0.07	0.12	3.50	1.10
	140	1.8	44	23	31	2200	ND	0.14	ND	0.09	0.03	0.07	ND	0.20	0.50	0.30
	131	ND	5.2	53	43	5100	0.58	0.58	ND	1.40	0.12	0.46	0.02	0.17	4.00	1.10
Southern	15A	1.6	79	ND	21	560	ND	ND	ND	0.041	0.026	0.091	0.0041	ND	0.0042	ND
	9	0.97	66	11	24	1100	ND	0.17	0.62	0.021	0.038	0.019	ND	0.022	0.63	0.11
	16	ND	1.4	63	38	2700	ND	0.094	0.73	ND	0.25	0.018	ND	ND	1.3	0.051
	80	0.38	19	43	38	2200	ND	0.26	ND	0.39	0.034	3.6	0.03	0.33	4.8	1.9

^a ND = Not detected

Model Parameters			
Lo : 170.00 m ³ / Mg ***** User Mode Selection *****			
k : 0.0500 1/yr ***** User Mode Selection *****			
NMOC : 4500.00 ppmv ***** User Mode Selection *****			
Methane : 56.0000 % volume			
Carbon Dioxide : 44.0000 % volume			
Landfill Parameters			
Landfill type : Co-Disposal			
Year Opened : 1967 Current Year : 2003 Closure Year: 1982			
Capacity : 197692 Mg			
Average Acceptance Rate Required from			
Current Year to Closure Year : 13179.47 Mg/year			
Model Results			
NMOC Emission Rate			
Year	Refuse In Place (Mg)	(Mg/yr)	(Cubic m/yr)
1968	1.318E+04	3.227E+00	9.002E+02
1969	2.636E+04	6.296E+00	1.757E+03
1970	3.954E+04	9.216E+00	2.571E+03
1971	5.272E+04	1.199E+01	3.346E+03
1972	6.590E+04	1.463E+01	4.083E+03
1973	7.908E+04	1.715E+01	4.784E+03
1974	9.226E+04	1.954E+01	5.451E+03
1975	1.054E+05	2.181E+01	6.085E+03
1976	1.186E+05	2.398E+01	6.689E+03
1977	1.318E+05	2.603E+01	7.263E+03
1978	1.450E+05	2.799E+01	7.809E+03
1979	1.582E+05	2.985E+01	8.328E+03
1980	1.713E+05	3.162E+01	8.822E+03
1981	1.845E+05	3.331E+01	9.292E+03
1982	1.977E+05	3.491E+01	9.739E+03
1983	1.977E+05	3.321E+01	9.264E+03
.	.	.	.
.	.	.	.
2001	1.977E+05	1.350E+01	3.766E+03
2002	1.977E+05	1.284E+01	3.583E+03
2003	1.977E+05	1.222E+01	3.408E+03
.	.	.	.
.	.	.	.
2201	1.977E+05	6.129E-04	1.710E-01
2202	1.977E+05	5.830E-04	1.627E-01
2203	1.977E+05	5.546E-04	1.547E-01

Figure 6-8. Rose Hill - Example LandGEM Model Run Output.

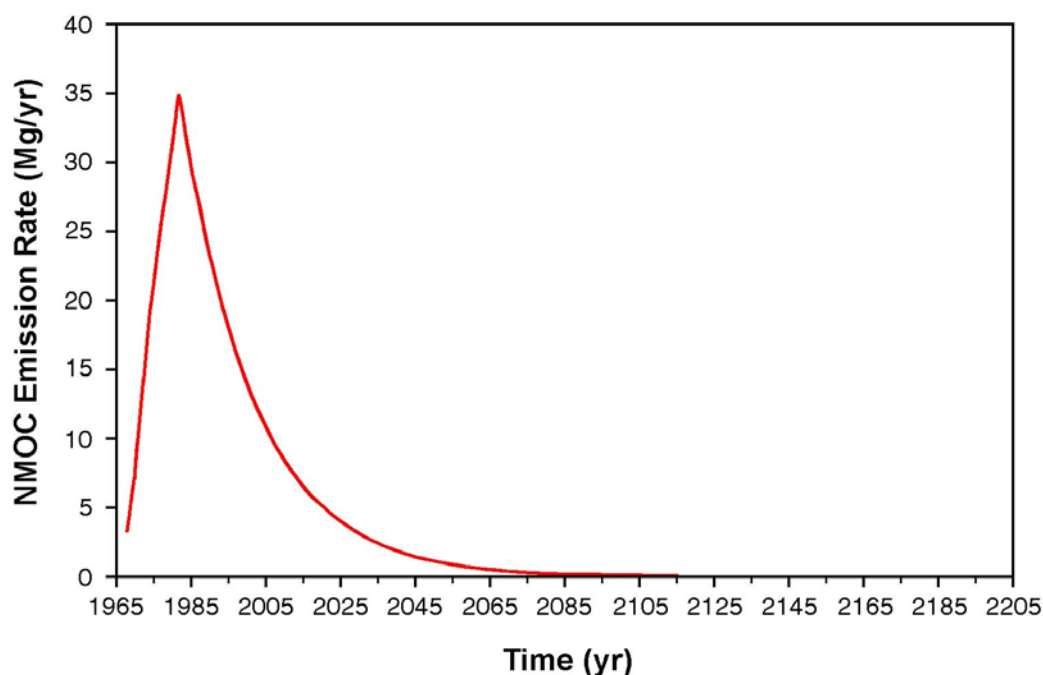


Figure 6-9. Rose Hill - NMOC Emission Rates versus Time.

Table 6-10. Rose Hill - Emission Rates of COPCs by Homogeneous Parcel.

COPC	Northern Parcel 2002 Emission Rates, Mg/yr	Southern Parcel 2002 Emission Rates, Mg/yr
NMOC	12.84	6.907
1,1,1-Trichloroethane	2.562×10^{-3}	
Benzene	4.243×10^{-3}	5.893×10^{-4}
Chlorobenzene	8.200×10^{-4}	2.547×10^{-3}
Chloroethane	6.324×10^{-3}	6.489×10^{-4}
1,4-Dichlorobenzene	4.868×10^{-4}	8.779×10^{-4}
Toluene	3.417×10^{-3}	7.385×10^{-3}
Trichloroethene	2.610×10^{-4}	1.239×10^{-4}
Vinyl Chloride	1.283×10^{-3}	5.893×10^{-4}
m, p-Xylene	2.366×10^{-2}	1.251×10^{-2}
o-Xylene	3.867×10^{-3}	5.139×10^{-3}

The next step in characterizing the LFG emissions is to evaluate the ambient impact of each of the COPCs. For this, it is necessary to use an atmospheric dispersion model. For demonstration purposes, SCREEN3 was used to provide a screening level assessment. In order to properly screen the landfill each parcel was again evaluated separately by treating each as an “area” source within the model. In order to accomplish this, each parcel was broken into its own rectangular area as shown in Figure 6-10. From these areas, each parcel was modeled at a unity emission rate of 1 g/s to provide maximum 1-h concentration for each parcel. Because each parcel was modeled on a unity basis, the emission rates generated by the LandGEM model could, in turn, be multiplied by this unity-derived concentration to determine the 1-h maximum concentrations for each COPC. To convert these concentrations to a representative annual concentration, all derived 1-h concentrations were multiplied by the appropriate multiplying factor of 0.08.



Figure 6-10. Rose Hill - Defined Modeling Areas for SCREEN3 .

Table 6-11 provides the maximum predicted annual concentrations for each COPC. For illustrative purposes, it was decided to use only the 2002 emission rates for calculating the ambient air concentrations because the LandGEM model runs for the Rose Hill Landfill predicted very low emission rates and the emission rate for every COPC was declining from 2002 forward. Hence, These predicted ambient air concentrations were then compared to the target concentrations presented in Table 6-12, which identifies target media concentrations

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corresponding to risk/hazard based concentrations for ambient air in residential settings. The target concentrations were derived using Equation 2-8 and the appropriate toxicity factor. Only air concentrations that satisfy both the prescribed cancer risk level and the target hazard index are included in the risk table. The approach described here also can be used to evaluate chemicals not listed in the tables. The reader is cautioned to recognize that the concentrations presented in the risk table are screening levels. They are not clean-up levels, preliminary remediation goals, nor are they intended to supercede existing criteria of the lead regulatory authority. The lead regulatory authority for a site may determine that criteria other than those provided herein are appropriate for their specific site or area.

Table 6-11. Rose Hill - Maximum Annual Concentrations.

COPC	Predicted Maximum Annual Concentrations				
	Northern Parcel		Southern Parcel		Total
	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)
NMOC	0.162	80.8	7.69×10^{-2}	38.4	119.
1,1,1-Trichloroethane	2.92×10^{-6}	1.61×10^{-2}			1.61×10^{-2}
Benzene	8.23×10^{-6}	2.67×10^{-2}	1.01×10^{-6}	3.28×10^{-3}	3.00×10^{-2}
Chlorobenzene	1.10×10^{-6}	5.16×10^{-3}	3.02×10^{-6}	1.42×10^{-2}	1.93×10^{-2}
Chloroethane	1.48×10^{-5}	3.98×10^{-2}	1.35×10^{-6}	3.61×10^{-3}	4.34×10^{-2}
1,4-Dichlorobenzene	5.01×10^{-7}	3.06×10^{-3}	7.98×10^{-7}	4.88×10^{-3}	7.95×10^{-3}
Toluene	5.62×10^{-6}	2.15×10^{-2}	1.07×10^{-5}	4.10×10^{-2}	6.26×10^{-2}
Trichloroethene	3.02×10^{-7}	1.64×10^{-3}	1.26×10^{-7}	6.89×10^{-4}	2.33×10^{-3}
Vinyl Chloride	3.11×10^{-6}	8.08×10^{-3}	1.26×10^{-6}	3.28×10^{-3}	1.14×10^{-2}
m, p-Xylene	3.38×10^{-5}	0.149	1.58×10^{-5}	6.95×10^{-2}	0.219
o-Xylene	5.52×10^{-6}	2.43×10^{-2}	6.49×10^{-6}	2.86×10^{-2}	5.29×10^{-2}

The sources of chemical data used in the calculations necessary to create Table 6-11 were EPA's Superfund Chemical Data Matrix (SCDM) database and EPA's Water 9 database whenever a chemical was not included in the SCDM database. EPA's IRIS is the preferred source of carcinogenic unit risks and non-carcinogenic reference concentrations (RfCs) for inhalation exposure. The following two sources were consulted, in order of preference, when IRIS values were not available: provisional toxicity values recommended by EPA's NCEA and EPA's HEAST. If no inhalation toxicity data could be obtained from IRIS, NCEA, or HEAST, extrapolated unit risks and/or RfCs were derived by using toxicity data for oral exposure (cancer slope factors and/or reference doses, respectively) from these reference sources using the same preference order. It is recognized that toxicity databases such as IRIS are constantly being updated; this table is current as of August 2002. Users of this guidance are strongly encouraged to research the latest toxicity values for contaminants of interest from the sources noted above.

Table 6-12. Rose Hill - Risk Assessment Analysis.

COPC	Basis of Target Concentration risk	Target Ambient Air Concentration to Satisfy Both the Prescribed Risk Level and the Target Hazard Index [R=10 ⁻⁶ , HI=1) C _{target}		Total Predicted Ambient Air Concentrations (µg/m ³)
		Cancer (µg/m ³)	Non-cancer (µg/m ³)	
1,1,1-Trichloroethane	NC ^a		2.3×10 ⁺³	1.6×10 ⁻²
Benzene	C ^b	0.25	0.31	3.0×10 ⁻²
Chlorobenzene	NC		62.	1.9×10 ⁻²
Chloroethane (ethyl chloride)	C	2.3	1.0×10 ⁺⁴	4.3×10 ⁻²
1,4-Dichlorobenzene	C	31.	8.4×10 ⁺²	7.9×10 ⁻³
Toluene	NC		4.0×10 ⁺²	6.3×10 ⁻²
Trichloroethylene	C	1.7×10 ⁻²	37.	2.3×10 ⁻³
Vinyl chloride (chloroethene)	C	0.11	1.0×10 ⁺²	1.1×10 ⁻²
m, p-Xylene	NC		1.1×10 ⁺²	0.22
o-Xylene	NC		1.1×10 ⁺²	5.3×10 ⁻²

^a NC = non-cancer^b C = cancer risk

The predicted ambient air concentrations in the table are risk-based screening levels calculated following an approach consistent with that presented in EPA 2001. Separate carcinogenic and non-carcinogenic target concentrations were calculated for each compound when both unit risks and reference concentrations were available. When inhalation toxicity values were not available, unit risks and/or reference concentrations were extrapolated from oral slope factors and/or reference doses, respectively. For both carcinogens and non-carcinogens, target air concentrations were based on an adult exposure scenario and assume maximum exposure of an individual (i.e., exposure to contaminants 24 hours per day, 7 days per week, 50 weeks per year over 30 years). An inhalation rate of 20 m³/day and a body weight of 70 kg are assumed and have been factored into the inhalation unit risk and reference concentration toxicity values. For comparative purposes, approximately 12 COPCs were identified in one or more of the ambient air samples that were collected approximately 3 feet above ground level at a location that was known or suspected of having LFG escaping either through a vent or through the cover material. The maximum concentration of the ambient air samples was always below 20 ppbv (0.3 µg/m³).

6.3 Summary of the Bush Valley Landfill Superfund Site

The Bush Valley Landfill (landfill) Site is located in Harford County, Maryland, one mile from the Town of Abingdon. The landfill occupies approximately 16 acres of a 29-acre parcel of land. The Bush Declaration Natural Resources Management Area, which is a 120-acre tidal cattail marsh, borders the site to the north, and the planned community of east Harford Town

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lies west of the site across Bush Road. Three single-family homes are located within 300 feet of the landfill's southern border.

The Bush Valley Superfund Landfill began operations in 1974 and took in household and industrial wastes. The operator abandoned the site in 1983 when the landfill reached capacity. During site investigations, several VOCs were detected, including benzene, vinyl chloride, and tetrachloroethene. Metals including beryllium, arsenic and manganese have shown up in samples of ground water, surface water, soil, and leachate. The VOCs have appeared in air samples.

EPA's 1993 Human Health Risk Assessment indicates that ground water is the only potential source of elevated risk if people are exposed to it. However, no residents currently use ground water in the area for their drinking or cooking. This assessment was not able to rule out air as potentially significant pathway, but additional air testing during the cleanup showed that the air is safe to breathe.

The site was added to the NPL in 1989. The final ROD was issued in 1995, and the final design for the remedial action was completed in 1999. The landfill was closed in 2001 with the installation of a flexible membrane single barrier cover system. As a part of the landfill closure, a passive LFG control system was installed. This passive system consists of 14 subsurface gas collection points that terminate below the landfill cap into a gas transmission layer. This layer is connected to five passive gas vent wells aligned along the ridge of the landfill. In December 2002, eight temporary gas monitoring probes (TMPs) were installed in the sand and gravel layer that exists approximately 15 feet below ground surface. These probes confirmed that a 15-foot thick layer of clayey soil is overlaying the sand. This study effort also demonstrated that CH₄ at concentrations between 62 and 65.4 percent exists in the sand layer, and the gas pressure within the sand layer is approximately 0.4 inches of Hg. Prior to this demonstration project, samples from the temporary probes had not been analyzed for speciated volatile organics. Monitoring has shown that the cap's passive gas venting system is not enough, by itself, to reduce the levels of underground LFG to acceptable levels. For this reason, the PRPs planned to modify the gas management system to include active gas venting. EPA approved the design for the active venting system in April 2004, and the vents were installed in June 2005.

The landfill itself consists of a mound of covered material sloping up from the southern site boundary. The mound peaks 25 feet above natural grade approximately in the center of the site, and then slope downward to the north at a somewhat steeper slope than on the south side of the site. The graded site also slopes gently to the east and west towards the marsh area and Bush Road, respectively. The landfill is capped with a geo-synthetic capping system. The cap is multilayered and includes:

- 2 ft of soil bedding material on top of the solid waste,
- Gas transmission layer (6 oz/yd² geotextile),
- Hydraulic barrier (40 mil low density polyethylene),
- Drainage layer (6 oz/yd² geotextile),
- Anchor trench (3 ft run out and 2 ft deep),
- Soil cover (2 ft thick) with shallow root vegetation,
- Five LFG vents (4 in. schedule 80 PVC) along ridge line,

- Nine permanent gas monitoring probes (2-in. diameter with 3/8-in. valves), and
- Five active LFG units along the eastern perimeter.

6.3.1 Bush Valley Landfill - Using the Procedure of Screening with Probes Placed Just Below the Cover

For reasons discussed above, this site was selected in order to compare the historical decisions concerning the number and location of the perimeter monitoring probes and the need to control LFG with the conclusions one would reach if the guidance document procedures were followed.

Field activities as described in the approved site activity plan for the Bush Valley Landfill located in Abingdon, Maryland were conducted on August 25 and August 26, 2003. Field activities included landfill surface screening analysis and data reduction, hot spot and homogeneity determinations, and sampling landfill soil gas, passive vent gas, perimeter well gas, and ambient air. To assist with the field activities a 30 m by 30 m sampling grid was developed across the extent of the landfill area prior to the field activities. This sampling grid was developed to include the entire extent of the landfill boundary area and to extend 30 m beyond it. This grid was then numbered for each node location forming a serpentine sampling pathway across the grid. A total of 108 sampling locations comprised the sampling grid layout developed for this site. A reference point was identified using an identifiable landmark on the site to locate the starting point. Figure 6-11 shows the sampling grid for the screening analysis.

Once on site, the reference point was visually located, and using a handheld GPS, the starting point (grid node No.1) was located to begin the screening analysis. This screening analysis encompassed measurements for NMOC using a PID and for CH₄ by using a FID. Both detectors were held no more than 1 in. above the ground while measurements were being made. It should be noted that the field instruments are very sensitive, and fluctuation due to gusts of wind across the landfill cover could have been significant. Readings were taken for approximately 1 min, and the average value, excluding the extreme highs and lows, was recorded.

In conducting the serpentine walk across the site, an effort was made to identify areas containing cracks and gaps in the landfill cover and to the extent possible measurements were made at those locations. As this site had previously installed passive vents, these passive vents were including in the screening analysis as a breach in the cover. The permanent and temporary installed gas monitoring probes were also included in these screening activities. Not all predetermined sampling locations were accessible due to a variety of reasons, ranging from being located on private property to extreme overgrowth. An attempt was made to collect a reading at each node, with measurements being collected not greater than 10 m from the predetermined locations. Duplicate readings were also taken at predefined nodes, selected based on a random number generator, as part of the QA/QC efforts. All screening data were recorded on field log data collection forms along with any field notes relevant to this specific location. There was 90 percent data collection efficiency. Table 6-13 provides the screening sample results for the first 29 nodes.

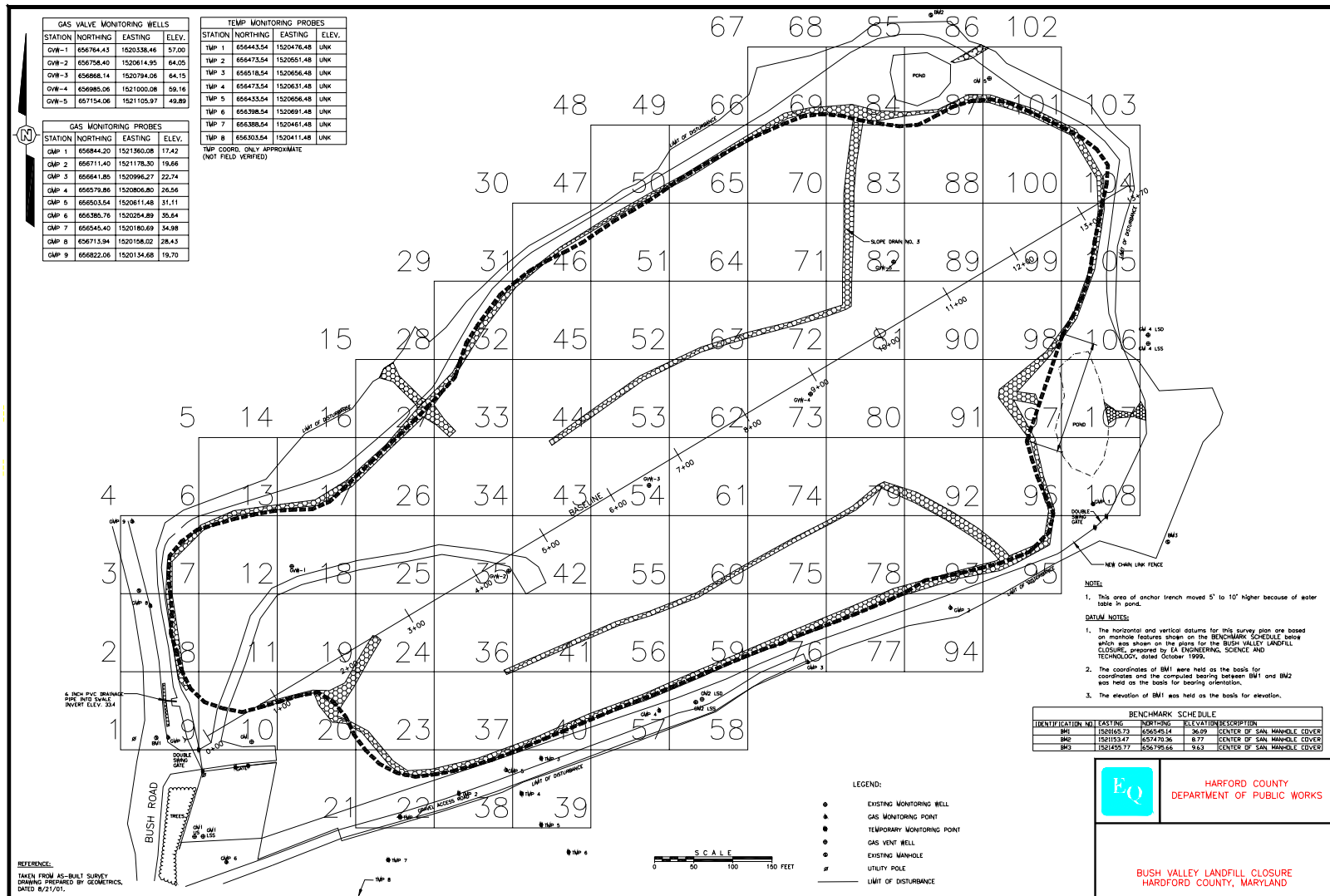


Figure 6-11. Bush Valley - Screening Sampling Grid.

Table 6-13. Bush Valley Screening Sample Results (partial).

Node No.	Sample ID No.	Actual UTM Coordinates		NMOC Conc. (ppm)	CH ₄ Conc. (ppm)
		Easting	Northing		
1	LSFG-02-082703- R- 001	18391264	4369160	ND ^a	1.29
2	LSFG-02-082703- R- 002	18391275	4369193	ND	1.29
3	LSFG-02-082703- R- 003	18391270	4369221	ND	1.05
4	LSFG-02-082703- R- 004	18391258	4369252	ND	1.58
5		NA ^b	NA	NA	NA
6	LSFG-02-082703- R- 005	18391296	4369251	ND	1.22
7	LSFG-02-082703- R- 006	18391311	4369216	ND	3.33
8	LSFG-02-082703- R- 007	18391314	4369185	ND	1.4
9	LSFG-02-082703- R- 008	18391313	4369140	ND	1.32
10	LSFG-02-082703- R- 009	18391327	4369141	ND	1.37
11	LSFG-02-082703- R- 010	18391330	4369191	ND	1.31
12	LSFG-02-082703- R- 011	18391329	4369221	ND	1.65
13	LSFG-02-082703- R- 012	18391325	4369248	ND	3.11
14		NA	NA	NA	NA
15		NA	NA	NA	NA
16	LSFG-02-082703- R- 013	18391353	4369267	ND	20.2
17	LSFG-02-082703- R- 014	18391357	4369250	ND	2.08
18	LSFG-02-082703- R- 015	18391355	4369220	ND	1.44
19	LSFG-02-082703- R- 016	18391359	4369189	ND	1.7
20	LSFG-02-082703- R- 017	18391354	4369160	ND	0.85
21	LSFG-02-082703- R- 018	18391357	4369141	ND	0.9
22	LSFG-02-082703- R- 097	18391384	4369133	ND	2.08
23	LSFG-02-082703- R- 019	18391385	4369154	ND	5.5
24	LSFG-02-082703- R- 020	18391391	4369189	ND	1.66
25	LSFG-02-082703- R- 021	18391386	4369214	ND	1.39
26	LSFG-02-082703- R- 022	18391386	4369252	ND	1.71
27	LSFG-02-082703- R- 023	18391383	4369280	ND	34
28		NA	NA	NA	NA
29		NA	NA	NA	NA

^a ND = not detected.^b NA = not available.

The screening data collected were used for two analyses. The first was for a hot spot analysis. This was done by importing the screening data set into a graphical contouring software package (Surfer) to produce concentration contours, which were layered over an aerial photograph of the site. This method enabled a visual determination of where the higher concentrations were recorded during the screening analysis. This method also allowed the data

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to be divided into two sets based on the contours derived from these data. This population division was used as part of the homogeneity determinations. NMOCs were only detected within the passive vents and gas monitoring probes. Therefore, CH₄ measurements were used to identify hot spots and to determine the number of near homogeneous subdivisions required to characterize the landfill surface. Figures 6-12 and 6-13 show the concentration contours for both NMOC and CH₄ data that were recorded during the screening analysis.

The second analysis provided a determination of the homogeneity of the site, which was done by the Wilcoxon Rank Sum statistical method. This method determines whether two data sets are statistically similar. If the two sets are determined to be similar, then the two populations are determined to be one nearly homogeneous area. If the two data sets are determined not to be statistically similar, then the two sets are said to be two non-homogeneous areas. For this task, the hot spot analysis was used to determine if there appeared to be two distinct population sets. For this site it was shown that there existed four nearly homogeneous areas. All non-detect and duplicate measurements were excluded from the statistical analysis.

As part of this demonstration, landfill soil gas samples were collected for COPCs. The samples were collected using a Summa canister and were sent to an off-site commercial laboratory for analysis. At each of the designated sampling locations, field instruments were used to measure fixed gases (CO₂, N₂, and O₂). The fixed gas concentration values were used to verify that LFG was being collected. As per the guidance, three landfill soil gas samples should be collected in each of the four homogeneous areas, yielding a total of 12 landfill soil gas samples required. However, a decision was made against using a slam-bar on this site in order to prevent damage to the flexible membrane cover that was already in place and to avoid the complexities of ensuring proper repair of damage to this cover that using a slam-bar would cause. Instead, it was determined that LFG samples would only be collected at the installed passive gas vents (GVW). For all GVW locations, a brass sampling valve was installed on each vent, and the vent exit was sealed to minimize leakage during sampling activities. The duplicate sample needed to satisfy QAPP requirements was collected at GVW 1.

As a further demonstration, sampling was conducted at all the site's 17 perimeter wells, which were designated as gas monitoring probes (GMPs) and TMPs. Sampling was conducted using sampling valves previously installed at each location. All 17 wells are located in close proximity to off-site receptors (i.e., residential dwellings). At each location, Summa canisters were used to collect the samples to be analyzed for COPCs, fixed gases, and methane. The Summa canister sampling rate was set to approximately 0.1 L/min to minimize the potential for ambient air leakage. Based on the fixed gas concentration data, it would appear that there is significant ambient air leakage associated with GMP-1, GMP-5, TMP-2, TMP-3, and TMP-5. The data from these probes was excluded from additional data analysis. It was observed that several of these excluded locations have elevated NMOC concentration even with the ambient air dilution. All probes had been installed for more than 7 months and some for as many as 3 years. It would appear that the grout and soils surrounding these probes had dried out and shrunk, allowing ambient air to leak into the annulus. Field instrumentation readings taken at each of the sampling locations prior to initiating sampling confirms this. These results demonstrated the presence of LFG via oxygen readings at levels of 0.4 percent. This theory is further supported in viewing the laboratory results of samples GMP-6 and TMP5 and

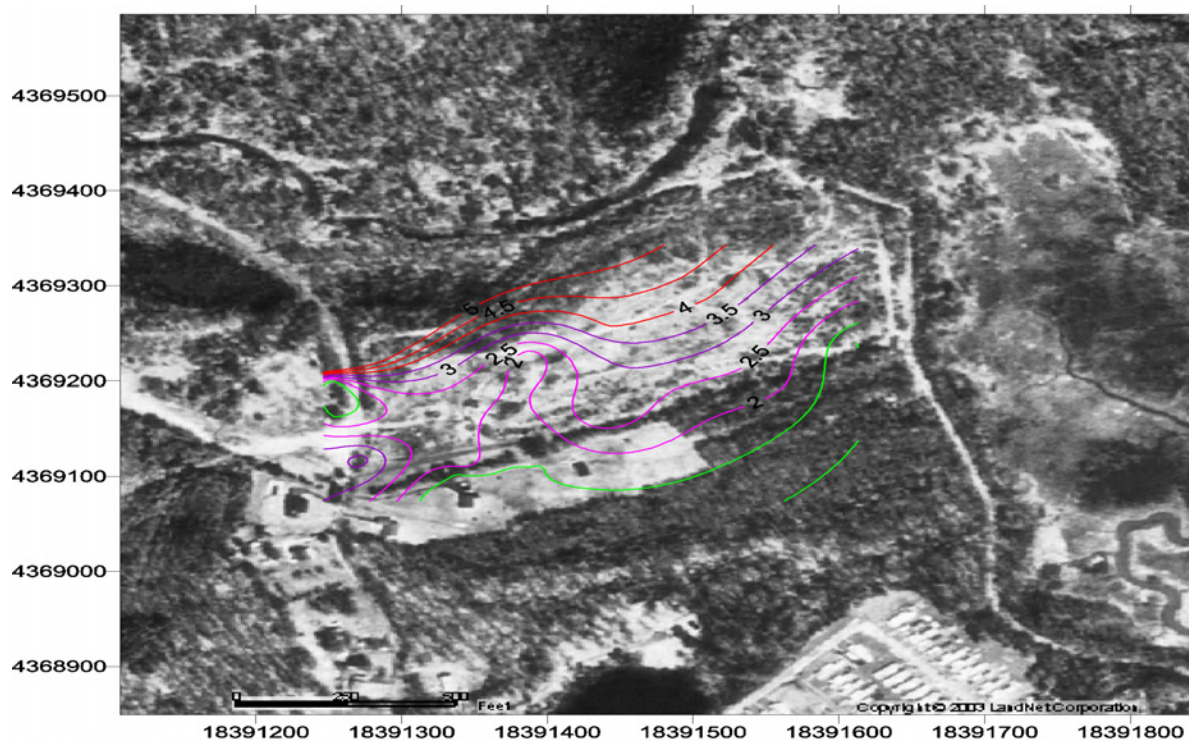


Figure 6-12. Bush Valley - Measured Screening Results for NMOC (ppm).

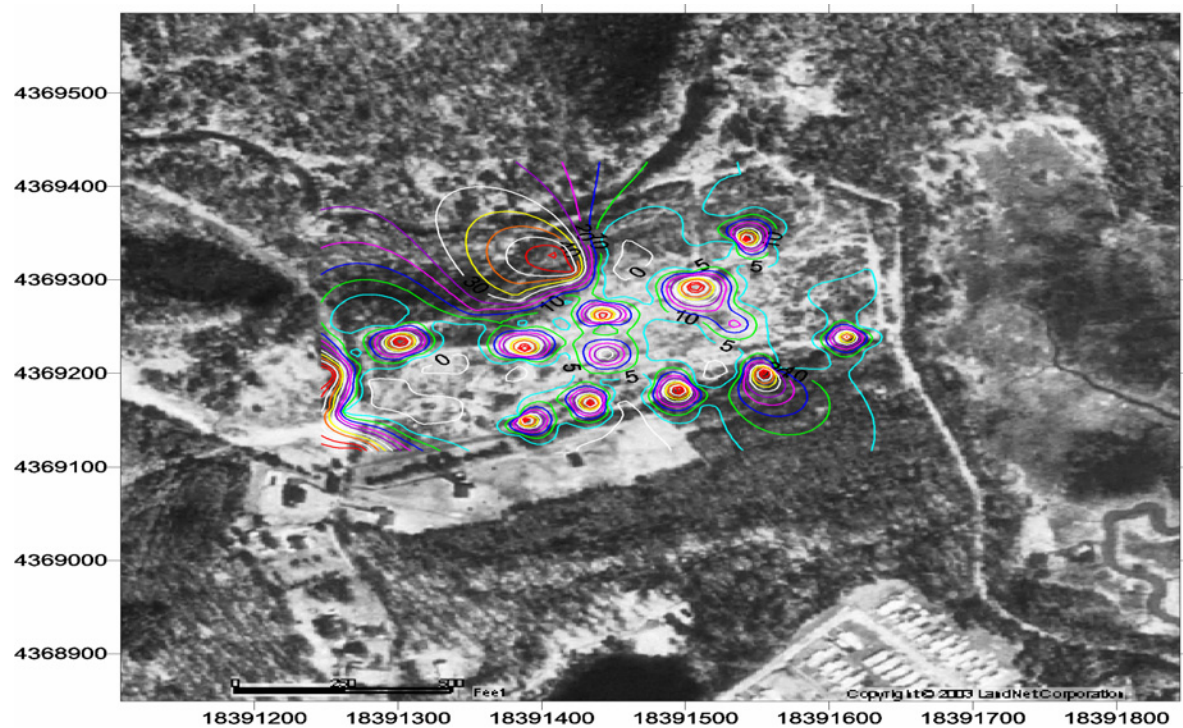


Figure 6-13. Bush Valley - Measured Screening Results for Methane (ppm).

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comparing them to the duplicate samples collected there. In both instances these laboratory results were nearly identical. For these reasons and because all of the existing probes were sampled, there was sufficient data to continue with the illustration of the guidance. One QA/QC sample was collected at each of the GMP and TMP sampling sets. These QA/QC samples were collected at GMP-6 and TMP-5.

Sampling was conducted of the ambient air at each of the passive vent locations (GVW). Five samples were collected using a Summa canister. The QAPP and field activity plan required the team to collect one duplicate ambient air Summa canister sample as a QA/QC validation.

Data quality objectives (DQOs) are a starting point of an interactive process, but they do not necessarily constitute definitive rules for accepting or rejecting results. Measurement quality objectives have been defined in terms of standard methods with accuracy, precision, and completeness goals. Uncertainty associated with the measurement data is expressed as accuracy and precision. The accuracy of a single value contains both a random error in a measurement and a systematic error, or bias. Accuracy thus reflects the total error for a given measurement. Precision values represent a measure of only the random variability for replicate measurements. In general, the purpose of calibration is to eliminate bias, although inefficient analyte recovery or matrix interferences can contribute to sample bias, which is typically assessed by analyzing matrix spike samples. At very low levels, blank effects (contamination or other artifacts) can also contribute to low-level bias. The potential for bias is evaluated by the use of method blanks. Instrument bias is evaluated by the use of control samples.

Accuracy of laboratory results has been assessed for compliance with the established QC criteria using the analytical results of method blanks, reagent/preparation blank, matrix spike and matrix spike duplicate samples, and field blanks. The laboratory detected 9.4 ppbv of acetone in a trip blank. This value is less than five times the value found in the sample results. The minimum and maximum percent recovery for the entire set of laboratory control samples was greater than 94 and less than 152. Out of 159 values, 154 were within the QC limits, and the data are deemed acceptable. The 4-bromofluorobenzene surrogate spike recovery was outside of the upper range for 56 field samples. The maximum 4-bromofluorobenzene surrogate spike recovery was 152 percent. The high 4-bromofluorobenzene surrogate recovery is indicative of matrix interference, and the results may be biased on the high side. All other spike surrogate recovery values were within the target range of 70 to 130 percent. The concentration of hexane in one sample exceeded the linear calibration range, and the value is assumed to be a lower end estimate.

The analytical results between MS/MSD analyses for each COPC have been assessed. The RPD was calculated for each pair of duplicate analysis. Methyl ethyl ketone (MEK) was reported in one of the duplicate ambient air samples, but not both. Chloroethane was reported in one of the duplicate GMP-6 samples, but not both. MEK, xylene, and dichloroethane (DCA) were reported for one of the duplicate TMP-5 samples, but not the other. The RPD for the duplicate samples ranged from -0.6 to 28.5, indicating that the laboratory was capable of reproducing the analytical results. Acetone was reported in the trip blank at 9.4 ppbv. Acetone in the LFG samples ranged from non-detect to 750 ppbv. Acetone is a common laboratory contaminant, and samples with concentrations less than five times that in the method/trip blank

should be considered to be estimates.

The sampling and analytical goal for completeness is 80 percent or more for all samples tested. Seventy-three percent of the targeted data was collection and validated. This is less than the DQO of more than 80 percent. The DQO was not achieved because of the air leakage problem discussed above.

From previous site activities and visual inspection of concentration isopleths generated from the laboratory results, the data were divided into the appropriate homogenous groups (corresponding to a parcel of land) for analysis. Figures 6-14 and 6-15 show the concentration isopleths of selected COPCs. These figures are a visual presentation of the laboratory results and were used to further understand the dynamics of this landfill and to quantify the division of this landfill into four distinct parcels. Table 6-14 provides the analytical results for GVW, GMP, and TMP sampling in the four homogeneous landfill parcels. For each parcel, the analytical results for each COPC were analyzed, and the 90th percentile concentrations shown in Table 6-15 were determined.

These data were used as input values for the LandGEM model to estimate the LFG emission rates for each COPC. It was necessary to model each of the four landfill parcels individually for CH₄ emissions. Figure 6-16 shows an example output file for NMOC emissions from the LandGEM model. Figure 6-17 shows the emission rate data for NMOC versus time. Table 6-16 provides the emission rates estimated for each COPC within each parcel of the landfill.

The next step in characterizing the emissions of LFG is to use an atmospheric dispersion model to evaluate the ambient impact of each of the COPCs. For demonstration purposes, SCREEN3 was used to provide a screening level assessment. In order to properly screen the landfill, each parcel shown in Figure 6-18 was evaluated separately and treated as an area source within the model. Each parcel was modeled at a unity emission rate of 1 g/s to obtain a 1-h concentration. Because each parcel was modeled on a unity basis, the emission rates generated from the LandGEM model could, in turn, be multiplied by this unity-derived concentration to determine the 1-h maximum concentrations for each COPC. To convert these concentrations to a representative annual concentration, all 1-h concentrations were multiplied by the appropriate multiplying factor of 0.08. Table 6-17 provides the predicted maximum annual concentrations for each COPC.

This time averaged emission rate is entered into the atmospheric dispersion model to estimate the average exposure point concentration of each COPC. Using this approach, a dispersion model run will be required for each chemical of concern. The dispersion model will generate a normalized air concentration at the receptor of concern if the model is run at 1 g/m²-s. The estimated ambient air concentration is determined by multiplying the dispersion coefficient by the time averaged emission rate. The LandGEM model runs for the Bush Valley Landfill predicted very low emission rates, and the emission rate for every COPC declines from 2003 forward. Hence, for illustrative purposes, only the 2003 emission rates were used for calculating the ambient air concentrations. These predicted ambient air concentrations were summed to identify the worst-case scenario and then compared to the target concentrations presented in Table 6-17.

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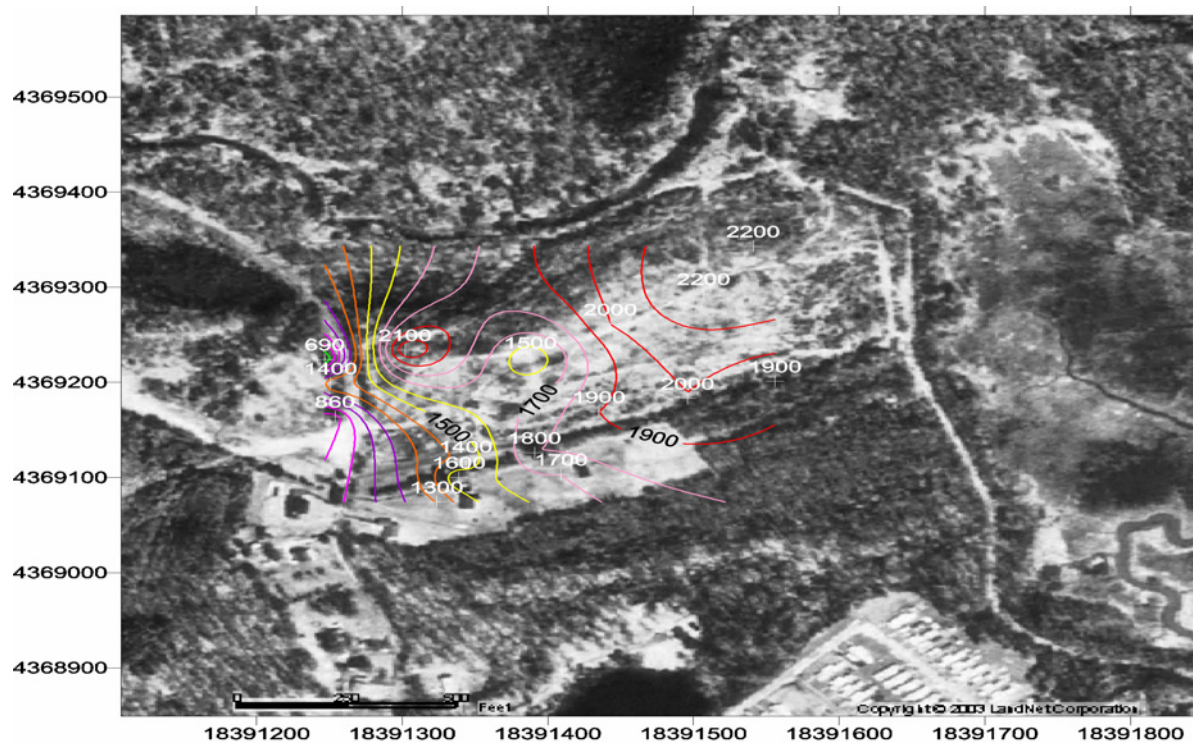


Figure 6-14. Bush Valley - NMOC Concentration (ppmvC) Isopleths from Summa Sampling.

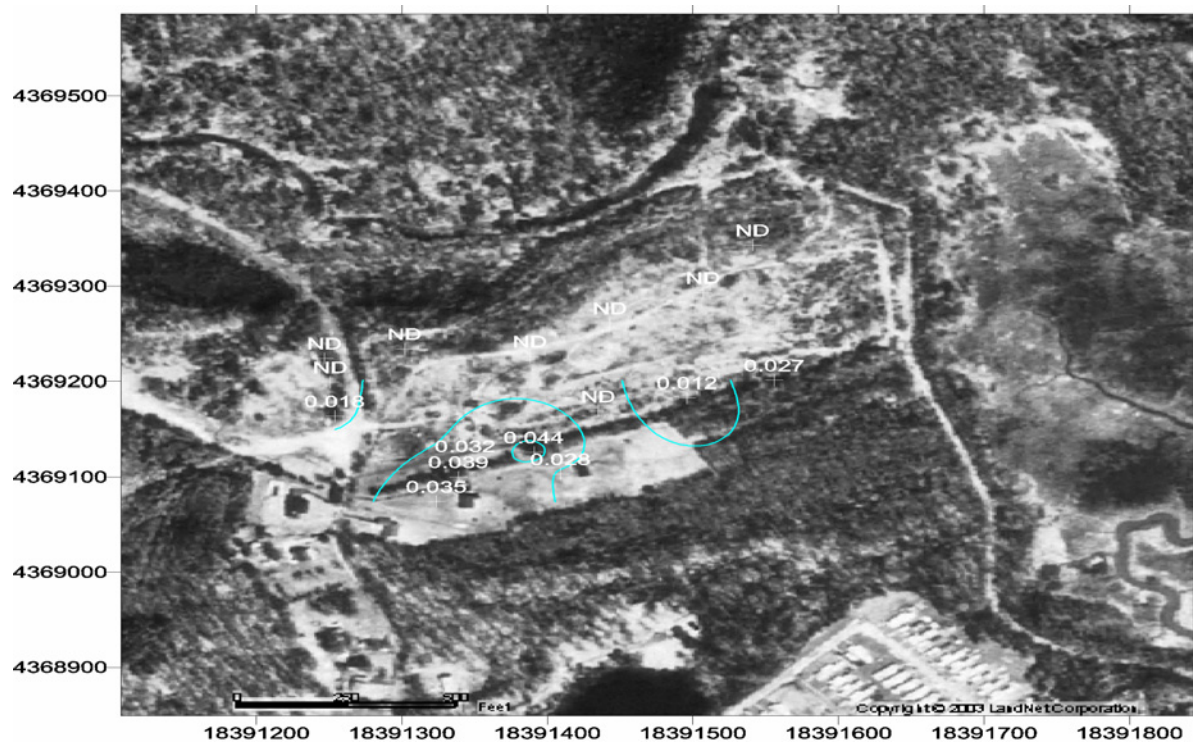


Figure 6-15. Bush Valley - 1,1-Dichloroethene Concentration (ppmv) Isopleths from Summa Sampling.

Table 6-14. Bush Valley - Analytical Results for Individual COPCs.

Parcel	Sample Location ID	Oxygen (%)	Nitrogen (%)	Methane (%)	Carbon Dioxide (%)	NMOCs (ppmv)	1,1,1-Trichloroethane (ppmv)	1,1-Dichloroethene (ppmv)	1,2-Dichloroethane (ppmv)	Benzene (ppmv)	Carbon tetrachloride (ppmv)	Chlorobenzene (ppmv)	Chloroethane (ppmv)	Chloroform (ppmv)	1,4-Dichlorobenzene (ppmv)	Methylene chloride (ppmv)	Tetrachloroethene (ppmv)	Toluene (ppmv)	Trichloroethene (ppmv)	Vinyl chloride (ppmv)	m,p-Xylene (ppmv)	o-Xylene (ppmv)
1	GVW-4	0.30	0.88	64.00	37.00	2200.00	ND ^a	ND	ND	0.72	ND	0.19	0.16	ND	0.32	ND	ND	4.00	ND	0.55	5.90	1.70
	GVW-5	0.37	1.00	62.00	40.00	2200.00	ND	ND	0.07	0.67	ND	0.25	0.10	ND	0.14	0.08	0.09	13.00	0.08	3.20	9.60	2.90
	GMP-2	ND	0.55	62.00	38.00	1900.00	0.09	0.03	ND	2.50	ND	ND	0.43	ND	0.20	0.20	0.31	0.18	0.27	1.40	0.45	0.18
	GMP-3	0.25	0.80	63.00	38.00	2000.00	ND	0.01	ND	0.95	ND	0.31	0.60	ND	0.17	0.13	0.68	ND	0.67	0.88	ND	ND
2	GVW-3	0.24	0.70	62.00	36.00	2000.00	ND	ND	ND	0.31	ND	0.21	0.16	ND	0.29	ND	ND	0.55	ND	0.22	8.00	2.40
3	GVW-1	0.42	1.20	63.00	36.00	2100.00	ND	ND	0.09	0.41	ND	0.41	0.12	ND	0.18	0.06	0.06	3.40	0.07	0.12	10.00	1.30
	GMP-7	1.00	34.00	36.00	27.00	860.00	ND	0.02	ND	0.05	ND	ND	0.10	ND	ND	0.01	0.08	ND	0.35	0.32	ND	ND
	GMP-8	0.21	1.70	68.00	32.00	1400.00	ND	ND	0.05	0.07	ND	ND	0.19	ND	0.02	ND	ND	0.02	0.10	1.10	ND	ND
	GMP-9	1.50	49.00	34.00	15.00	690.00	ND	ND	ND	ND	ND	ND	0.03	ND	ND	ND	ND	ND	0.03	0.07	ND	ND
	TMP-1	3.60	12.00	54.00	31.00	1400.00	ND	0.03	0.27	0.22	ND	0.15	0.18	ND	0.03	1.30	1.10	0.03	1.00	0.53	0.08	0.04
	TMP-7	0.24	1.70	64.00	37.00	1600.00	0.03	0.04	0.22	0.19	ND	0.31	0.26	ND	0.09	0.49	1.20	0.01	1.4	0.61	0.02	0.04
	TMP-8	0.47	7.90	60.00	33.00	1300.00	ND	0.04	0.28	0.40	ND	0.13	0.15	ND	0.03	2.20	1.30	0.12	1.00	0.43	0.30	0.13
4	GVW-2	0.46	1.50	64.00	36.00	1500.00	ND	ND	ND	0.42	ND	0.17	0.29	ND	0.03	ND	ND	0.08	ND	0.05	1.60	0.39
	GMP-4	1.20	8.40	57.00	38.00	1900.00	ND	ND	ND	0.94	ND	0.18	0.28	ND	0.06	ND	0.80	0.13	0.84	0.93	0.48	0.07
	TMP-4	0.27	1.20	64.00	39.00	1800.00	0.05	0.04	0.10	0.60	ND	0.23	0.49	ND	0.09	0.18	0.72	0.08	0.72	0.48	0.11	0.10
	TMP-6	0.19	0.72	64.00	36.00	1700.00	ND	0.03	ND	0.45	ND	0.18	0.00	ND	0.06	0.10	0.92	0.05	0.75	0.66	0.09	0.02

^a ND = not detected

Table 6-15. Bush Valley - 90th Percentile Concentrations for Individual COPCs.

COPC	Parcel 1		Parcel 2		Parcel 3		Parcel 4	
	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)
NMOC	1.10×10^6	2200	9.98×10^{-5}	2000	8.99×10^{-5}	1800	9.33×10^{-5}	1870
1,1,1-Trichloroethane	515.	0.093			166.	0.03	282.	0.051
1,1-Dichloroethene	103.	0.0255			152.	0.0378	171.	0.0424
1,2-Dichloroethane	280.	0.068			1140.	0.276	412.	0.1
Benzene	6610.	2.035	1010.	0.31	1300.	0.405	2720.	0.838
Chlorobenzene	1400.	0.298	987.	0.21	1790.	0.38	1010.	0.215
Chloroethane	1470.	0.549	429.	0.16	585.	0.218	1150.	0.43
1,4-Dichlorobenzene	1740.	0.284	1770.	0.29	881.	0.144	503.	0.0822
Methylene chloride	657.	0.186			6500.	1.84	607.	0.1718
Tetrachloroethene	4180.	0.606			8700.	1.26	6190.	0.896
Toluene	4.29×10^4	11.2	2110.	0.55	8000.	2.088	439.	0.1147
Trichloroethene	3220.	0.59			6320.	1.16	4480.	0.822
Vinyl chloride	6920.	2.66	572.	0.22	2100.	0.806	2210.	0.849
m, p -Xylene	3.91×10^4	8.86	3.53×10^4	8	3.13×10^4	7.09	5570.	1.264
o-Xylene	1.17×10^4	2.66	1.06×10^4	2.4	4180.	0.949	1330.	0.3024

Model Parameters			
Lo : 170.00 m ³ / Mg			
k : 0.0500 1/yr			
NMOC : 2200.00 ppmv			
Methane : 64.0000 % volume			
Carbon Dioxide : 36.0000 % volume			
Landfill Parameters			
Landfill type : Co-Disposal			
Year Opened : 1974 Current Year : 2004 Closure Year: 2004			
Capacity : 303128 Mg			
Average Acceptance Rate Required from			
Current Year to Closure Year : 0.00 Mg/year			
Model Results			
Year	Refuse In Place (Mg)	NMOC Emission Rate	
		(Mg/yr)	(Cubic m/yr)
1975	3.031E+04	3.175E+00	8.857E+02
1976	6.063E+04	6.195E+00	1.728E+03
1977	9.094E+04	9.067E+00	2.530E+03
1978	1.213E+05	1.180E+01	3.292E+03
1979	1.516E+05	1.440E+01	4.017E+03
1980	1.819E+05	1.687E+01	4.707E+03
1981	2.122E+05	1.922E+01	5.363E+03
1982	2.425E+05	2.146E+01	5.987E+03
1983	2.728E+05	2.359E+01	6.581E+03
.	.	.	.
2001	3.031E+05	1.095E+01	3.054E+03
2002	3.031E+05	1.041E+01	2.905E+03
2003	3.031E+05	9.906E+00	2.764E+03
.	.	.	.
2201	3.031E+05	4.970E-04	1.387E-01
2202	3.031E+05	4.728E-04	1.319E-01
2203	3.031E+05	4.497E-04	1.255E-01

Figure 6-16. Bush Valley - Example LandGEM Model Run Output.

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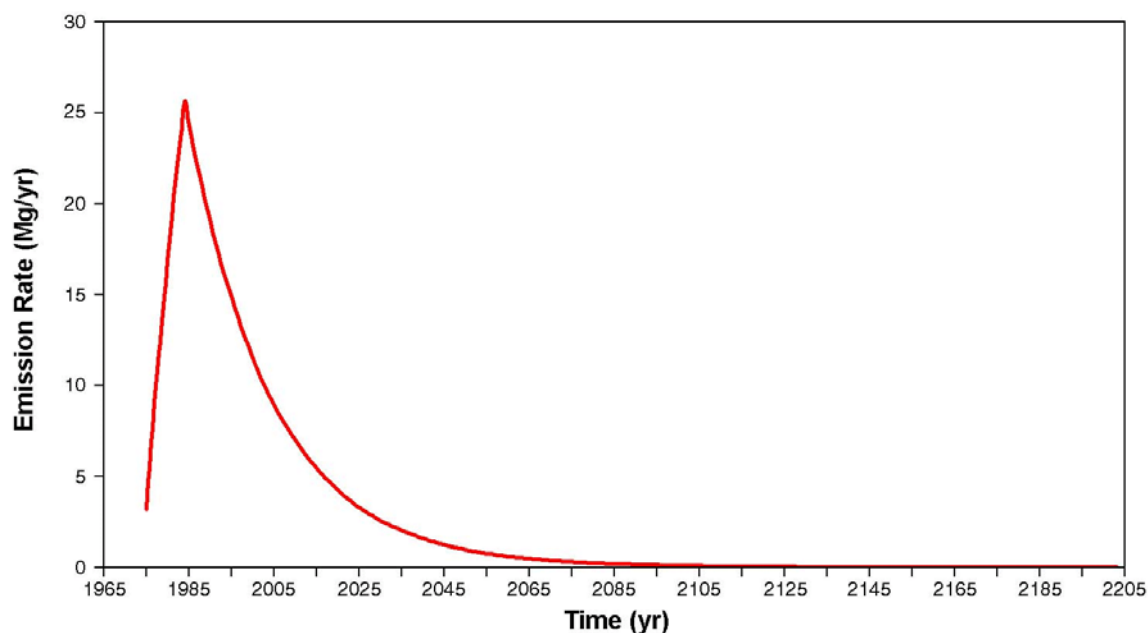


Figure 6-17. Bush Valley - NMOE Emission Rates versus Time.

Table 6-16. Bush Valley - Emission Rates of COPCs by Parcel.

COPCs	Parcel 1 2003 (Mg/yr)	Parcel 2 2003 (Mg/yr)	Parcel 3 2003 (Mg/yr)	Parcel 4 2003 (Mg/yr)
NMOE	9.91	1.48	1.38	8.54
1,1,1-Trichloroethane	6.27×10^{-4}		3.55×10^{-5}	3.54×10^{-5}
1,1-Dichloroethene	1.52×10^{-4}		3.44×10^{-5}	2.06×10^{-5}
1,2-Dichloroethane	3.62×10^{-4}		2.46×10^{-4}	5.25×10^{-5}
Benzene	8.33×10^{-3}	2.08×10^{-4}	2.84×10^{-4}	3.48×10^{-4}
Carbon tetrachloride				
Chlorobenzene	1.76×10^{-3}	2.03×10^{-4}	3.79×10^{-4}	1.31×10^{-4}
Chloroethane	1.85×10^{-3}	8.88×10^{-5}	1.26×10^{-4}	1.47×10^{-4}
Chloroform				
1,4-Dichlorobenzene	2.15×10^{-3}	3.67×10^{-4}	1.82×10^{-4}	6.23×10^{-5}
Methylene chloride	8.43×10^{-4}		1.39×10^{-3}	7.65×10^{-5}
Tetrachloroethene	5.29×10^{-3}		1.85×10^{-3}	7.91×10^{-4}
Toluene	5.39×10^{-2}	4.36×10^{-4}	1.71×10^{-3}	5.37×10^{-5}
Trichloroethene	4.05×10^{-3}		1.35×10^{-3}	5.71×10^{-4}
Vinyl chloride	8.69×10^{-3}	1.18×10^{-4}	4.49×10^{-4}	2.82×10^{-4}
m,p-Xylene	4.92×10^{-2}	7.30×10^{-3}	6.67×10^{-3}	7.09×10^{-4}
o-Xylene	1.48×10^{-2}	2.19×10^{-3}	8.94×10^{-4}	1.69×10^{-4}

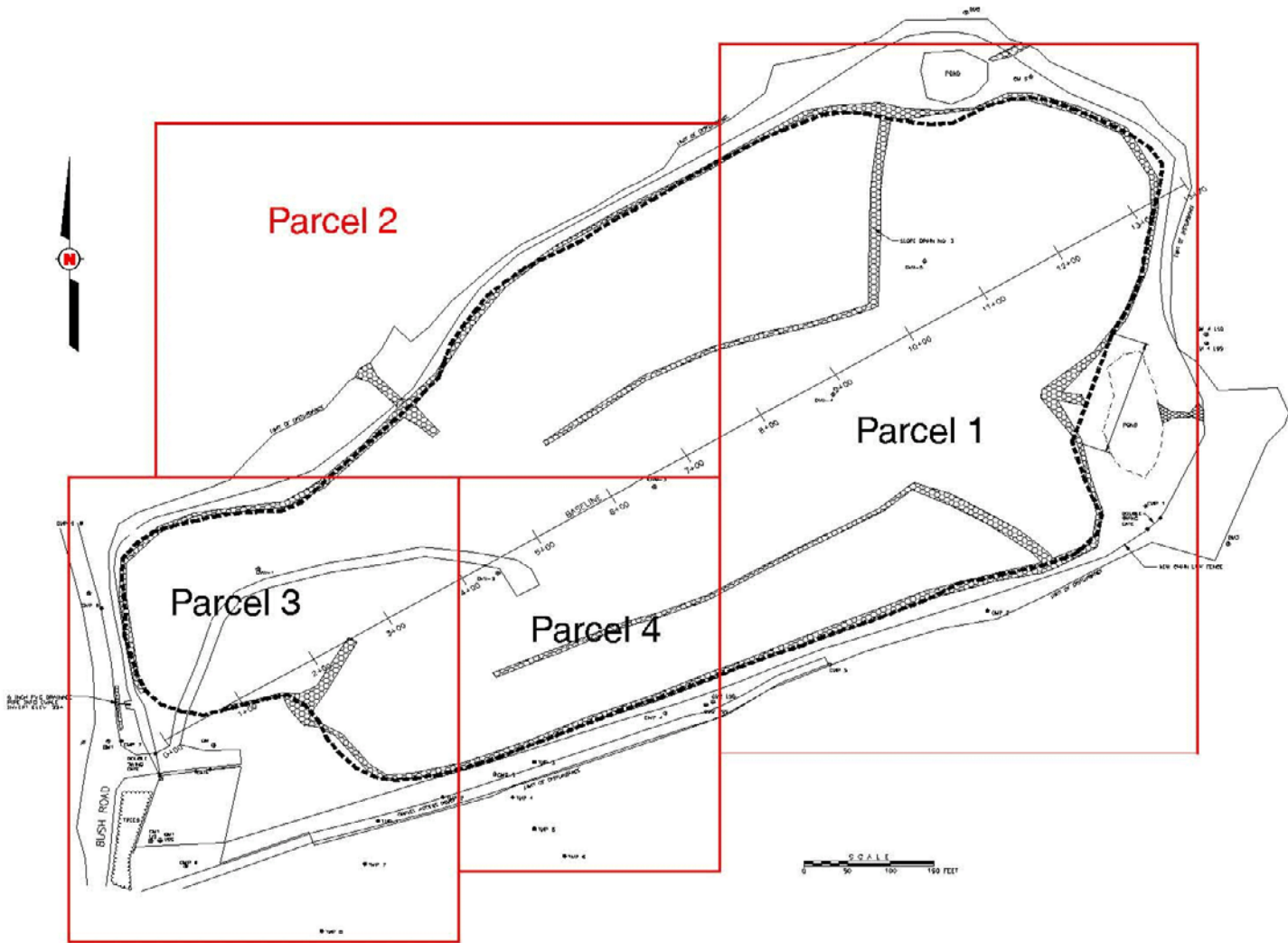


Figure 6-18. Bush Valley - Defined Modeling Areas for SCREEN3.

Table 6-17. Bush Valley - Maximum Predicted Ambient Air Annual Concentrations.

COPC	Parcel 1		Parcel 2		Parcel 3		Parcel 4		Total
	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	(ppmv)	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)
Methane		4449.		1102.		1301.		1251.	8103.
Carbon Dioxide		6867.		1854.		1871.		1931.	1.252×10^4
NMOC		82.17		19.11		19.17		19.65	140.1
1,1,1-Trichloroethane	9.41×10^{-7}	5.204×10^{-3}		0.000	8.94×10^{-8}	4.948×10^{-4}	1.47×10^{-7}	8.132×10^{-4}	6.512×10^{-3}
1,1-Dichloroethene	3.13×10^{-7}	1.260×10^{-3}		0.000	1.19×10^{-7}	4.793×10^{-4}	1.17×10^{-7}	4.726×10^{-4}	2.212×10^{-3}
1,2-Dichloroethane	7.29×10^{-7}	3.002×10^{-3}		0.000	8.32×10^{-7}	3.425×10^{-3}	2.93×10^{-7}	1.206×10^{-3}	7.633×10^{-3}
Benzene	2.13×10^{-5}	6.907×10^{-2}	8.26×10^{-7}	2.684×10^{-3}	1.22×10^{-6}	3.959×10^{-3}	2.46×10^{-6}	7.999×10^{-3}	8.371×10^{-2}
Chlorobenzene	3.11×10^{-6}	1.463×10^{-2}	5.57×10^{-7}	2.620×10^{-3}	1.12×10^{-6}	5.288×10^{-3}	6.42×10^{-7}	3.020×10^{-3}	2.556×10^{-2}
Chloroethane	5.73×10^{-6}	1.538×10^{-2}	4.26×10^{-7}	1.144×10^{-3}	6.54×10^{-7}	1.754×10^{-3}	1.26×10^{-6}	3.383×10^{-3}	2.166×10^{-2}
1,4-Dichlorobenzene	2.92×10^{-6}	1.783×10^{-2}	7.73×10^{-7}	4.725×10^{-3}	4.16×10^{-7}	2.544×10^{-3}	2.34×10^{-7}	1.433×10^{-3}	2.654×10^{-2}
Methylene chloride	1.98×10^{-6}	6.991×10^{-3}			5.47×10^{-6}	1.931×10^{-2}	4.98×10^{-7}	1.759×10^{-3}	2.806×10^{-2}
Tetrachloroethene	6.35×10^{-6}	4.384×10^{-2}			3.74×10^{-6}	2.583×10^{-2}	2.63×10^{-6}	1.819×10^{-2}	8.786×10^{-2}
Toluene	1.17×10^{-4}	0.4473	1.47×10^{-6}	5.617×10^{-3}	6.21×10^{-6}	2.380×10^{-2}	3.22×10^{-7}	1.235×10^{-3}	0.4779
Trichloroethene	6.17×10^{-6}	3.360×10^{-2}			3.46×10^{-6}	1.884×10^{-2}	2.41×10^{-6}	1.313×10^{-2}	6.557×10^{-2}
Vinyl chloride	2.77×10^{-5}	7.205×10^{-2}	5.86×10^{-7}	1.524×10^{-3}	2.41×10^{-6}	6.258×10^{-3}	2.49×10^{-6}	6.476×10^{-3}	8.631×10^{-2}
m, p -Xylene	9.25×10^{-5}	0.4077	2.14×10^{-5}	9.415×10^{-2}	2.11×10^{-5}	9.305×10^{-2}	3.7×10^{-6}	1.631×10^{-2}	0.6112
o-Xylene	2.78×10^{-5}	0.1224	6.14×10^{-6}	2.825×10^{-2}	2.83×10^{-6}	1.247×10^{-2}	8.8×10^{-7}	3.882×10^{-3}	0.1670

Table 6-18 identifies target media concentrations corresponding to risk/hazard based concentrations for ambient air in residential settings. Only air concentrations that satisfy both the prescribed cancer risk level and the target hazard index are included in this table. The approach described here also can be used to evaluate chemicals not listed in the tables. The reader is cautioned to recognize that the concentrations presented in Table 6-18 are screening levels. They are not clean up levels, or preliminary remediation goals, nor are they intended to supercede existing criteria of the lead regulatory authority. The lead regulatory authority for a site may determine that criteria other than those provided herein are appropriate for their specific site or area.

Table 6-18. Bush Valley - Risk Assessment Analysis.

CAS No.	Chemical	Basis of Target Concentration	Target Ambient Air Concentration to Satisfy Both the Prescribed Risk Level and the Target Hazard Index (R=10 ⁻⁶ , HI=1) C _{target}		Total Predicted Ambient Air Concentrations (µg/m ³)
			Cancer (µg/m ³)	Non-cancer (µg/m ³)	
71556	1,1,1-Trichloroethane	NC ^a		2.2×10 ⁺³	6.5×10 ⁻³
75354	1,1-Dichloroethylene	NC		2.0×10 ⁺²	2.2×10 ⁻³
107062	1,2-Dichloroethane	C ^b	7.4×10 ⁻²	9.4×10 ⁻²	7.6×10 ⁻³
71432	Benzene	C	0.25	0.31	8.4×10 ⁻²
108907	Chlorobenzene	NC		60.	2.6×10 ⁻²
75003	Chloroethane (ethyl chloride)	C	2.3	1.0×10 ⁺⁴	2.2×10 ⁻²
106467	1,4-Dichlorobenzene	C	0.31	8.0×10 ⁺²	2.7×10 ⁻²
75092	Methylene chloride	C	4.1	5.2	2.8×10 ⁻²
127184	Tetrachloroethylene	C	0.32	0.81	8.8×10 ⁻²
108883	Toluene	NC		4.0×10 ⁺²	0.48
79016	Trichloroethylene	C	1.7×10 ⁻²	37.	6.6×10 ⁻²
75014	Vinyl chloride (chloroethene)	C	0.11	1.0×10 ⁺²	8.6×10 ⁻²
108383	m, p-Xylene	NC		1.1×10 ⁺²	0.61
95476	o-Xylene	NC		1.1×10 ⁺²	0.17

^a NC = non-cancer risk.

^b C = cancer risk.

The sources of chemical data used in the calculations necessary to create Table 6-18 were EPA's Superfund Chemical Data Matrix (SCDM) database or EPA's Water 9 database whenever a chemical was not included in the SCDM database. EPA's IRIS is the preferred source of carcinogenic unit risks and non-carcinogenic RfCs for inhalation exposure. The following two sources were consulted, in order of preference, when IRIS values were not available: provisional toxicity values recommended by EPA's NCEA and EPA's HEAST. If no inhalation toxicity data could be obtained from IRIS, NCEA, HEAST, extrapolated unit risks

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and/or RfCs were derived by using toxicity data for oral exposure (cancer slope factors and/or reference doses, respectively) from these reference sources using the same preference order. It is recognized that toxicity databases such as IRIS are constantly being updated; this table is current as of August 2002. Users of this guidance are strongly encouraged to research the latest toxicity values for contaminants of interest from the sources noted above.

The ambient air concentrations in the table are risk-based screening levels calculated following an approach consistent with that presented in EPA 2001. Separate carcinogenic and non- carcinogenic target concentrations were calculated for each compound when both unit risks and reference concentrations were available. When inhalation toxicity values were not available, unit risks and/or reference concentrations were extrapolated from oral slope factors and/or reference doses, respectively. For both carcinogens and noncarcinogens, target air concentrations were based on an adult exposure scenario and assume maximum exposure of an individual (i.e., exposure to contaminants 24 hours per day, 7 days per week, over 70 years). An inhalation rate of 20 m³/day and a body weight of 70 kg are assumed and have been factored into the inhalation unit risk and reference concentration toxicity values.

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Appendix A

Monitoring Landfill Gas Chemicals of Potential Concern (COPCs)

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1.0 Introduction

Monitoring air pollutants at MSW landfills through various routes of exposure is required in almost all regulations. Monitoring provides the regulator with information and data that can be used to determine compliance with applicable emission limits. Specifically, monitoring requirements are identified in the NSPS and EG regulations, the RCRA regulations, and as part of any risk evaluation procedures performed at MSW landfills. Each of these regulations specify specific monitoring procedures identified in various Federal reference methods and compendia methods used in assessing MSW landfill gas emissions applicable to the regulations.

The NSPS (40 CFR 60, Subpart WWW) and EG (Subpart Cc) promulgated under Section 111(b) of the CAA are in place to control emissions of NMOCs from MSW landfills. As discussed in Chapter 4, NMOC is used under the NSPS and EG as a surrogate measurement of VOCs. As discussed in Chapter 4, the determination of the need for controls under the NSPS/EG is a three-tier protocol, for which sampling plays a major role:

- Tier 1 determination of the NMOC emission rate is performed through the application of the LandGEM model using default input parameter values.
- Tier 2 involves determining the NMOC concentration generated by the landfill via Federal Reference Method 25C or Federal Reference Method 18.
- Tier 3 employs Federal Reference Method 2E for determining the site-specific methane generation rate constant.

In addition, the NSPS and EG regulations specify that each landfill must meet a surface methane operational standard. Compliance with the standard is determined by Federal Reference Method 21, a portable organic vapor analyzer, for measuring surface concentrations of methane along the entire perimeter of the collection area and along a serpentine pattern spaced 30 meters apart for each collection area on a quarterly bases. The portable organic vapor analyzer must meet all instrument specifications provided in Section 3 of Federal Reference Method 21.

For an evaluation of the risks from exposure to MSW landfill gases, the route of human exposure is inhalation of COPCs transported by the landfill gas. In addition, State and Federal requirements dictate that the MSW landfill must be in compliance with air pathways ARARs, as appropriate. The three routes of exposure are ambient air, subsurface convection, and subsurface vapor intrusion. Each of these pathways must be considered by the RPM or OSC:

- For assessing the ambient air pathway, EPA's *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* is used to quantify the various COPCs. For instance, Compendium Method TO-10/13A is used for quantifying semi-volatiles/PAHs, Compendium Method TO-15 for VOCs, Compendium Method TO-12 for NMOCs, Inorganic Compendium Method IO-5 for mercury and Inorganic Compendium Methods IO-1/IO-2 for suspended particulate matter.
- For assessing subsurface convection, Federal Reference Method 21 can be employed to quantify subsurface methane vapor transport and indoor concentrations.
- Finally, for subsurface vapor intrusion into a building from contaminated ground water or for vapor intrusion from subsurface convection, EPA's *Compendium of Methods for the Determination of Air Pollutants in Indoor Air* is used to quantify the various COPCs. Method IP-1-A uses specially-treated canisters and portable gas chromatographs for initial screening investigation for VOCs. Method IP-7/8 uses polyurethane foam for capture of pollutants with subsequent analysis by GC/MS for quantifying dioxin furans, polychlorinated biphenyls (PCBs) and semi-volatiles. Method IP-10 provides for monitoring of particulate matter using a single-stage impactor.

Under RCRA, Subtitle D, the owners or operators of all MSW landfill units must implement a routine

methane monitoring program to ensure that the standards set forth in the regulations are met. The frequency and type of methane monitoring system must be based on site-specific soil conditions. Federal Reference Method 21 meets the monitoring specifications and other requirements of the Subtitle D rules.

The purpose of this Appendix is to provide the RPM and/or the OSC with information associated with the monitoring techniques and instrumentation needed to quantify landfill gas constituents. This appendix discusses the nature of landfill gases, the development of a target compound list (TCL), technologies for monitoring landfill gases, including time-integrated and real-time monitoring for inorganic, organic, and suspended particulate matter (SPM). Additionally, this appendix provides guidance on the use and application of Federal Reference Methods (FRMs) and Compendia methods for quantifying COPCs found in landfill gas.

2.0 Municipal Solid Waste Landfill Air Emission Mechanisms

Emissions from municipal solid waste (MSW) landfill sites are classified as either point or area sources. Point sources include landfill gas vents and landfill gas combustion equipment exhausts (controlled emissions), whereas area sources are generally associated with fugitive emissions (e.g., from landfill cover materials, lagoons, material handling and contaminated surface areas).

Air contaminant emissions can be classified into two categories (i.e., gas phase emissions and particulate matter emissions). The mechanisms associated with gas phase emissions are quite different from those associated with particulate matter releases.

2.1 Gas Phase Emissions

Gas phase emissions primarily involve organic compounds but can also include inorganic compounds and certain metals. Gaseous emissions from an MSW landfill site can be released through a variety of mechanisms, including:

- Volatilization,
- Biodegradation,
- Photo-decomposition,
- Hydrolysis, and
- Combustion.

Volatilization is typically the most important mechanism for air releases and occurs when molecules of a dissolved or pure substance escape to an adjacent gas layer. For wastes at the surface, this action results in immediate transport into the atmosphere. Volatilization from subsurface wastes results in a concentration gradient in the soil-gas from the waste to the surface. The rate of emissions is usually limited by the rate of diffusion of contaminants to the soil-air interface. For MSW landfills still generating methane, convective vapor transport due to pressure gradients can also be significant. The rate of volatilization of contaminants at a soil-air boundary is a function of the concentration and properties of the escaping chemical (molecular weight, vapor pressure, Henry's Law constant, boiling temperature), soil properties (moisture, temperature, clay content, and organic content), and properties of the air at soil level (temperature, relative humidity, and wind speed). The rate of volatilization from liquid surfaces depends on the concentration of the contaminants at the liquid-air interface. Any factors that enhance mixing in the bulk liquid and replenishment of contaminants in the boundary layer will enhance the volatilization rate.

2.2 Particulate Emissions

Particulate matter (PM) emissions from MSW landfill sites can be released through wind erosion, mechanical disturbances, and combustion. COPCs, such as semi-volatiles (polycyclic aromatic hydrocarbons—PAHs), dioxin/furans (D/Fs), polychlorinated biphenyls (PCBs), and metals, can also

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be adsorbed onto PM and thereby transported with the inert material.

The importance of each of these mechanisms varies as a function of source type. The hazardous constituents of concern in a particulate release (which include PM and semi-volatiles) may involve constituents that are either absorbed or adsorbed onto the particulate or constituents that actually comprise the particulate. These constituents may include volatile and semi-volatile organic compounds, metals, and non-volatile toxic organic compounds.

Significant atmospheric dust can arise from the disturbance of soil exposed to the air. Dust generated from these area sources is referred to as “fugitive” because it is not discharged to the atmosphere in a confined stream. The dust generation process is caused by two physical phenomena: (1) entrainment of dust particles by the action of wind erosion of an exposed surface under moderate-to-high wind speeds and (2) pulverization and abrasion of surface materials by mechanical disturbances.

For airborne particles, the particle size distribution plays an important role in inhalation exposure. Large particles tend to settle out of the air more rapidly than small particles but may be important in terms of non-inhalation exposure. Very small particles (i.e., those that are less than 10 μm in diameter) are considered to be respirable and, thus, present a greater inhalation health hazard than the larger particles.

2.3 Transport and Diffusion

Once released to the ambient air, a contaminant or COPC is subject to simultaneous transport and diffusion processes in the atmosphere. Atmospheric transport/diffusion conditions are significantly affected by meteorological, topographic, and source factors.

The contaminant will be carried by the ambient air, following the spatial and temporal characteristics of the wind flow as determined by the ambient temperatures and the wind direction and speed. The turbulent motions of the atmosphere (as characterized by atmospheric stability conditions) promote diffusion of airborne gases and particulate matter. Thus, the local meteorology during and after the release determines where the contaminant moves and how it is diluted in the atmosphere.

2.4 Transformation, Deposition, and Depletion

Contaminants emitted to the atmosphere are subjected to a variety of physical and chemical influences. Transformation processes can result in the formation of more hazardous substances or may result in hazardous constituents being converted into less harmful ones. A variety of inorganic and organic materials may be present along with the natural components of the air. The emissions may remain in the atmosphere for a considerable time and undergo a myriad of reactions. Both primary and secondary products are exposed to further changes through oxidation and photochemical reactions. In general, however, these effects are secondary to transport and diffusion in importance and are subject to more uncertainty.

3.0 Defining COPCs

Ambient air around a MSW landfill site is a very complex, dynamic system of interacting chemicals. As previously discussed, the pollutants can be found in the gas phase, in the particulate phase, or in a liquid aerosol surrounded by a gaseous atmosphere. The complex nature of the dynamic air system in and around a MSW landfill site controls the complexity of the solution of sampling method and analytical requirements in the identification and quantification of these chemicals. Each COPC has its own unique characteristics, yet many fall within basic classes such as volatiles, semi-volatiles, aromatics, halogenated compounds, etc.

3.1 Volatile Organic Compounds (VOCs)

VOC is a general term used to describe the gaseous nonmethane organic emissions from a MSW land-

fill. These compounds have vapor pressures greater than 10^{-1} mm Hg and boiling points less than 200 °C. A capped landfill usually maintains a stable temperature between 77 and 150 °F. Temperature rises promote volatilization and chemical reactions, and as a general rule, emissions of VOCs and NMOCs double with every 18 °F increase in temperature. Maximum temperatures usually occur in the first year.

Temperature for years 5 to 10 are typically 100 to 115 °F. VOCs are predominantly found in the gaseous state in the atmosphere, as identified in Table A-1, and illustrated in Figure A-1.

Table A-1. Defining Hazardous Air Pollutants

Category	Vapor pressure (mm Hg)	Boiling point (°C)
PM	$< 10^{-7}$	> 500
SVOCs	10^{-1} to 10^{-7}	200 to 50
VOCs	$> 10^{-1}$	< 200

3.2 Semi-volatile Organic Compounds (SVOCs)

Semi-volatile organic compounds (SVOCs) are not as easily collected or analyzed as the VOCs. However, attention has been focused on resolving the problems associated with SVOCs found around

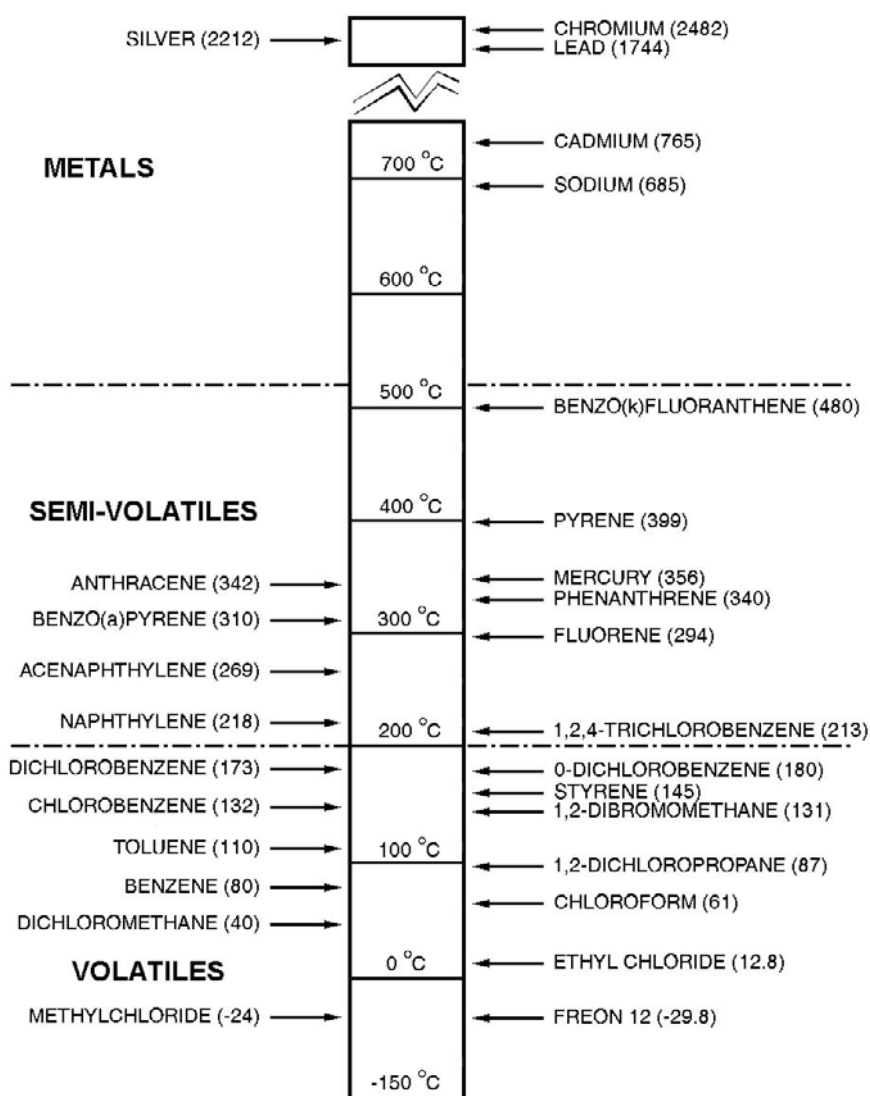


Figure A-1. Example of Defining COPCs by Boiling Point.

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MSW landfill sites. Members of this class include PAHs with three or more fused rings; halogenated compounds such as PCBs; organopesticides with chlorine and phosphorus; and various pesticides and herbicides. Vapor pressures of these compounds range from 10^{-1} to 10^{-7} mm Hg, and their boiling points range from 200 to 500 °C, as illustrated in Table A-1 and Figure A-1. These less volatile compounds are present in the atmosphere, both in gaseous phase and in particle-bound phase. Their point of origin can be landfill gas vents, LFG combustion equipment exhaust, or fugitive emissions from the surface of the landfill.

3.3 Non-volatile Organic Compounds

Ambient air contains relatively low amounts of non-volatile organic compounds, which are organic compounds with vapor pressures less than 10^{-7} mm Hg and boiling points greater than 500 °C. These compounds are almost always found in the condensed particle-bound state. Polycyclic hydrocarbons with more than four rings, and their nitrogenous and oxygenated derivatives, are the major constituents of this category.

3.4 Inorganic Compounds

Inorganic compounds are those compounds with vapor pressures less than 10^{-12} mm Hg. These compounds are almost always found in the particle state. Heavy metals, such as lead, chromium, cadmium, zinc, beryllium copper, and other earth metals represent this category of COPCs.

4.0 Developing a Site-specific Target Compound List and Monitoring Design Elements

Developing a site-specific target compound list (TCL) is a key factor in the long-term monitoring at a MSW landfill site. MSW landfill sites often contain a complex mixture of contaminants, and not every contaminant will pose a significant risk via the air pathway. Selection of too broad a range of compounds can lead to excessive cost, whereas selection of too few may result in not meeting the data quality objectives (DQOs) of the project. In most cases, the selection of a TCL at a MSW landfill site is a compromise between technical feasibility and environmental significance.

The objective of developing a site-specific TCL is to establish a prioritized list of compounds for which there are sampling and analytical protocols and to provide a tool for optimizing the air monitoring design. The TCL includes compounds most commonly found at the MSW landfill site that pose the most significant threat to human health and are most likely to enter the air pathway.

Certain compounds typically are considered to “drive” both the listing of target compounds and the risk assessment as part of the air pathway analysis (APA). These compounds pose the most significant risk during various phases of the life of a MSW landfill. Consequently, the objective of the APA is to focus available resources and effort on those compounds thought to pose the most significant risk rather than including an evaluation of every compound found at the MSW landfill site. The selected analytes, therefore, become the COPCs. Compounds of interest for MSW landfills are categorized into four broad classifications based on the compound and its physical and chemical properties. As previously discussed, the four classifications are:

- NMOCs and VOCs, especially benzene and chlorinated solvents such as vinyl chloride, methylene chloride, chloroform, etc.,
- SVOCs, such as PAHs, pesticides, dioxin/furans, and other semi-volatile inorganic compounds,
- Particulate matter and non-volatile compounds such as asbestos and cyanides, and
- Heavy metals, such as lead, chromium, cadmium, zinc, beryllium, copper, and arsenic.

Table A-2 summarizes the compound classes and the representative compounds in each of the four classifications. Table A-3 provides typical concentrations of the different categories of COPCs in ambient air.

Table A-2. Example of Classification of COPCS (Organic and Inorganic Compounds) for Monitoring Programs at MSW Landfill Sites.

Contaminant type	Compound class	Representative compounds	
Volatile organic compounds	Aromatics	benzene toluene ethylbenzene	total xylenes styrene chlorobenzene
	Halogenated species	carbon tetrachloride chloroform methylene chloride chloromethane 1,2-dichloropropane trans-1,3-dichloropropene cis-1,3-dichloropropene bromoform bromomethane	bromodichloromethane dibromochloromethane 1,1,2,2-tetrachloroethane 1,1,1-trichloroethane 1,1-dichloromethane chloroethane tetrachloroethane trichloroethane vinyl chloride
	Oxygenated species	acetone 2-butanone	2-hexanone 4-methyl-2-pentanone
	Sulfur containing species	carbon disulfide	
	Nitrogen containing species	benzonitrile	
Volatile inorganic compounds	Acids	hydrogen cyanide	hydrochloric acid
	Sulfur containing	hydrogen sulfide	
Semi-volatile organic compounds	Phenols	phenol 2-methylphenol 4-methylphenol 2,4-dimethylphenol 2-chlorophenol 2,4-dichlorophenol 2,4,5-trichloropheno	2,4,6-trichlorophenol pentachlorophenol 4-chloro-3-methylphenol 2-nitrophenol 4-nitrophenol 2,4-dinitrophenol 4,6-dinitro-2-methylphenol
	Esters	bis(2-ethylhexyl)phthalate di-n-butyl phthalate vinyl acetate	di-n-octyl phthalate diethyl phthalate
	Chlorinated	1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene 1,2,4-trichlorobenzene hexachlorobenzene	nitrobenzene 2,6-dinitrotoluene 2,4-dinitrotoluene 3,3-dichlorobenzidine
	Amines	n-nitrosodimethylamine n-nitrosodi-n-propylamine n-nitrosodiphenylamine aniline	2-nitroaniline 3-nitroaniline 4-nitroaniline 4-chloroaniline
	Ethers	bis(2-chloroethyl)ether	bis(2-chloroisopropyl)ether
	Alkadienes	hexachlorobutadiene	hexachlorocyclopentadiene
	Miscellaneous and aromatics	benzoic acid bis(2-chloroethoxy)methane dibenzofuran isophorone	benzyl alcohol hexachloroethane

continued

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Contaminant type	Compound class	Representative compounds	
	Polychlorinated biphenyls (PCBs)	Arochlor 1016 Arochlor 1221 Arochlor 1232 Arochlor 1242	Arochlor 1248 Arochlor 1254 Arochlor 1260
Non-volatiles	Inorganic metals and nonmetals	aluminum antimony arsenic asbestos barium beryllium cadmium calcium chromium cobalt copper iron	lead magnesium manganese nickel potassium selenium silver sodium thallium tin vanadium zinc

Table A-3. Example of Typical Concentrations of Groups of COPCS in the Atmosphere.

Category	Concentration range
PAHs	10–100 ng/m ³
PCBs, Dioxins, Furans	1–10 pg/m ³
Pesticides/Herbicides	10–100 ng/m ³
Particles/Metals	10–50 µg/m ³
Volatiles	0.5–5.0 ppb

Monitoring all emissions at an MSW landfill site is not realistic; so, when developing an air monitoring program, target compounds are usually selected to represent either a broad classification or a specified class of compounds. These target compounds (i.e., indicator compounds), at a minimum, should include all contaminants with concentrations greater than or equal to 10% of the appropriate health-based action level.

This approach provides a practical basis to address the large number of potentially emitted compounds at the site. Many factors should be reviewed in the decision process for selecting COPCs, including:

- Types of air contaminants (organic, inorganic, biohazard),
- Physical state of air contaminants (gas, liquid, solid),
- Level of air contaminant emissions,
- Air monitoring objectives,
- Potential availability of standard sampling and analytical techniques,
- Homogeneity of the waste material, and
- Potential analytical interferences from the site.

The rate at which gaseous contaminants are emitted into the air depends, in part, on their volatilities, which depend on vapor pressures and Henry's Law constants. Highly volatile compounds will typically be emitted at a higher rate than compounds of similar concentration in the waste but with lower volatility. Computer models that rely, in part, on compound vapor pressure and Henry's Law data as input are often used to estimate potential emissions to the air. Emission rates can then be used as input to an atmospheric dispersion model to gauge concentration levels at the property line of the MSW landfills and at off-site receptors. Semi-volatile and nonvolatile compounds may also be of concern

when they exist in significant concentrations within the waste or are contained in any wind-blown dust. It often is not practical to monitor for every compound present in the waste or ambient air because of the limitations of available technical or financial resources. In these cases, potential target compounds should be ranked in terms of predicted concentration levels and applicable health-based action levels. Note that the potential for adverse health effects varies from compound to compound, and the health-based action levels may vary by orders-of-magnitude between compounds with relatively similar structures and physical properties. For example, 1,2-dichloroethane is considered to be a much more potent carcinogen than 1,1-dichloroethane, and benzene is considered to pose a much more significant risk than equal amounts of toluene or xylene. Therefore, the most significant compounds at the site from a health risk standpoint might not necessarily be those present in higher concentrations in the waste.

Basically, the objective is to find the type and/or species of COPCs that could be used to assess emissions from the site (both point source and fugitive) and their air quality impact on the surrounding community. The ideal target compound should be:

- Found in air emissions from the site in a fixed ratio to other constituents,
- Non-reactive or stable species,
- Found at levels above analytical detection limits,
- Unique to the MSW landfill site, and
- Of known toxicity and acceptable exposure criteria.

The objective of developing a site-specific TCL is to provide a prioritized list of COPCs associated with the MSW landfill site. The TCL should be composed of those compounds that are most commonly found at the MSW landfill site, pose the most significant threat to human health, and that are likely to enter the air pathway. The number of target compounds to be monitored varies depending on the DQOs of the MSW landfill site monitoring program, as identified in Table A-4.

Table A-4. Relationship Between Monitoring Design Elements and MSW Landfill Site Activities.

Design element	Site Activities		
	Level I: Screening or baseline study	Level II: Short-term investigation	Level III: Long-term investigation
Number of target compounds	Multiple compound classes; full analyte list	1–20	<10
Data quality objectives	Identify compounds accurately; semi-quantitatively for NMOCs and methane	Quantify level of specified compound(s); NMOC and methane	Quantify level of specified compound(s)
Sampling			
Period	24 hours	8–24 hours	24 hours
Duration	5 days to 1 year	Duration of investigation	5 days to 1 year
Frequency	Daily to once every 6 days	Daily	Daily to quarterly
Type of sampling	Mobile, walking the site and taking a sample every 30 meters along the path and along the perimeter	Fixed or mobile site from vent tubes, bore holes, sample wells, or perimeter air monitoring stations	Fixed or mobile site from vent tubes, bore holes, sample wells, or perimeter air monitoring stations
			continued
Monitoring method characteristics	Low detection limits Applicable to broad range of compounds Typically portable FIDs/PIDs	Rapid data turnaround Low detection limits Specific target compound list	Low detection limits Specific target compound list

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5.0 Composition of Landfill Gas

Landfill gas is made up primarily of methane (CH₄) and carbon dioxide (CO₂), but small quantities of other gases are also present. EPA has determined that some of these compounds are carcinogenic or associated with non-carcinogenic health effects. A list of COPCs often found in landfill gas is provided in Table A-5.

Table A-5. COPCs Commonly Found in LFG.

Classification	Analyte
Very Volatile Organic	Methane
	Non-methane Organic Compounds (NMOCs)
Speciated Volatile Organic Compounds	1,1,1-Trichloroethane (Methyl Chloroform)
	1,1-Dichloroethene (Vinylidene Chloride)
	1,2-Dichloroethane (Ethylene Dichloride)
	Acrylonitrile
	Benzene
	Carbon Tetrachloride
	Chlorobenzene
	Chloroethane (Ethyl Chloride)
	Chlorofluorocarbons (as Dichlorodifluoromethane)
	Chloroform
	Dichlorobenzene ^a
	Ethylene Dibromide
	Dichloromethane (Methylene Chloride)
	Perchloroethylene (Tetrachloroethylene)
	Toluene
	Trichloroethylene (Trichloroethene)
	Vinyl Chloride
	Xylenes (all isomers)
Inorganic Constituents	Mercury (total) ^b
	Hydrogen Sulfide

^a The para-isomer is a CAA Title III listed HAP.

^b No data was available to speciate total mercury into the elemental and organic forms.

6.0 Technologies for Monitoring COPCs at MSW Landfill Sites

A variety of sampling methods can be used to monitor emissions from MSW landfill sites. The methods vary according to sample type (i.e., volatile compounds, semi-volatile compounds, inorganics, and particulate-borne compounds), sample duration and detectability, and applicability to the monitoring objectives of the program. The greatest number of available methods for any one type are for the volatile fraction. Semi-volatile pollutants exist in both the vapor and particulate phases, so the sampling methodology must address both. Finally, the concentration of particulate-borne contaminants (inorganic and non-volatile organic) can be monitored by collection of the total mass loading during sampling.

Sampling techniques may be divided into broad classes, regardless of the analyte of concern. They are grab sampling, time-integrated sampling, real-time monitoring, passive sampling, and portable real-time monitoring.

- **Grab sampling**—grab sampling involves collecting an instantaneous air sample. This technique usually requires some form or type of container (i.e., canister, TEDLAR bag, etc.) to contain the instantaneous sample.
- **Time-integrated sampling**—time-integrated sampling involves collecting a sample over a fixed time period (e.g., 1 hr, 4 hr, 8 hr or 24 hr) and provides a single, integrated value. Methods included in time-integrated sampling are whole air canister sampling, solid adsorbent tube monitoring, and most particulate matter and semi-volatile collection systems.
- **Real-time monitoring**—real-time monitoring involves sample extraction, conditioning, analyzing, and reporting within a fixed time period, usually less than 15 minutes.
- **Passive sampling**—passive sampling involves collecting a sample over an extended period of time without assistance from a pump. This sampling technique is usually exclusively associated with monitoring volatile organics.
- **Portable real-time monitoring**—portable real-time systems provide sampling and analysis of a limited target compound set. The use of portable systems allows one to survey the site and identify hot spots, thus making it a very feasible tool during the investigation.

6.1 Grab Sampling

Grab sampling involves extracting a sample at a single point-in-time. The hardware for this sampling is usually a whole-air sample container (i.e., specially-treated canister, glass sampling bulb, Tedlar bags, or solid adsorbent tubes for colorimetric gas detection). In the grab sample mode, a sample is taken over a very short period of time, from a few seconds to a few minutes.

Grab sampling is usually used in EPA's air pathway analysis program as a screening technique to identify contaminants that might be present in an area of interest and to determine their approximate concentrations. As an example, grab sampling can be used to collect volatile organics during the site investigation stage using Tedlar bags or specially-treated canisters to help develop future long-term monitoring plans or to assess the preliminary risks at the site.

Some of the advantages of grab sampling are that the methodology is simple to apply and sampling costs are at a minimum. Several disadvantages, however, are associated with grab sampling. One major disadvantage is that the value acquired is a single point in time and cannot be related to typical health effect exposure durations. Another disadvantage is that the sample volume acquired is relatively small, thus requiring very sensitive analytical techniques if the data is to be used for comparison with ambient air regulatory limits. Finally, inward and outward diffusion of gases in some of the collection containers has been observed, thus creating uncertainty in the data.

6.2 Time-Integrated Sampling

This category of monitoring is the most commonly used technique for monitoring COPCs at MSW landfill sites. Time-integrated is most applicable if the pollutant is present in very low concentrations because sampling can be conducted long enough to provide the analytical system sufficient sample to meet required detection limits. Appropriate time-integrated sampling techniques are available for collecting volatiles, semivolatiles, inorganics, and PM in the ambient air.

In time-integrated sampling, the sampling period can be as short as minutes or as long as weeks or months depending upon the detection limits associated with the analytical system. The results from the analysis of integrated samples are expressed as average concentrations over the sampling period.

Integrated sampling for PM can be done by high and low volume samplers, dichotomous samplers, or size-select inlet samplers. The sophistication of the samplers ranges from manually operated hand-held units to fully automated units that can run for weeks unattended.

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Integrated sampling for gaseous pollutants can be done by extracting a sample over a period of time through solid absorbents, specially-treated canisters, impingers, or other collection devices that can capture the analytes of interest over a period of time. In general, the greater the sampling time, the more analyte is trapped on the collection media, thus allowing for lower health-based detection limits. Thus, integrated sampling methods may not be adequate for evaluating compliance with short-term (e.g., 15 min, 1 hr) action levels that might be imposed at the site boundary. As an example, a high-volume particulate monitor at the site boundary may not be adequate to determine compliance with a 1-hr emission limit for selected inorganic metals. Integrated sampling methods are therefore useful for determining pollutant concentrations when the regulatory limit is based on a time similar to the 8-hr personnel exposure level or EPA's 24-hr national ambient air quality standards (NAAQS). For some analytes, like semivolatiles, a sampling period of 72 hr may be required to obtain adequate sample to meet the desired health-based detection limits.

Integrated sampling techniques offer additional advantages. They can be cost effective, require fewer personnel than continuous monitoring and are sufficiently flexible to achieve the detection sensitivity to meet the health-based detection limits needed in most regulatory monitoring programs. In addition, samples can be analyzed at a more convenient time or place offsite. Several drawbacks of integrated sampling include the lack of immediate feedback on the data that is acquired, thus preventing modification of activities on site. In addition, time-integrated sampling methods typically do not give site decision makers timely data so that they can determine worker and community acute exposure to pollutants or the need for implementing emission controls. Another disadvantage is that short-term information is also lost. Finally, time-integrated monitoring requires the collected sample to be transported to another location for analysis, thus leading to possible sample integrity problems involving sample deterioration, loss of analytes, and contamination from the surrounding environment.

6.3 Real-Time Monitoring

Real-time monitoring refers to methods that provide nearly instantaneous concentration values, thus allowing multiple measurements over a very short time period of several minutes. In general, real-time means the ability to extract, condition, concentrate, analyze, and report data nearly instantaneously. The samples may be analyzed directly at the collection point, or the sample may be transported through heat-traced lines to a central analytical center for analysis. In the former situation, a single analytical system is used at each of the sampling points around the MSW landfill site or from vent tubes at the site. In the latter case, a single analytical device is used to analyze samples from multiple sampling points around the MSW landfill site. In this case, the analytical system cycles through each of the sampling points in the network. Analytical systems may involve gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) or mass spectrometry/mass spectrometry (MS/MS).

Real-time monitoring usually occurs when personnel at the MSW landfill site must make timely decisions on the emissions from the site. Real-time monitoring also enables the investigator to see peak, short-term concentrations that may have important health effects. Variations in concentration as a function of time can be correlated with source emissions. The major advantage that real-time monitoring has over portable real-time monitors is that most portable monitors react with entire classes of compounds and tend not to be specific for a given compound that might be of concern. As an example, photo-ionization detectors (PID) are very sensitive to aromatic hydrocarbons but significantly less sensitive to aliphatic hydrocarbons or methane. In essence, a portable system does not have the capability to differentiate between compounds if it does not have a GC column attached to it.

Although real-time monitoring systems have numerous benefits, they also have disadvantages. Such systems are expensive and require frequent calibration and routine maintenance. In addition, real-time systems are usually complex, requiring highly trained field personnel, rigorous quality-control (calibration) procedures, and independent performance audits of routine monitoring and data handling

operations. Finally, securing electrical power and a suitable location for housing the real-time system and the adaptation of sampling lines and cables for the system can require long-term planning and entail considerable expense.

6.4 Passive Sampling

In recent years, the development of passive sampling devices (PSD) has drawn much attention. These devices sample by means of gas diffusion or permeation of the COPC (usually VOCs or volatile inorganic compounds) on an adsorbent (i.e., Tenax, charcoal, CarboTrap 300) rather than by means of a pump. They have been shown to be simple, convenient, inexpensive, and valid alternatives for assessing time-weighted average concentrations for personal exposure monitoring.

Analysis of adsorbed compounds on sampling tubes is done by thermal desorption and chromatographic separation. Specificity can be introduced into a passive sampling technique by choice of a suitable adsorbent substrate that is unique to capturing a specific compound. As an example, a passive sampler using chemically-coated glass fiber filter has been developed for formaldehyde. A comparison of recoveries of trichloroethylene from active charcoal tubes and a thermal desorbable personal monitor revealed the passive sampler to exhibit better recovery efficiency. A personal dosimeter based on molecular diffusion and direct detection by room temperature phosphorescence has been developed to monitor vapors of polynuclear aromatics.

6.5 Portable Real-Time Monitoring

Probably one of the most attractive sampling and analysis approaches is that of portable sampling methods based upon real-time monitoring. Portable sampling techniques are mostly used in screening applications at MSW landfill sites. Portable monitoring allows instantaneous results to be acquired so on-site decisions can be made for the protection of workers and off-site communities. Portable monitoring allows rapid turn-around of data with relatively inexpensive instrumentation.

Two of the most common detectors utilized in portable gas sampling techniques are portable flame ionization detectors (FIDs) and PIDs. These detectors, used in conjunction or separately, are generally used to give background levels of NMOCs, methane, and total VOCs. Portable sampling techniques are used to identify hot spots of NMOC, CH₄, or total VOCs within a test locale. Two of the most important attributes of these detectors are their ever-increasing levels of sensitivity and their ability to specifically characterize and/or identify VOCs when used in conjunction with a chromatographic column.

The operation of a FID involves the pollutant entering a flame where it is mixed with hydrogen and burns. Ions and electrons formed in the flame enter an electrode gap, decreasing the gap resistance, thus permitting a current to flow. The flow of electrons determines the pollutant concentration. The FID is a universal detector, responding to a host of organic compounds and classes. One of the major advantages of the FID is its lack of response to air and water. The FID therefore serves as a basis for most commercially available “total hydrocarbon” and “non-methane hydrocarbon” analyzers. The detection limits for most FIDs is about 100 ppbv.

Portable PIDs operate on the principle of photo ionization. In operation, the gas stream is subjected to a high-intensity beam of UV radiation from a lamp of a particular energy. If the molecule ionization potential is lower than that of the lamp, absorption occurs by the gas molecule, leading to the formation of a positive ion and free electron. The positive ion is collected at the electrode and the resultant current is directly proportional to the analyte concentration. Consequently, the ionization potential of the lamp is very important in the detection of certain classes of compounds. Compounds having a high ionization potential will be less easily detected than those with a lower ionization potential. Thus, a PID can readily detect aromatic hydrocarbons but will not detect aliphatic hydrocarbons having a higher ionization potential.

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The manufacturers of photo ionization lamps usually provide lamps in four energy levels:

- 8.3 eV,
- 9.5 eV,
- 10.2 eV, or
- 11.7 eV.

It is more difficult to ionize an alkane (i.e., butane) than a chlorinated aromatic (i.e., chlorobenzene). The selection of the lamp, therefore, allows the user to screen out certain organics based on their ionization potential. If the lamp does not have enough energy to ionize the molecule, the detector does not see it. Consequently, aromatics can be selectively detected in the presence of halogenated hydrocarbons with a low-energy lamp (e.g., 9.5. eV), whereas both groups can be detected with a high-energy lamp (11.0 eV). The sensitivity of the PID is considerably better than the FID in most cases (10 ppb or better). Recent models have shown sensitivity in the sub-parts per billion range.

7.0 Sources of Sampling and Analytical Methodologies

As documented in Chapter 5, various Federal Reference Methods (FRMs) have been identified in the MSW landfill regulations in support of characterizing emissions for these facilities. Although FRMs are specific for a few of the COPCs, there are no methods for many others. It is appropriate that the correct sampling and analytical method be selected. Accurate and reliable data can only be generated if the correct samples of analytical method for each COPC is used. Where possible, the user should use FRMs. However, there are available other sampling and analytical methods which are applicable to quantifying emissions from MSW landfills, as identified in EPA's Compendia. This section will review both the FRMs and Compendia methods which are applicable to MSW landfill gas monitoring.

7.1 Federal Reference Methods

7.1.1 Federal Reference Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. This method can be considered a self-validating method since it requires method performance data for particular applications prior to full use. Direct on-line GC analysis is preferred, but this is frequently impossible for reasons of safety or access. When using direct analysis, a dilution interface is often required. Alternatively, samples of the gas may be captured for later analysis. Several types of sampling media for this alternative are discussed, including glass sampling bulbs, evacuated stainless steel spheres (evacuated canisters are not mentioned specifically, but sometimes can be used), and various sorbents.

Method 18 is useful for situations for which a specific method has not been developed and in which the stack conditions are relatively mild. For example, high temperatures, high moisture, or a corrosive matrix in a stack or vent may necessitate the use of other methods such as SW-846 Volatile Organic Sampling Train (VOST).

Once the gas containing the pollutant of interest is cleaned of particulate matter and at ambient temperature, there is the choice of several sample media. Most directly, a whole-gas sample is captured in an inert container. Either Tedlar bags or evacuated specially-treated stainless steel canisters are used, although there are differences in opinion on the use of evacuated canisters. Tedlar bags are relatively cheap, light weight, and transparent so that the sample being collected may be observed. For example, if water condenses inside the bag, it may be necessary to go to the VOST sampling train. However, since the bags are transparent, gases collected in them must be protected from light if they are photosensitive. Also, the gas must be drawn into the bag using some pumping apparatus. Evacuated canisters, on the other hand, use the vacuum in the canister to draw the sample. Flow regulators are often used in conjunction with canisters to guarantee a uniform flow and at such a rate that the sampling

will last for a desired period (a few minutes up to 24 hours). In some cases, pumps are used with canisters, which will withstand pressures above atmospheric, if necessary. Canisters must be pre-cleaned (Tedlar bags should never be reused), but they are rugged and very easy to use. Both Tedlar bags and canisters have limitations on the types of gases they may be used for. For example, canisters should not be used for acid gases (e.g., HCl) nor for any sulfur compounds (e.g., H₂S).

Along with the choice of sampling media, a range of gas chromatographic detectors can be used, as long as they are appropriate for the target species. The detectors most frequently in current use are flame ionization, photo-ionization, and electron capture detectors. Although the mass spectrometric detector should, in principle, function similarly to non-specific detectors mentioned above for detecting eluting species from the GC column, EPA is developing a MS-specific Method 18, which takes advantage of the additional information available from GC/MS.

7.1.2 Federal Reference Method 25C: Determination of Non-methane Organic Compounds (NMOC) in MSW Landfill Gases. Federal Reference Method 25C is applicable to the sampling and measurement of nonmethane organic compounds (NMOCs) as carbon in MSW landfill gases. In operation, a stainless steel sample probe that has been perforated at the bottom third is driven or augered to a depth of 1.0 m below the bottom of the landfill cover and connected to an evacuated cylinder. Once the gas is trapped within the evacuated cylinder, the cylinder valve is closed and the tank returned to the laboratory for analysis. The NMOC content of the gas is determined by injecting a portion of the gas into a gas chromatographic column to separate the NMOCs from CO, CO₂, and CH₄; the NMOCs are oxidized to CO₂, then reduced to CH₄, and measured by a FID. In this matter, the variable response of the FID associated with different types of organics is eliminated.

Prior to field deployment, the sample tank is evacuated, cleaned, and leak checked. In addition, the analytical system must pass an initial performance test which includes an oxidation catalyst efficiency check, a reduction catalyst efficiency check, NMOC calibration, and a system performance check. The analytical system must also pass a daily NMOC analyzer calibration check before field samples are analyzed.

7.1.3 Federal Reference Method 2E: Determination of Landfill Gas Production Flow Rate. Federal Reference Method 2E is used to calculate the NMOC flow rate from landfills. In operation, extraction wells are installed either in a cluster of three or at five locations dispersed throughout the landfill. A blower is used to extract LFG from the landfill. LFG composition, landfill pressures near the extraction well, and volumetric flow rate of LFG extracted from the wells are measured and the landfill gas production flow rate is calculated. The well head assembly used to determine production flow rate involves a well head control valve, water knockout jar, orifice meter to measure pressure drop across an inline orifice plate, blower assembly, and an outlet sample port.

7.1.4 Federal Reference Method 3C: Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources. Federal Reference Method 3C is applicable to the analysis of CO₂, CH₄, N₂, and O₂ concentrations by using a GC coupled with a thermal conductivity detector (TCD). In operation, a gas sample is extracted directly to the analyzer or captured in a whole-air container (canister/Tedlar bag), similar to Federal Reference Method 3 or Federal Reference Method 25C. If captured in a whole-air container, the sample is taken back to the laboratory for analysis.

Analysis involves passing a portion of the sample through a chromatographic column that has the capability to separate the listed gases. Once separated, their concentrations are determined with a TCD. As with other GC methods, the GC analyzer is optimized, calibrated, and checked for linearity prior to analysis of the field sample.

7.2 Compendia of Methods

Over the last several years, EPA's Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL) and the Center for Environmental Research Information (CERI) has supported technology transfer programs involving peer-reviewed ambient air monitoring methods presented in a standard format for use by regulatory and industrial personnel via publication of a series of methods Compendia. These Compendia represent a series of documents reflecting EPA's commitment to use standardized sampling and analytical procedures in environmental applications. Presently, there are three Compendia:

1. *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*, EPA/625/R-96-010a, June 1999 (Winberry et al., 1999a).
2. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition*, EPA/625/R-96-010b, January 1999 (Winberry et al., 1999b).
3. *Compendium of Methods for the Determination of Air Pollutants in Indoor Air*, EPA/600/4-90-010, April 1990 (Winberry et al., 1990).

While EPA has published numerous Federal Reference Methods (FRMs), there has been a lack of standardized ambient air sampling and analytical methodologies which address the Clean Air Act Amendments of 1990, Title III list of now 188 hazardous air pollutants (HAPs). The Compendia address methodologies for characterizing various HAPs, both inorganic and organic constituents, including sulfuric acid, nicotine, metals, PM_{2.5} (particulate matter having an aerodynamic diameter equal to or less than 2.5 µm), mercury (particle/vapor), SVOCs, and specific VOCs.

The intent of the Compendia is to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date technology involving the sampling and analysis of organic and inorganic compounds in ambient air. Historically, regulatory agency personnel have used a variety of monitoring and analytical techniques to obtain results that varied widely in data quality. The absence of the use of standardized procedures raised serious concern about the compatibility of the data collected and its ultimate use. Ensuring data compatibility is critical, because environmental regulators make major decisions based upon the interpretation of such data relating to public health issues and applicable control options. The Compendia provide standardized procedures for the sampling and analysis of organic and inorganic compounds in the ambient air, thus providing high quality data to the regulatory community and making industry accountable for HAP emissions as part of their source compliance strategy.

7.2.1 Compendium Methods for Analysis of Volatile Organics. Compendium Methods TO-14 and TO-15 are applicable to specific VOC compounds and allow an analyst to reach the sub- ppb level. Numerous compounds, many of which are chlorinated and more toxic than non chlorinated compounds, have been successfully tested for storage stability in pressurized canisters. Method TO-15 is significant in that it extends the Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Method TO-15 incorporates a multisorbent/dry purge technique or equivalent for water management, thereby addressing a more extensive set of compounds than addressed by Method TO-14A.
- The Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs..
- Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme, which is generally more desirable than using single or even multiple specific detectors.
- In addition, Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment.
- Method TO-15 includes enhanced provisions for inherent quality control. The method uses

internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

7.2.1.1 Compendium Method TO-14. This method is applicable to non-polar VOCs that have been tested and determined to be stable when stored in pressurized and sub-atmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. However, minimal documentation is currently available demonstrating stability of VOCs in sub-atmospheric pressure canisters. Both sub-atmospheric pressure and pressurized sampling modes typically use an initially evacuated canister and pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated specially prepared passivated canister. The analytical strategy for Method TO-14A involves using a high-resolution GC coupled to one or more appropriate GC detectors. Historically, detectors for a GC have been divided into two groups: non-specific detectors and specific detectors. The non-specific detectors include, but are not limited to, the nitrogen-phosphorus detector (NPD), the FID, the electron capture detector (ECD) and the PID. The Method TO-14A analytical system employs a Nafion permeable membrane dryer to remove water vapor from the sample stream. Polar organic compounds permeate this membrane in a manner similar to water vapor and rearrangements can occur in some hydrocarbons due to the acid nature of the dryer. Compendium Method TO-15 provides guidance associated with alternative water management systems applicable to the analysis of a large group of VOCs in specially-treated canisters.

7.2.1.2 Compendium Method TO-15. This method is applicable to polar and non-polar VOCs that have been tested and determined to be stable when stored in pressurized and sub-atmospheric pressure canisters. This method documents sampling and analytical procedures for the measurement of subsets of the 97 VOCs that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25 °C and 760 mm Hg. This method applies to concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. Use of Method TO-15 for many of the VOCs is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how to obtain audit standards. The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister. The analytical strategy for Method TO-15 involves using a high resolution GC coupled to a mass spectrometer.

Method TO-15 has been applied to the sampling and analysis of COPCs involving VOCs for emission monitoring of landfill gases, soil gases, and in particular, ambient air around the perimeter of the landfill, as illustrated in Figure A-2.

7.2.1.3 Compendium Method TO-16. This method is intended for the use of an FT-IR system that acquires data using a long, open air path and does not require the acquisition of a sample for subsequent analysis. The system produces data that is a time sequence of the path-averaged atmospheric concentrations of various gases. Because the FT-IR can potentially measure the concentration of a large number of atmospheric gases, this method does not address the requirement for measuring a particular gas or a set of gases. The primary geometric configurations of FT-IR instruments that are commercially available are the monostatic configuration and the bistatic configuration. Once a set of target gases has

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been selected, the wave number regions to be used in the analysis are chosen. For the monostatic instrument geometry, the stray light component must be subtracted from each single beam spectrum. For the bistatic case, the black body radiation spectrum must be subtracted from each single beam spectrum.

The method of trace gas monitoring using FT-IR-based, long-path, open-path systems has a number of advantages that are significant over traditional methods. Some of these advantages are related to the path monitoring aspect of this method which, by its very nature, distinguishes the method from all point monitoring methods. The main advantages of these systems are:

- Integrity of the sample is assured since no sampling actually occurs;
- Multi-gas analysis is possible with a single field spectrum;
- Path-integrated pollutant concentrations are obtained;
- Spatial survey monitoring of industrial facilities is possible if scanning optics are used;
- Rapid temporal scanning of line-of-sight or multiple lines-of-sight is possible; and
- Monitoring of otherwise inaccessible areas is possible.



Figure A-2. Example of Compendium Method TO-15 Application for Landfill COPCs at the Perimeter of the Site.

The ultimate significance of remote sensing with FT-IR systems is a matter of cost effectiveness and of technological advances. Technological advances are required in at least two important areas: (1) the improvement in the characteristics of the instrumentation itself and (2) the development of “intelligent” software. The software is required to improve the means for short-term adjustment of background and water vapor spectra to account for the continual variation of ambient conditions that can adversely affect the accuracy and precision of FT-IR based systems.

7.2.2 Compendium Method IO-1/IO-2 for Suspended Particulate Matter (SPM). Compendium Method IO-1/IO-2 involves time-integrated and real-time monitoring for total suspended particulate (TSP) matter and PM_{10} (particulate matter with an aerodynamic diameter equal to or less than $10\ \mu m$). TSP and PM_{10} monitoring at the perimeter of a MSW landfill site may be required and can be integrated within the MSW landfill gas monitoring program. From a regulatory standpoint, sampling options for TSP and PM_{10} monitoring fall into two categories: reference methods and equivalent methods. Reference methods are those sampling procedures that were initially established by EPA for determining average TSP and PM_{10} concentrations during a fixed time period. Hence, these methods are also termed time-integrated. These are by far the most commonly used TSP and PM_{10} measurement methods. Alternatively, EPA has more recently designated certain continuous reading instruments as equivalent methods for measuring ambient air concentrations of TSP and PM_{10} at or near real-time. Real-time

measurements are useful when parameters such as the diurnal variation in concentration or changes in concentration associated with specific site activities of interest.

The reference, or time-integrated, method for TSP is codified at 40 CFR 50, Appendix B. This method uses a high-volume (hi-vol) sampler to collect particles with aerodynamic diameters of approximately 100 μm or less. The TSP sampler is a compact unit consisting of a protective housing; a high-speed, high-volume electric blower; a filter holder capable of supporting an 8 by 10-inch filter; and a flow-controller and blower assembly capable of maintaining the air-flow rate through the instrument at 40 to 60 ft^3/min throughout the sampling period. The hi-vol sampler design causes the TSP to be deposited uniformly across the surface of the fixed filter. The TSP hi-vol can be used to determine the average ambient TSP concentration over the sampling period, and the collected material subsequently can be analyzed to determine the identity and quantity of inorganic metals present in the TSP.

The reference method for PM_{10} is codified in 40 CFR 50, Appendix J. Two technologies have qualified as meeting the sampling requirements of the reference method for PM_{10} : a hi-vol with a 10 μm inlet and a dichotomous sampler. The PM_{10} hi-vol is identical to the TSP hi-vol except that it is equipped with a sampling inlet that directs only particles with aerodynamic diameter of 10 μm or less to the filter.

A dichotomous sampler collects both PM_{10} and $\text{PM}_{2.5}$. The sample is further split into fractions above and below 2.5 μm at the sample inlet. Both the hi-vol and dichotomous samplers deposit the particulate matter uniformly across the surface of fixed filters. Both can be used to determine average ambient PM_{10} concentration over the sampling period, and the collected material from both subsequently analyzed for inorganic metals and other materials present.

Both the hi-vol and the dichotomous sampler can be equipped with either of two basic types of flow control systems, a mass-flow-control (MFC) system and a volumetric-flow-control (VFC) system. The calibration and standard operating procedures differ considerably between these two types of flow-control systems, and therefore operational procedures are control-system-specific.

The flow rate in an MFC system is actively sensed and controlled at a predetermined set point. Air is pulled through the filter into the intake of the blower and subsequently exits the sampler through an exit orifice, which facilitates measurement of the flow with a manometer or pressure recorder. The flow rate is controlled by an electronic mass-flow controller, which uses a flow sensor installed below the filter holder to monitor the mass flow rate and related electronic circuitry to control the speed of the blower motor accordingly. The controlled flow rate can be changed by an adjustment knob on the flow controller.

Real-time monitoring for TSP or PM_{10} can be done by utilizing the principle of micro-balance oscillation impaction. A micro-balance oscillation impaction monitor (TEOM Monitor) utilizes the filter-based measurement system for providing real-time mass monitoring capability.

The TEOM ambient particulate monitor is comprised of two main components: the TEOM sensor unit and the cabinet assembly. The enclosure cabinet houses the mass flow controller with an in-line filter cartridge and silicone tubing and an electronic circuit chamber with the appropriate wiring and frequency signal output.

The microbalance is a rectangular metal enclosure which houses a metal cylinder (the sensor head) and inner inlet tube. The metal cylinder contains an oscillating tapered element, an electronic feedback system, and a filter cartridge. The tapered element is attached to a platform at its wide end (bottom) and has a small metal tip onto which the filter cartridge sits. The electronic feedback system consists of an amplifier board, which maintains the elements oscillation, and the electronics, which allow frequency

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signals to be transcribed to mass units. At the bottom of the microbalance, a silicone tube that is connected to the mass flow controller carries the air sample.

In operation, the particle-laden air is drawn in through a heated air inlet followed by an exchangeable filter cartridge, where the particulate mass collects. The filtered air then proceeds through the sensor unit, which consists of a patented microbalance system and an automatic flow controller. As the sample stream moves into the microbalance system (filter cartridge and oscillating hollow tube), it is heated to the temperature specified by the software. The automatic flow controller pulls the sample stream through the monitor at flow rates between 0.5 to 1 L/min. The hollow tube is attached to a platform at its wide end and is vibrated at its natural frequency. As particulate mass gathers on the filter cartridge, the tube's natural frequency of oscillation decreases, and the electronic microbalance system continually monitors this frequency. Based on the direct relationship between mass and frequency, the instrument's microcomputer computes the total mass accumulation on the filter, as well as the mass rate and mass concentration, in real-time. The data processing unit contains software which allows the user to define the operating parameters of the instrumentation through menu-driven routines. During sample collection, the program plots total mass, mass rate and/or mass concentration on the computer screen in the form of scalars. The program allows two y-axis scales to be displayed and up to 10 variables to be plotted simultaneously. In addition, the scales and variables used in plotting the data may be changed during collection without affecting stored data.

7.2.3 Compendium Method TO-12 for NMOCs. A whole air sample is either extracted directly from the MSW landfill vent, bore hole, landfill surface, or ambient air and analyzed on site by the GC system or is collected into a precleaned specially-treated canister and analyzed offsite.

The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead filled trap that is cooled to approximately -186 °C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOCs (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to, pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.

After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap in the opposite direction to the sample flow and into a FID. When the residual air and methane have been flushed from the trap and the FID baseline stabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90 °C.

The organic compounds previously collected in the trap volatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.

By convention, concentrations of NMOCs are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration in parts per million by volume multiplied by the number of carbon atoms in the compound.

7.2.4 Compendium Method TO-13A/TO-10 for Semi-Volatiles/PAHs. Compendium Methods TO-13A and TO-10 utilize a polyurethane foam plug and filter to trap semi-volatiles (PAHs, dioxins, furans, PCBs, etc.) from landfill gas. Filters and adsorbent cartridges (containing XAD-2 or PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars

wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.

Approximately 325 m³ of landfill gas over a 24-hour period is drawn through the filter and adsorbent cartridge using a calibrated high-volume sampler for Method TO-13A. Method TO-10A uses the same type filter/PUF adsorbent, but only the air is pulled through the PUF cartridge at a rate of 1 L/min. This allows the collection of semi-volatiles from landfill gas vents and bore holes without disturbing the air from the source.

The amount of air sampled through the filter and adsorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and adsorbent cartridges to the analytical laboratory for analysis.

The filters and adsorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by a Kuderna-Danish (K-D) evaporator followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis.

The eluent is further concentrated by the K-D evaporator, then analyzed by either GC equipped with a FID or by MS detection or high performance liquid chromatography (HPLC). The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions, each analyzed in triplicate. The amount of semi-volatiles detected on the extracted PUF/filter is related to the concentration of the COPCs in the sample.

7.2.5 Compendium Method IO-5 for Mercury. Elemental mercury (Hg⁰) and most of its derivatives are metabolic poisons which bioaccumulate in aquatic food chains, ultimately reaching concentrations capable of causing neurological and reproductive damage in terrestrial, as well as, aquatic organisms.

Atmospheric Hg, although present only in trace amounts, has been established as a significant source of mercury to aquatic environments.

Mercury compounds in the atmosphere exist in vapor and particulate forms, preferentially partitioning into the vapor phase. Mercury species fall within two main categories; inorganic Hg compounds and organic Hg compounds. The most common form of inorganic mercury is elemental mercury vapor. Other inorganic forms of Hg include mercuric chloride (HgCl₂) and mercurous chloride (HgCl). The organic compounds include those compounds in which Hg is covalently bonded to a carbon atom, as in the case of methyl and dimethyl mercury.

Method IO-5 describes procedures for collection and analysis of vapor phase and particulate Hg in order to provide an EPA-approved accessible sampling and analytical methodology for uniform monitoring of Hg levels. The collection of mercury from ambient air, vent tubes, and bore holes involves using gold-coated bead traps and glass-fiber filters. The amalgamation process for vapor-phase Hg requires a flow rate low enough to allow adsorption of the mercury in the air to the gold surface. On the other hand, the significantly lower levels of particle-phase Hg requires a much higher flow rate in order to collect sufficient particle mass for mercury determination. Therefore, separate sampling systems are needed for the collection of Hg in the vapor and particle phases. Accurate flow determinations through both sampling systems are critical in providing accurate Hg concentrations in air.

Vapor-phase mercury is collected using gold-coated glass bead traps. A Teflon filter pack with a glass fiber filter is placed in front of the traps to remove particulate material from the air being sampled. Air is pulled through the vapor-phase sampling system using a mass-flow controlled vacuum pump at a nominal flow rate of 0.3 L/min.

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Particle-phase Hg is collected using a glass-fiber filter in an open-faced Teflon filter pack. Air is pulled through the particulate sampling system using a vacuum pump at a nominal flow rate of 30 L/min.

Determination of vapor- and particle-phase Hg in ambient air is accomplished using cold-vapor atomic fluorescence spectrometry (CVAFS); more specifically, dual-amalgamation CVAFS. The amount of vapor-phase Hg collected on a gold-coated bead trap is determined directly by CVAFS. The sample trap is heated to release the collected mercury. The desorbed mercury is carried in an inert gas stream (He or Ar) to a second gold-coated analytical bead trap. The Hg collected on the analytical trap is then thermally desorbed and carried into the CVAFS analyzer. The resulting voltage peak is integrated to produce the peak area for the sample.

Determination of Hg in the particle phase requires acid extraction of the glass-fiber filters prior to analysis. The sample filters are extracted in a nitric acid solution using microwave digestion to yield "acid-extractable" particulate mercury. The extract is oxidized to convert all forms of Hg to Hg^{+2} (ionized Hg), and SnCl_2 is added to the extract to reduce the Hg^{+2} to volatile Hg^0 . The Hg^0 is liberated from the extract by purging with an inert gas (N_2) and collected on a gold-coated bead analytical trap. The amount of mercury collected on the trap is then determined using dual-amalgamation CVAFS. The detection limits achieved using Inorganic Compendium Method IO-5 are 30 pg/m^3 for particulate mercury and 45 pg/m^3 for vapor mercury.

Table A-6 documents the availability of both FRMs and Compendia methods available for characterizing MSW landfill gas, soil gas, landfill gas combustion equipment exhaust, indoor air, and ambient air. Table A-7 list the various advantages and disadvantages of EPA's Compendium Methods.

Table A-6. Applicability of FRMs and Compendia Methods for MSW Landfill COPCs.

Analyte	Media					
	Landfill Gas	Soil Gas	Landfill Surface	LFG Combustion	Ambient Air	Indoor Air
COPCs Commonly Found						
1,1,1-Trichloroethane	TO-14/TO-15 ¹	TO-14/TO-15	Mod. FRM-21 ²	Method 0030 ³ , SW-846	TO-14/TO-15	TO-1/TO-14/TO-15 ⁴
1,1-Dichloroethene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
1,2-Dichloroethane	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Acrylonitrile	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Benzene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Carbon Tetrachloride	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Chlorobenzene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Chloroethane	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Chlorofluorocarbons	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15

continued

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Analyte	Media					
	Landfill Gas	Soil Gas	Landfill Surface	LFG Combustion	Ambient Air	Indoor Air
Chloroform	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Dichlorobenzene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Ethylene Dibromide	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Mercury	IO-5 ⁴	IO-5	IO-5	Method 0060 ³	IO-5	IO-5
Methylene Chloride	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Perchloroethylene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Toluene	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Vinyl Chloride	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
Xylenes	TO-14/TO-15	TO-14/TO-15	Mod. FRM-21	Method 0030	TO-14/TO-15	TO-1/TO-14/TO-15
NMOC	TO-12/FRM-25C	TO-12/FRM-25C	Portable Real Time	FRM-25C	TO-12/FRM-25C	TO-12/FRM-25C
Other COPCs						
Chlorinated Organics	TO-14/TO-15	TO-14/TO-15	TO-14/TO-15	Method 0030	TO-14/TO-15	IP-1A
Total Reduced Sulfur	TO-14/TO-15	TO-14/TO-15	Portable Real Time	FRM 15/15A	TO-14/TO-15	IP-1A
Methane	Portable Real Time/TO-14/TO-15	Portable Real Time/TO-14/TO-15	Portable Real Time/TO-14/TO-15	FRM 18	Portable Real Time/TO-14/TO-15	Portable Real Time/IP-1A
CO/CO ₂	FRM 3C	FRM 3C	FRM 3C	FRM 3C	FRM 3C	FRM 3C
Semi-Volatiles (PAHs, D/Fs, PCBs)	TO-10A ¹	TO-10A	NA	Method 0010 ³	TO-13A ¹	IP-7 ⁴
Suspended Particulate Matter	FRM-5i ²	FRM-5i	FRM-5i	FRM 5	IO-1 ⁴	IP-10 ⁴
Speciated Reduced Sulfur						
Hydrogen Sulfide	FRM-15	Portable Real Time	Portable Real Time	FRM-15	FRM-15	Portable Real Time
Carbonyl Sulfide	FRM 15	Portable Real Time	Portable Real Time	FRM-15	FRM-15	Portable Real Time
Carbon Disulfide	FRM-15	Portable Real Time	Portable Real Time	FRM-15	FRM-15	Portable Real Time
Flow Rates	FRM-2E	FRM2-E	NA ⁵	FRM-2E	NA	NA

continued

- ¹ Winberry, W.T., Jr., "Compendium of Methods For The Determination of Organic Compounds in Ambient Air-Second Edition," U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, EPA-625/R-96/010b, January 1999 <http://www.epa.gov/ttn/amtic/inorg.html> (accessed August 2005).
- ² 40CFR Part 60, Appendix A <http://www.epa.gov/ttn/emc/promgate.html> (accessed August 2005).
- ³ Test Methods for Evaluating Solid Waste: Physical/Chemical Methods: SW-846 <http://www.epa.gov/epaoswer/hazwaste/test/main.htm> (accessed August 2005).
- ⁴ Winberry, W.T., Jr., Stephen Edgerton, and Linda Forehand, "Compendium of Methods For the Determination of Inorganic Compounds in Ambient Air," U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, EPA-625/R-96-010a, June 1999 <http://www.epa.gov/ttn/amtic/airtox.html> (accessed August 2005).
- ⁵ NA = not applicable.

8.0 Real-Time Monitoring for Organic Gases

Many varieties of organic species analyzers are available. Gas chromatographic systems include all devices that separate organic species through use of a packed or capillary column and measure the organic concentration using a detector at the end of the column. Several analyzers are hybrid chromatographs, in that organic/inorganic separation is performed through chemical or thermal techniques and analysis using typical detectors (i.e., flame ionization, electron capture, etc.).

8.1 Gas Chromatography/Mass Spectroscopy (GC/MS)

Gas chromatography is a common technique used for separating and analyzing mixtures of gases and vapors. A gas mixture is percolated through a column of porous solids or liquid coated solids which selectively retard sample components. A carrier gas is used to bring the discrete gaseous components to a detector, and the sample can be identified and quantified through analysis of the detector response and the component retention time. Gas chromatography has been in use in the laboratory since 1905; however, it has only recently been used in environmental applications.

A compound in a gas matrix can be more fully identified through analysis of retention time in a GC/MS. Identification can be established by comparing the total ion current profile of an eluted compound to a published standard spectrum. GC/MS techniques are particularly suited for analysis of organics in air through a concentration step. GC/MS has also been used to identify organic ambient air contaminants. The concentration step involves passing the air sample through an absorber column that traps the organic analytes followed by thermal desorption of that material in the GC. This technique is semi-continuous, and overall response time of a GC/MS is typically greater than 3 minutes. This powerful tool has been adapted to identify and quantitate organic compounds at landfills in close to real-time. At present, many GC/MS instruments are in routine use as continuous monitors. Double mass spectrometry (MS/MS) and laser multi-photon ionization mass spectrometry have been identified as potential on-line or real time instruments for the identification of PAHs. These instruments do not use the GC for separation of components and therefore do not involve the same delays in response time.

A disadvantage of GC/MS and MS/MS techniques is the complexity and cost of the instrumentation, and investments of more than \$75,000 are usually required. The mass spectra produced is complex and close to real-time results can only be provided through a computer with extensive library searching capabilities. The MS can scan for certain compounds within seconds; however, full spectrum scans usually take greater than 3 minutes. These advantages should be weighed against the high sensitivity and resolution capabilities of the GC/MS system.

Table A-7. Advantages and Disadvantages of EPA's Compendia Methods.

Method Desig.	Types of Compounds Determined	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-1 (See also Methods TO-14A, TO-15, and TO-17)	VOCs (80 to 200 °C) ¹ [e.g., benzene, toluene, xylenes]	<u>Tenax-GC Adsorption and GC/MS OR GC/FID Analysis</u> Ambient air is drawn through organic polymer sorbent where certain compounds are trapped. The cartridge is transferred to the laboratory, thermally desorbed, and analyzed using GC/MS or GC/FID.	.01–100 ppbv	• Good data base. • Large volume of air can be sampled. • Water vapor is not collected. • Wide variety of compounds collected. • Low detection limits. • Standard procedures available. • Practical for field use.	• Highly volatile compounds and certain polar compounds are not collected. • Rigorous clean-up of adsorbent required. • No possibility of multiple analysis. • Low breakthrough volumes for some compounds. • Desorption of some compounds difficult. • Structural isomers are the most common interferences. • Contamination of adsorbent and blank. contaminants may be a problem. • Artifact formation.
TO-2 (See also Methods TO-14A, TO-15, and TO-17)	Highly volatile VOCs (-15 to +120 °C) [e.g., vinyl chloride, chloroform, chlorobenzene]	<u>Carbon Molecular Sieve Adsorption and GC/MS or GC/FID Analysis</u> Selected volatile organic compounds are captured on carbon molecular sieve absorbents. Compounds are thermally desorbed and analyzed by GC/MS or GC/FID techniques.	0.1–200 ppbv	• Trace levels of volatile organic compounds are collected and concentrated on sorbent material. • Atmospheric moisture not collected. • Efficient collection of polar compounds. • Wide range of application. • Highly volatile compounds are adsorbed. • Easy to use in field.	• Some trace levels of organic species are difficult to recover from the sorbent. • Structural isomers are common interferences. • Water is collected and can de-activate adsorption sites. • Thermal desorption of some compounds may be difficult.
TO-3 (See also Methods TO-14A, TO-15, and TO-17)	VOCs nonpolar (-10 to +200 °C) [e.g., vinyl chloride, methylene chloride, acrylonitrile]	<u>Cryogenic Preconcentration and GC/FID/ECD Analysis</u> Vapor phase organics are condensed in a cryogenic trap. Carrier gas transfers the condensed sample to a GC column. Adsorbed compounds are eluted from the GC column and measured by FID or ECD.	0.1–200 ppbv	• Collects wide variety of volatile organic compounds. • Standard procedures are available. • Contaminants common to adsorbent materials are avoided. • Low blanks. • Consistent recoveries. • Large data base.	• Moisture levels in air can cause freezing problems with cryogenic trap. • Difficult to use in field. • Expensive. • Integrated sampling is difficult. • Compounds with similar retention times will interfere.

continued

Method Desig.	Types of Compounds Determined	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-4 (See also Method TO-10A)	Pesticides/PCBs [e.g., PCBs, 4,4-DDE, DDT, DDD]	<u>High Vol Filter and PUF Adsorbent Followed by GC/FID/ECD or GC/MS Detection</u> Pesticides/PCBs trap on filter and PUF adsorbent trap. Trap returned to lab, solvent extracted and analyzed by GC/FID/ECD or GC/MS.	0.2pg/m ³ –200 ng/m ³	• Low detection limits. • Effective for broad range of pesticides/PCBs. • PUF reusable. • Low blanks. • Excellent collection and retention efficiencies for common pesticides and PCBs.	• Breakdown of PUF adsorbent may occur with polar extraction solvents. • Contamination of glassware may limit detection limits. • Loss of some semi-volatile organics during storage. • Extraneous organics may interfere. • Difficulty in identifying individual pesticides and PCBs if using ECD.
TO-9A	Dioxins/Furans/ PCBs	<u>PUF Adsorbent Cartridge and HRGC/ HRMS Analysis</u> Ambient air is drawn through a glass fiber filter and a PUF adsorbent cartridge by means of a high volume sampler. The filter and PUF cartridge are returned to the laboratory and extracted using toluene. The extract is concentrated using the Kuderna-Danish technique, diluted with hexane, and cleaned up using column chromatography. The cleaned extract is then analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).	0.25–5000 pg/m ³	• Cartridge is reusable. • Excellent detection limits. • Easy to preclean and extract. • Excellent collection and retention efficiencies. • Broad database. • Proven methodology.	• Analytical interferences may occur from PCBs, methoxybiphenyls, chlorinated hydroxydiphenylethers, naphthalenes, DDE, and DDT with similar retention times and mass fractions. • Inaccurate measurement—Ds/Fs are retained on particulate matter and may chemically change during sampling and storage. • Analytical equipment required (HRGC/HRMS) is expensive and not readily available. • Operator skill level important. • Complex preparation and analysis process. • Can't separate particles from gaseous phase.

continued

Method Desig.	Types of Compounds Determined	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-12	NMOCs (non-methane organic compounds)	<u>Canister Sampling--cryogenic Preconcentration and FID Detection</u> Ambient air is drawn into a cryogenic trap where the NMOCs are concentrated. The trap is heated to move the NMOCs to the FID. Concentration of NMOCs is determined by integrating under the broad peak. Water correction is necessary.	0.1–200 ppmvC	• Standard procedures are available. • Contaminants common to adsorbent materials are avoided. • Low blanks. • Consistent recoveries. • Large data base. • Good sensitivity. • Useful for screening areas or samples. • Analysis much faster than GC.	• Moisture levels in air can cause freezing problems. • Non-speciated measurement. • Precision is limited.
TO-13A	PAHs [e.g., benzo(a)pyrene, naphthalene, fluorene]	<u>PUF or XAD-2 Adsorbent Cartridge and GC/MS Analysis</u> Ambient air is drawn through a glass fiber filter and a PUF or XAD-2 adsorbent cartridge by means of a high volume sampler. The filter and PUF cartridge are extracted using 10% diethyl ether. The extract is concentrated using Kuderna-Danish technique, diluted, and cleaned up using column chromatography. The cleaned extract is then analyzed by GC/MS.	0.5–500 ng/m ³	• Allows for sample dilution if concentration is too high during analysis. • Repeated analysis is possible. • High-volume sampling provides for lower detection limits. • Filter and PUF are low cost.	• Method has interferences due to contamination of solvents, reagents, glassware, and sampling hardware. • Coeluting contaminants may cause interference with target analytes. • Heat, ozone, NO₂, and ultraviolet light may cause sample degradation.

continued

Method Desig.	Types of Compounds Determined	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-14A	VOCs (non-polar) [e.g., toluene, benzene, chlorobenzene]	<u>Specially-prepared Canister and GC/FID/ECD or GC/MS Detection</u> Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.	0.2–25 ppbv	• Best method for broad speciation of unknown trace volatile organics. • Simple sampling approach. • Good QA/QC database. • Proven field and analytical technology.	• Limited to non-polar compounds due to use of permeation type dryer. • Sample components may be adsorbed or decompose through interaction with container walls. • Water condensation at high humidity may be a problem at high concentrations (ppm). • Complex equipment preparation required. • Expensive analytical equipment.
TO-15	VOCs (polar/non-polar) [e.g., methanol, benzene, xylene, nitrobenzene]	<u>Specially-prepared Canister and GC/MS Analysis</u> Whole air samples are collected in a specially- prepared canister. VOCs are concentrated on a solid sorbent trap or other arrangement, refocused on a second trap, separated on a GC column, and passed to an MS detector for identification and quantification.	0.2–25 ppbv	• Incorporates a multisorbent/ dry purge technique or equivalent for water management, thereby addressing a more extensive set of compounds. • Establishes method performance criteria for acceptance of data. • Provides enhanced provisions for quality control. • Unique water management approach allows analysis for polar VOCs.	• Expensive analytical equipment. • Operator skill level important.

continued

Method Desig.	Types of Compounds Determined	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-16	VOCs (polar/ non-polar) [e.g., ammonia, ethylene, carbon monoxide, chlorobenzene]	<u>FTIR Open Path Spectroscopy</u> VOCs are monitored using real-time long-path open-path Fourier transform infrared spectroscopy (FTIR).	25–500 ppbv	• Open path analysis maintains integrity of samples. • Multi-gas analysis saves money and time. • Path-integrated pollutant concentration measurement minimizes possible sample contamination, and provides real-time pollutant concentration.. • Applicability for special survey monitoring. • Monitoring at inaccessible areas possible using open-path FTIR.	• High level of operator skill level required. • Requires spectra interpretation. • Limited spectra library available. • Higher detection limits than most alternatives. • Must be skilled in computer operation. • Substantial limitations from ambient CO₂ and humidity levels associated with spectral analysis.
TO-17	VOCs (polar/non-polar) [e.g., benzene, toluene, o- xylene, chlorobenzene]	<u>Multi-bed Adsorbent Tube Followed by GC/MS</u> Ambient air is drawn through a multi-bed sorbent tube where VOCs are trapped. The cartridge is returned to the laboratory, thermally desorbed, and analyzed by GC/MS or other methods.	0.2–25 ppbv	• Placement of the sorbent as the first element minimizes contamination from other sample train components. • Large selection of sorbents to match with target analyte list. • Includes polar VOCs. • Better water management using hydrophobic sorbents than Method TO-14A. • Large database, proven technology. • Size and cost advantages in sampling equipment.	• Distributed volume pairs required for quality assurance. • Rigorous clean-up of sorbent required. • No possibility of multiple analysis. • Must purchase thermal desorption unit for analysis. • Desorption of some VOCs is difficult. • Contamination of adsorbent can be a problem.

¹ Numbers in parenthesis are the boiling point range of the organics applicable to that Compendium Method.

8.2 Ion Mobility Spectrometry (IMS)

Ion mobility spectrometry (IMS) has traditionally been used for the study of ion molecule reactions and the qualitative analysis of ultra trace levels of organic compounds. Advances in technology have resulted in the development of small, rugged, and dependable cells using this technology. These advances have allowed the use of this technology in industrial applications, where superior performance characteristics have been achieved when compared to traditional monitoring methods. The ability of IMS to provide real-time response, specificity, low temperature performance, and low maintenance of IMS-based devices present decided advantages over electrochemical, paper tape detection, UV, and GC/MS systems. IMS has the advantage of active sampling without moving parts.

Maintenance disadvantages of techniques such as electrochemical cells and paper tape detectors are thus overcome by the elimination of expendables. Most IMS instruments are under microprocessor control, allowing the same basic configuration to be used for the specific detection of a wide variety of gases. Specificity is achieved by programming the instrument to monitor the unique drift time for the compound of interest. An algorithm converts the peak heights to a concentration by way of a calibration table. Thus, even nonlinear responses are converted into a linear output. The concentration is displayed on the front of the instrument and is also converted to a 4 to 20 ma signal for remote monitoring. Although drift has not been seen to be a problem, recalibration is easily achieved in a two step semi-automated procedure.

In operation, ambient air is drawn in the IMS instrument through a semi-permeable membrane on the outside of the cell by use of a sampling pump. The membrane allows materials of interest to pass into the detection cell while attenuating many possible interferences. Purified dry air from a self-contained scrubbing system sweeps the membrane on the inside of the cell and delivers the sample to the reaction region. The sample, consisting of one or more components, is ionized by reactions with a weak plasma of positive and negative ions, formed by ionization of the purified air by a radioactive source. The ionized sample molecules and reactant ions drift through the cell under the influence of an applied electric field. A shutter grid allows periodic introduction of the ions into a drift tube where they separate based on charge, mass, and shape. Smaller ions move through the drift tube faster than larger ions and arrive first at the detector. The ability of an ion to move through another gas is called "mobility." Because different ions have different mobilities, the ions arrive at the collector with different drift times. The current created at the detector is amplified, measured as a function of time, and a spectrum is generated. The mobility of the molecules can then be determined using pattern recognition algorithms using a computer or microprocessor to analyze and compare features of the IMS signature with information stored in memory. The electric field is periodically reversed so that ions of both polarities can be studied.

8.3 Diffusion-Limited Technique (Passive Sampling Devices)

Passive sampling devices (PSDs) have been used extensively over the past decade by industrial hygienists to assess the effects of respiratory exposures to hazardous pollutants on workers. Only recently, however, has there been interest in using PSD's as part of a landfill gas monitoring program.

To obtain an accurate estimate of organic/inorganic species, the EPA has developed a PSD monitor. The device is unobtrusive and lightweight. It operates quietly, and places little or no burden on the sampling system. Passive devices, which require no pump, are much lighter in weight than traditional devices and are not power-limited. They have the additional advantages of small size and relatively low cost, which make them ideally suited as personal exposure monitors for toxic chemicals in air, bore-hole monitoring, and unattended area monitoring, especially when electrical power sources are not readily accessible.

Passive air monitors may be either permeation or diffusion-controlled. In each case, a collector or sorbent material is separated from the external environment by a physical barrier that determines the sampling characteristics of the device. Permeation-limited devices employ a membrane in which the test compounds are soluble. Because of this solubility requirement, it is possible to achieve some selective function with permeation devices by choice of the membrane material. However, because of solubility variation even within a congeneric series of compounds, permeation devices must be calibrated for each individual chemical that is sampled.

With diffusion-limited devices, the collector is isolated from the environment by a porous barrier containing a well-defined series of channels or pores. The purpose of these channels is to provide a geometrically well-defined zone of essentially quiescent space through which mass transport is achieved

solely by diffusion. As a general criterion for this condition, the length/diameter ratio (L/D) of the pores should be at least three.

Despite the potential limitations of applying passive monitors to quantitatively measure air pollutants, these devices have in recent years been used quite successfully in ambient and indoor monitoring applications. Their application to ambient atmospheres, which requires detection limits from 0.1 to 50 ppbv, presents a greater challenge. Most commercial devices use activated carbon as the collector. Solvents such as carbon disulfide or a mixture of CS_2 in methanol must be used to desorb the chemicals for analysis. Concentration by evaporation of the solvent extract is impractical for the analysis of VOCs. Consequently, carbon-based commercial dosimeters generally do not have adequate sensitivity for ambient air monitoring.

8.4 Radial Plume Mapping

These techniques were developed in research and development programs funded by the EPA National Risk Management Research Laboratory (NRMRL). Detailed spatial information is obtained from path-integrated ORS measurements by the use of optimization algorithms. The method involves the use of an innovative configuration of non-overlapping radial beam geometry to map the concentration distributions in a plane. This method, radial plume mapping (Hashmonay et al., 1999; Wu et al., 1999; Hashmonay et al., 2002), can also be applied to a vertical plane downwind from an area emission source to map the crosswind and vertical profiles of a plume. By incorporating wind information, the flux through the plane is calculated, which leads to an emission rate of the upwind area source. The RPM method can be used with any ORS instrument. An extensive validation study of the RPM method was conducted during 2003 using tracer gas releases, and the results of this validation study led to the creation of an EPA draft protocol, which is currently under review by EPA, for using the RPM method to characterize emissions from area sources.

8.4.1 Horizontal Radial Plume Mapping (HRPM). The radial plume mapping approach provides spatial information to path-integrated measurements by optical remote sensing. This technique yields information on the two-dimensional distribution of the concentrations in the form of chemical-concentration contour maps (Hashmonay et al., 1999; Wu et al., 1999; Hashmonay et al., 2002). This form of output readily identifies chemical hot spots, the location of high emissions. This method can be of great benefit for performing site surveys prior to remediation activities.

HRPM is usually performed with the ORS beams located as close to the ground as practical. This enhances the ability to detect minor constituents emitted from the ground because the emitted plumes dilute significantly at higher levels above the ground. The survey area is divided into a Cartesian grid of n times m rectangular cells. A mirror is located in each of these cells, and the OP-FTIR sensor scans to each of these mirrors in the order of either increasing or decreasing azimuth angle, dwelling on each for a set measurement time. The path-integrated concentrations measured at each mirror are averaged over a several scanning cycles to produce time-averaged concentration maps. Meteorological measurements are made concurrent with the scanning measurements.

Figure A-3 represents a typical horizontal RPM configuration in which $n = m = 3$. The lines represent the nine optical paths, each terminating at a mirror (Hashmonay et al., 2002).

8.4.2 Vertical Radial Plume Mapping (VRPM). The vertical radial plume mapping method maps the concentrations in the vertical plane of the measurement. By scanning in a vertical plane downwind from an area source, one can obtain plume concentration profiles and calculate the plane-integrated concentrations. The flux is calculated by multiplying the plane-integrated concentration by the wind speed component perpendicular to the vertical plane. The flux leads directly to a determination of the emission rate (Hashmonay et al., 1998; Hashmonay and Yost, 1999; Hashmonay et al., 2001). Thus, vertical scanning leads to a direct measurement-based determination of the upwind source emission rate.

Figure A-4 shows a schematic of the experimental setup used for vertical scanning. Several mirrors are placed in various locations in a vertical plane in-line with the scanning OP-FTIR. Two of the mirrors used in the configuration are mounted on a scissors jack (which is a piece of equipment used to create a vertical platform for mounting mirrors in the configuration). The location of the vertical plane is selected so that it intersects the mean wind direction as practical.

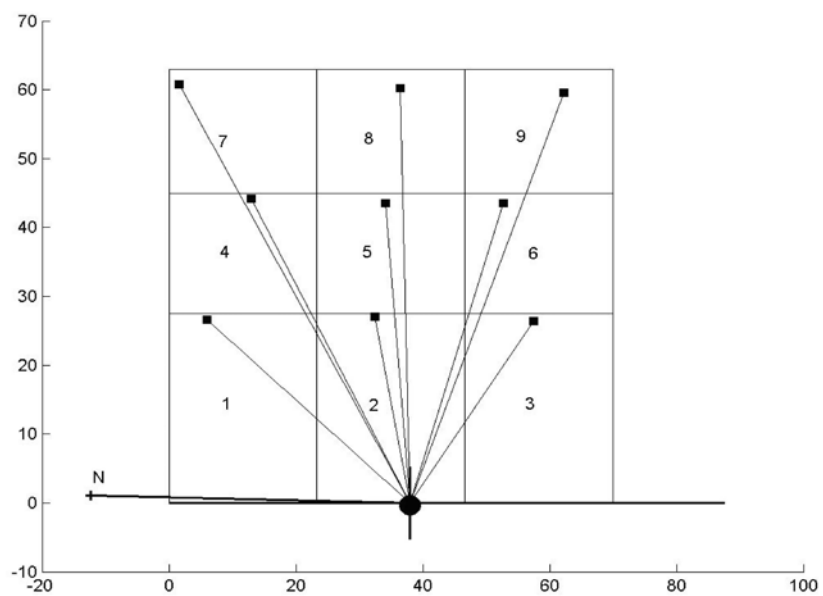


Figure A-3. Overhead View of an Example HRP Configuration.

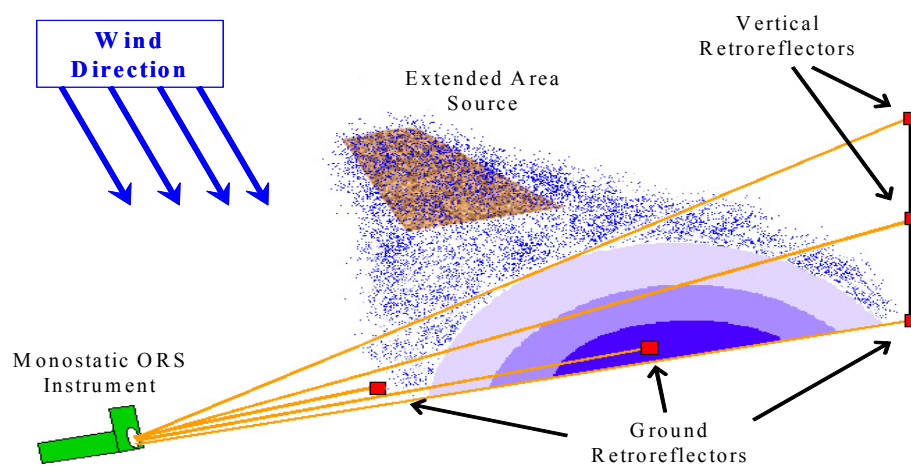


Figure A-4. Example of a Vertical RPM Configuration.

8.4.3 Open-Path Fourier Transform Infrared Spectroscopy (OP-FTIR). The OP-FTIR Spectrometer combined with the RPM method is designed for both fence-line monitoring applications and for real-time, on-site, remediation monitoring and source characterization. An infrared light beam, modulated by a Michelson interferometer is transmitted from a single telescope to a retro-reflecting mirror target, which is usually set up at a range of 100 to 500 meters from the transmitter. The returned light signal is received by the single telescope and directed to a detector. The light is absorbed by the molecules in the beam path as the light propagates to the retro-reflecting mirror and again as the light is reflected back to the analyzer. Thus, the round-trip path of the light doubles the chemical absorption signal.

8.4.4 Open-Path Tunable Diode Laser Absorption Spectroscopy (OP-TDLAS). The OP-TDLAS instrument is an interference free technique for making continuous concentration measurements of many gases. Concentrations in the range of part per billions are suitable for measurements over an open path up to 1 km, for gases such as CO, CO₂, NO_x, NH₃, and CH₄. The laser emits radiation at a particular wavelength when an electrical current is passed through it. The light wavelength depends on the current and therefore allows scanning over an absorption feature and analyzing for the target gas concentration using Beer's law. Recent development of a multiple channel OP-TDLAS instrument allows scanning electronically very fast (few seconds) among many beam-paths (presently, 8 beams). The multiple channel OP-TDLAS applies a small 4-inch telescope, which launches the laser beam to a retro-reflecting mirror. The laser beam is returned by the mirror to the telescope, which is connected with fiber optics to a control box that houses the laser and a multiple channel detection device. The potential advantages of the OP-TDLAS instrument include near real-time air concentrations, no requirement for sample collection, no additional analytical costs (i.e., laboratory costs), and concentrations that are path-averaged values instead of concentrations at specific sampling points. The disadvantage of the OP-TDLAS instrument is the ability to measure only one gas (in most cases) with one instrument.

8.4.5 Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS). The UV-DOAS is a subset of long-path absorption spectroscopy. In long-path absorption, a known intensity of light is generated and allowed to propagate through a predetermined space. UV-DOAS technology utilizes the ability of molecules to absorb light as a basis for calculation of the concentration of molecules in a gas, and the attenuation of light energy through the path length is assumed to be due to absorption by the target species. The basic concept of the DOAS is the same as the above except multiple wavelengths are measured. Concentrations are determined on the basis of Lambert-Beer's law. The light from the receiver is sent over an optic cable to the spectrometer, where it is resolved into spectra by a grating. For the specific wavelength area, about 100 spectra are obtained per second. These spectra are converted to digital signals and stored in a multi-channel memory. The computer compares the spectra for each wavelength with a precalibrated reference spectrum. The system can store data for a maximum of 1,000 wavelengths. On the basis of these comparisons, a program calculates the quantities of the substances which are being monitored. The computer reports the margin of error for each measurement. Currently, the simultaneous measurements for up to 50 organic/inorganic compounds are possible. The reference beam is created mathematically, and only the measurement beam is necessary. By recording the various shades of color in the light and analyzing them mathematically, the concentration of the different molecules can be determined with great accuracy.

9.0 Real-time Monitoring for Suspended Particulate Matter

Suspended particulate matter (SPM) must be considered as part of the APA because PM can be emitted from landfills that do not have covers. It is understood that particulate emissions from landfills normally do not constitute a major source of COPCs. However, if the waste is excavated or disturbed by mechanical processes, one should consider the possibility of toxic PM emissions as part of the APA. This section will discuss four of the more popular real-time methods for monitoring ambient air particulate matter. They are:

- Forward scatter near-infrared (RAM and MINIRAM) monitors,
- Cascade impaction-piezoelectrical balance monitors,
- Beta attenuation monitors, and
- TEOM particle monitors.

9.1 Forward Scatter Near-Infrared (RAM and MINIRAM)

The RAM is a stationary or portable self-contained aerosol monitor whose sensing principle is based on the detection of near-forward scattered electromagnetic radiation in the near-infrared. The instrument uses a pulsed semiconductor light emitting diode which generates a narrow-band emission centered on

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940 nm. The scattered radiation is detected by means of a silicon photo-voltaic-type diode with integral low noise preamplifier.

Signal processing is performed by employing a lock-in synchronous scheme that allows continuous cancellation of detector and electronic circuitry drift and noise. The standard instrument is supplied with three selectable ranges (0–2, 20, 200 mg/m³) to allow for high resolution over a concentration range of five decades. Further readout flexibility is obtained through four selectable time constants (0.5, 2, 3 and 32 seconds); thus, the operator has complete control over both the range and the speed of response.

The concentration data are continually displayed by a three and one-half digit liquid crystal display. Included in the display are two diagnostics to alert the operator; a flashing “k” on the right-hand side of the display indicates that the reference scatterer is inserted, and a flashing “VDC” indicates a low battery voltage. An analog voltage (0–10 FDC) output proportional to the concentration is also available for strip chart recording, data logging and/or telemetry.

The flow system employs a diaphragm pump to produce the desired sampling flow to 2 L/min. A secondary clean air stream of 0.2 L/min provides continuous flushing of filtered air over all critical optical surfaces. Also, the entire inlet airflow is filtered during a zero check to effect a self-cleaning of the optical sensing chamber. The flow meters are provided to allow for continuous monitoring of the total and filtered flows.

The instrument is designed to operate continuously for 6 to 8 hours after the internal battery has been fully charged. A separate charger is provided with which the RAM can operate indefinitely from the AC line.

The MINIRAM (Miniature Real-time Aerosol Monitor) is a light scattering aerosol monitor of the nephelometric type (i.e., the instrument continuously senses the combined scattering from the population of particles present within its sensing volume—approximately 1 cm³—whose dimensions are large compared with the average separation between the individual airborne particles).

The MINIRAM operating principle is based on the detection of scattered electromagnetic radiation in the near infrared. The MINIRAM uses a pulsed gallium (GA) light emitting source, which generates a narrow-band emission centered at 880 nm. This source is operated at an average output power of about 2 mW. The radiation scattered by airborne particles is sensed over an angular range of approximately 45 to 95 degrees from the forward direction by means of a silicon-photovoltaic hybrid detector with internal low-noise preamplifier. An optical interference-type filter is incorporated to screen out any light whose wavelength differs from that of the pulsed source.

In operation, air surrounding the MINIRAM passes freely through the open aerosol sensing chamber as a result of air transport caused by convection, circulation, and ventilation. The MINIRAM requires no pump for its operation, and the scattering sensing parameters have been designed for preferential response to the particle size range of 0.1 to 10 µm, ensuring high correlation with standard gravimetric measurements of both the respirable and inhalable size fractions. Optional flow accessories are available for applications requiring specific inertial particle precollection, extractive sampling, concurrent filter collection, etc.

9.2 Cascade Impaction (Piezoelectrical Balance)

The cascade impaction piezoelectrical balance air particle analyzer is an aerosol particle mass concentration and size distribution analyzer that gives data in real time. The monitor is based on the principle of cascade impaction. However, it achieves its real-time capability by using the piezoelectric quartz crystal microbalance (QCM) mass sensor to electronically weigh particles in each impactor stage. The sensing component consists of dual-crystal design involving a sensing and reference crystal. Only one of the two unsealed crystals collects particles. The other acts as a reference to null out temperature and humidity effects. The frequency difference between the crystals is the QCM signal, and it changes in proportion to particles collected on the sensing crystal. A built-in microcomputer processes the QCM signals and provides the data output in a printout.

The QCM sensing crystal with particles on it can be recovered from the sampler after a period of time and analyzed for metals through scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy.

9.3 Beta Attenuation Monitor

The beta attenuation monitor samples at ambient temperatures, relative humidities, and gas concentrations to minimize particle volatilization biases. These monitors operate at a low-volume flow rate (nominally 16.7 L/min) using either a virtual impact or cyclonic flow operating principal to determine the 50 percent cut-point. For beta attenuation monitors, low energy beta rays (i.e., 0.01–0.1 MeV electrons) are focused on deposits on a filter tape and attenuated according to the approximate exponential function of particulate mass (i.e., Beer's Law). These automated samples employ a continuous filter tape. Typically, the attenuation through an unexposed portion of the filter tape is measured, and the tape is then exposed to the ambient sample flow where a deposit is accumulated. The beta attenuation is repeated, and the difference in attenuation between the blank filter and the deposit is a measure of the accumulated concentration. Blank corrected attenuation readings can be converted to mass concentrations for averaging times as short as 30 minutes. Although these monitors are capable of producing half-hourly average mass concentrations, a 24-hour averaging period is required for typical ambient concentrations to obtain sufficient particulate deposition for an accurate determination. The two types of beta-gauges are the Andersen Beta-Gauge (Inorganic Compendium Method 10-1.1) and the Thermo Environmental, Inc. (formally Wedding and Associates) Beta-Gauge (Inorganic Compendium Method 10-1.2).

The Andersen monitor directly measures particulate mass at concentrations of 0.005–20 mg/m³ on a real-time basis. With the Andersen instrument, ambient air enters the monitor through an inlet head. The inlet head can be designed for either total suspended particulate matter (TSP), PM₁₀, or PM_{2.5} sampling. If the sampling requirement is for PM₁₀, then the flow rate is 16.7 L/min. The air containing the PM enters the instrument where it is pulled through a glass fiber filter tape, and the particles are deposited on the tape. Low level beta radiation is emitted from a stainless steel capsule containing Krypton-85 gas towards the filter tape containing deposited particulate matter. The particulate matter on the tape reduces the intensity of the beta radiation reaching the measuring chamber on the opposite side of the tape. To compensate for the effect of the filter tape on the reduction of the level of beta radiation, the source directs a second beam of beta particles through a "foil" that mimics clean filter tape to a second measuring chamber (compensation chamber). No air flow is directed to the compensation foil, so the effect of the foil on the beta radiation intensity remains constant. The instrument compares the measurement of the compensation foil to the measurement of the filter tape with deposited PM to determine the mass of the particulate matter. Because changes in temperature, pressure, or humidity can affect measurement of PM on the filter tape, the measurements made through the compensation foil are impacted to the same degree. The foil measurements provide baseline data to compensate for these meteorological effects. Therefore, this monitor is less sensitive to temperature, pressure, and humidity fluctuations than some other types of continuous particle monitors because the compensation foil measurements provide baseline data. Because the measuring mechanism lacks moving parts, the instrument is not as sensitive to vibrational effects as other types of continuous particulate monitors. The Andersen monitor has certain limitations or interferences. In high-humidity or rainy climates, water may collect on the filter tape and cause artificially high mass readings. In these same climates where the instrument is housed in an air-conditioned environment, the ambient air inlet tube should be insulated to avoid condensation or the inlet tube should be heated to ensure that any water drawn into the unit is vaporized.

The Thermo Environmental, Inc. beta gauge operates under the same basic principles as the Andersen monitor, but with some differences. The Thermo monitor can measure ambient mass concentration with a resolution of about 3 µg/m³ for a 1-h sampling period. A constant volumetric flow rate for the PM₁₀ inlet of 18.9 L/min is used compared to the 16.7 L/min for the Andersen unit. A major difference between the two monitors is the beta source. The Thermo monitor uses a carbon-14 beta source compared to Krypton-85 gas for the Andersen monitor. The carbon-14 source does not require a license by the Nuclear Regulatory Commission, whereas the Krypton-85 does.

9.4 TEOM Particle Monitor

Different from the beta-gauges, the Rupprecht and Pataschnick (R&P) real-time particulate monitor is based upon a tapering element oscillating microbalance (TEOM) as the filter-based measurement system to continuously measure particulate mass at concentrations between 5 pg/m³ and several grams per cubic meter on a real-time mass monitoring basis. The instrument calculates mass rate, mass concentration, and total mass accumulation on exchangeable filter cartridges that are designed to allow for future chemical and physical analysis. In addition, this instrument provides hourly and daily averages. This

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system operates on the principal that particles are continuously collected on a filter cartridge mounted on the tip of a tapered hollow glass element. The element oscillates in an applied electric field. With this monitor, particle-laden air enters through an air inlet and then passes to the sensor unit containing the patented microbalance system. The inlet system is equipped with a sampling head for either TSP, PM₁₀, or PM_{2.5}.

In operation, the sample stream passes into the microbalance system, which consists of a filter cartridge (½ inch diameter) and oscillating hollow tube, where the stream is heated to a predetermined temperature. The filter cartridge is a ½ inch diameter thin aluminum base (foil-like) assembly. A water resistant plastic cone, which fits onto the oscillating element, is attached to the aluminum base. An automatic flow controller pulls the sample stream through the monitor at flow rates between 0.5 and 5 L/min. The wider end of the hollow element is fixed to a platform and is vibrated at its natural frequency. The oscillation frequency of the glass element is maintained based on the feedback signal from an optical sensor.

As mass accumulates on the filter cartridge, the resonant frequency of the element decreases, resulting in a direct measurement of inertial mass. Based on the direct relationship between mass and frequency, the monitor's microcomputer calculates the total mass accumulation on the filter and the mass rate and mass concentration in real-time.

The TEOM monitor is very sensitive to mass concentration changes and can provide precise measurements for sampling duration of 1-h or less. To achieve this level of precision, the hollow glass element must be maintained at a constant temperature to minimize the effects of thermal variations. Because the instrument's primary operating mechanism is the microbalance system, the instrument should be isolated from mechanical noise and vibration. The operating temperature of the element can be lowered to minimize the potential particle loss bias for more volatile compounds but must be maintained above the maximum ambient temperature encountered during the field sampling.

Table A-8 outlines the various weaknesses and strengths of each of the discussed systems. The RPM and/or the OSC should examine each of these items before incorporating them into a MSW landfill gas monitoring program.

10.0 Federal Reference Method 21

The various fugitive emission regulations—New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), and state implementation plans (SIPs)—require the use of Federal Reference Method 21 (FRM 21) for determining the concentrations of fugitive VOCs with reference to methane. In particular, FRM 21 is specified as the sampling and analytical methodology for the fugitive leak detection program applicable to petroleum refineries. This same technology is now being applied to the monitoring of fugitive CH₄ and VOC emissions at MSW landfills. It is therefore imperative to become familiar with FRM 21 and its application to landfill gas monitoring.

FRM 21 can be found in 40 CFR 60, Appendix A. 40 CFR 60 covers the NSPS and EG, and Appendix A contains the Federal Reference Methods that must be used in determining emission compliance with the limits specified in the rules. FRM 21 does not recommend specific analyzers or manufacturers, but it does define analyzer performance specifications.

10.1 Portable VOC Analyzers

Portable VOC analyzers take two forms: (1) single hand-held units containing all the instrumentation in one unit, and (2) multi-component units that separate the inlet from the analytical section of the system by way of an umbilical cord. This approach allows greater flexibility in the field to reach difficult locations.

Each analyzer comprises two functional units: the probe mechanism and the analytical assembly. In addition, each analyzer should contain a power supply (battery) and support gas(es). In the case of the multi-component analyzer, there should be an umbilical connector between the probe and the analysis unit, as illustrated in Figure A-6.

Table A-8. Weaknesses and Strengths of Real-Time Monitoring Systems Applicable to MSW Landfill Gas Monitoring.

Monitoring Technique	Weakness	Strength
NDIR	• Other gases absorb in spectral region. • Optical maintenance high. • Pressure/Temperature sensitive.	• Relative low cost. • Can be applied to multiple gases.
NDUV	• Other gases absorb in spectral region. • Narrow absorption bands limit detection.	• Use of differential absorption. • More sensitive than NDIR. • Water not an interference.
Electrochemical	• High-temperature required to detect O₂. • Cell interface must remain moist.	• Inexpensive and portable. • Cells can be easily interchanged or replace for different pollutants. • Multiple cells in one analyzer allows flexibility.
GFC	• Requires pressure cells in monitoring. • Gas cells may leak. • Applicability limited to small number of gases .	• Improved specificity over conventional NDIR/NDUV. • Ability to monitor various constituents at one time.
OP-FTIR	• Must use library comparison of spectra. • Complex spectra interpretation.	• Ability to analyze complex spectrum. • Can be used as extractive or remote monitor. • No consumables. • On-site fast/instantaneous analysis.
Ion Mobility Spect. (IMS)	• Inability to discriminate between two compounds with similar mass. • Linear range small. • Variable day-to-day response. • Gases must be able to accept an electrical charge in order to be detected.	• No moving parts. • Low detection limits. • Sample matrix interference may be minimized by GC. • IMS universal detector.
GC/MS	• Greater equipment cost. • Requires high vacuum source. • Routinely requires preconcentration of sample.	• Positive compound identification. • Systems now very portable. • System more specific to analyte identification. • Less operator interpretation.
Remote Monitoring	• Operating cost are higher than traditional methods. • High degree of education required to operate system.	• More representative of emissions in open path. • On-line 24 hr per day. • Multi-pollutant analysis routine. • On-site analysis; no off-site analysis required.
Passive Sampling Devices	• Must have high concentration or integrated over a longer time period than traditional systems. • Many interferences which have not been completely studied.	• Lost cost. • Small and less obtrusive, lightweight. • No pump requirements. • Quiet operation. • Easy to use.



Figure A-6. Typical Federal Reference Method 21 Portable Fugitive VOC Analyzer.

The objective of the probe assembly is to extract a representative fugitive emission sample from the source (i.e., inlet or outlet to LFG combustion equipment, bore hole/soil gas sampling, landfill surface monitoring, or ambient air monitoring) and move it to the detector for analysis. To minimize dilution of the gas stream as it is being pulled into the system, FRM 21 specifies that the probe opening cannot be greater than 1/4 inch outside diameter. Optional components of the probe and the interface assembly include meter-readouts and particulate filters.

The analytical assembly normally contains the detector, electronics processing boards, pump, flow control devices, high pressure gas cylinders, power supply, and service panel.

FRM 21 does not specify a particular manufacturer's instrument to be used in determining CH₄ and VOC emissions. Rather, FRM 21 requires that portable VOC detection equipment must meet specific instrumentation specifications and certain performance criteria.

10.2 Instrument Specifications

FRM 21 has eight instrument specifications that must be met in order for the portable instrument to be part of an emission monitoring program:

- VOC monitor response to the process chemical being tested,
- Measurement range must include the "leak definition,"
- Scale resolution,
- Response time,
- Intrinsically safe,
- Probe dimensions specifications,
- Response factor requirements, and
- Accuracy requirements.

10.2.1 Monitor Response. The portable VOC analyzer must be able to respond to compounds being processed and regulated. Two of the most commonly used detectors in fugitive VOC monitoring are

- Flame ionization detector and
- Photoionization detector.

By far the most widely used detector for portable total hydrocarbon analysis is the FID. The gas sample is introduced into a hydrogen/air flame, the CH₄ and VOCs are burned, ionized, and detected. The technique is specific for organic compounds and gives relatively uniform response for the various compounds.

The PID is the second most popular VOC analyzer. The PID analyzer also ionizes the VOCs in the gas stream. Instead of burning the gas stream, it uses high intensity ultraviolet light (UV). Since the ionization potential of a particular compound must be less than the ionization of the UV light energy in order to be detected, this means that the PID is not as universal a detector as the FID.

10.2.2 Measurement Range. The portable fugitive VOC analyzer must have a measurement range that encompasses the leak definition for landfill gas applications; this means that the instrument must be able to detect fugitive CH₄ and VOCs as high as 500 ppmv above background.

10.2.3 Scale Resolution. The third instrumentation specification is that the scale reading on the analyzer must be readable to within ± 2.5 % of the specified leak definition concentration when performing a “no detectable emission” survey. For a leak definition of 500 ppmv, this means that the scale reading must be readable to 12.5 ppmv.

10.2.4 Response Time. The response time (RT) instrument specification is defined as the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached and displayed on the instrument readout meter. In operation, zero gas is introduced into the instrument and a stable reading is obtained. Then, quickly switch to the calibration gas and measure the time from switching to the time when 90 percent of the final stable reading is attained. The user then performs this activity two additional times to obtain an average of 3 readings for the average response time. FRM 21 specifies that the average must be less than 30 s.

10.2.5 Safety. The instrument must be intrinsically safe. This is a very important requirement because of CH₄ emissions at MSW landfills and because many of the organic emissions are explosive.

10.2.6 Probe Dimensions. To minimize biases from dilution, the maximum outside diameter (OD) of the sample probe can be no greater than 1/4 inch. A larger probe OD has the ability to pull surrounding air into the probe, thus diluting the sample and producing a bias in the sampling system. The specification also states that the pump in the instrument must be able to draw sample gas at a rate of 0.10 to 3.0 L/min into the 1/4 inch OD probe opening. The flow rate range was selected after field studies indicated that this range limited the biases of the sampling technique due to sample extraction.

10.2.7 Response Factor (RF). This instrument specification requires that the RF be less than 10 for the specific VOC being tested. This specification requires the user to use an instrument that responds within a certain level of reliability and accuracy to the VOC being monitored. The specification requires the user to determine the RF for each of the VOCs being monitored.

A response factor of 1.0 means that the instrument readout is identical to the actual concentration of the chemical in the gas sample. As the RF increases, the instrument readout is proportionally less than the actual concentration. A high RF means that the instrument does not detect the compound very well. A low RF means that the instrument is very sensitive to the compound of interest.

10.2.8 Accuracy. Similar to the response time test, this instrument specification associated with calibration precision (accuracy) requires a calibration gas to be introduced into the analyzer three times and that the average response of the analyzer must be within 10 % of the certified calibration gas value recorded on the calibration gas cylinder. This specification assures that the user is using a well characterized instrument in determining CH₄ and VOC concentrations.

10.3 Performance Criteria

FRM 21 requires the following checks for each analyzer to ensure that the analyzer meets FRM 21 performance criteria:

- The response factor (RF) must be determined for each compound that is to be measured before placing the analyzer into service.

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- A response time (RT) test must be performed prior to placing the analyzer into service and whenever there is a change to the sample pump or flow system of the analyzer.
- A calibration precision test must be completed prior to placing the analyzer into service and every 3 months thereafter (or at the next use, whichever is later).

The performance criteria specifications require that a calibration precision test be performed before the analyzer is placed-in-service and at a minimum every 3-months.

The calibration precision test is performed by three analyses of zero gas being introduced, then an analysis of the certified calibration gas (CH₄) being introduced into the analyzer to determine the analyzer's response to the calibration gas. The acceptance criteria is $\pm 10\%$ of the certified calibration gas concentration as recorded on the gas cylinder or on the certification papers.

Calibration tests must be performed prior to placing the monitor in service and should be done at the inspector's dedicated facility for maintaining monitors. The basic components for performing calibration checks on the analyzer are

- NIST traceable gas cylinders,
- Tedlar bags,
- Appropriate tubing, and
- Field portable VOC analyzer.

Detailed procedures are described in the regulations and with the manuals that accompany the analyzers covering the proper operation, use and storage of the analyzer.

10.4 Selecting an Analyzer

There are no specific rules for selecting an analyzer since many factors that enter into the selection are agency/site specific. However, the list below provides some items to consider when selecting an analyzer to place in service as part of a landfill emission monitoring program.

- Determine the amount of use and type of emission points to monitor as part of the landfill emission monitoring program.
- Specify needs for the portable fugitive analyzer to be used in order to minimize time and labor associated with landfill gas monitoring requirements (i.e., bar code scanning needs, audible alarm level capability, data logger capability, etc.).
- Size, weight and bulk of instrumentation.
- Ease of instrument data logger interface with project data management software.
- Enhanced speciation capability for future VOC emission inventory.
- Durability of analyzer, power supply system, and data logger under unique conditions (for example, cold weather impacts).
- Ease of operation, calibration, and on-the-job repairs.
- Level of manufacturer's technical support.

11.0 Application of Different Sampling Techniques

Monitoring at a MSW landfill may involve landfill surface monitoring, soil gas monitoring, and LFG combustion equipment monitoring.

11.1 Landfill Surface Monitoring

Landfill surface monitoring is usually performed to verify that the LFG collection system is working adequately and that there are no detectable leaks in the system. Using a FRM 21 portable analyzer allows the investigator to examine the property and certify control of fugitive emissions. However, the likelihood of landfill surface monitoring success depends on how the investigator performs the soil gas sampling methodology. The application of the methodology should be guided by the objectives of the project and the perceived spatial and temporal array of the potential sampling targets. Of course, if the landfill is controlled by an impermeable membrane, this type of sampling is unnecessary except at membrane seams, suspected openings or tears, and at any membrane penetration (i.e., LFG vents).

Historically, the ability to obtain data distributed over a geographic area allows the investigator to obtain scientific and accurate data so regulatory decisions can be made. The use of a grid design with patterns of variable design and spacing can serve very effectively toward the objectives of obtaining a

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11.1.2 Sampling Methods and Procedures. A maximum surface concentration of 500 ppmv CH₄ above background indicates proper operation of the landfill cap and recovery system. The following test methods and procedures should be followed, as outlined in 40 CFR 60, Appendix A, FRM 21.

A portable hydrocarbon analyzer that satisfies 40 CFR 60, Appendix A, FRM 21 should be used to determine the CH₄ concentration at each sampling point, and the instrument should be operated according to manufacturer's instructions.

1. Assemble and start-up the instrument according to manufacturer's instructions.
2. Evaluate the response factor with a known concentration of certified methane gas and document.
3. Calibrate with a certified methane standard reference (80% of emission limit), also using zero gas as background, certifying that the instrument returns to zero.
4. Repeat twice more to obtain three measurements of the methane standard and zero gas concentration.
5. Calculate three individual and one average response factors.
6. Calibration Precision.
 - Make three measurements by alternately using zero gas and calibration gas.
 - Calculate the calibration algebraic difference between the meter reading and the known value.
 - Calculate calibration precision (%).
7. Response Time.
8. Leak-check sample system.
9. Set electronic zero and alarm levels (if applicable).
10. Set zero using background (<10 ppm VOC) air.
 - Sampling should be performed during typical meteorological conditions.
 - Measure the background methane concentration by moving the analyzer probe inlet upwind, outside the boundary of the landfill at a distance of at least 98 ft (30 m) from the limits of the landfill. Record on the field test data sheet.
 - The predetermined grid layout of the landfill with the grid mark separations no more than 30 m apart are the sampling points.
 - The field portable detector probe should be no greater than 1 inch from the surface of the landfill.

11.1.3 Sampling Grid Pattern. A pattern of parallel lines approximately 98 ft (30 m) apart should be established over a majority of the surface area of the landfill that contains buried refuse. Per 40 CFR Part 60, Section 60.53 (c)(d), areas with steep slopes or dangerous areas will not be monitored. The tester should walk the path and record a sampling result at approximately 98 ft (30 m) intervals as illustrated in Figure A-7. The tester should first obtain a reading upwind of the site for background information. Then, the tester should start at a known location and begin walking the perimeter of the site, noting readings every 30 m. Perform parallel surveys until the complete landfill surface has been evaluated using the grid approach. Any cracks, holes, passive vents breaches in the surface, or interfaces with undisturbed native soil should also be tested.

Any reading 500 ppmv or more above background should be noted, and the locations of the readings should be marked and recorded. Landfill cover maintenance or adjustments to the LFG collection system should be made, and the location should be re-monitored within 10 calendar days of the initial exceedance. If remonitoring the location shows a second high reading, additional corrective action should then be taken, and the location should be re-monitored within 10 days of the second high reading. A proposed corrective action plan and corresponding time line should then be prepared for any location where monitored methane concentrations equal or exceed 500 ppmv above background three times within a quarterly period.

11.1.4 Monitoring Frequency. Surface emissions testing for the entire landfill should be performed quarterly.

11.1.5 Recordkeeping. The location and concentration of each high reading recorded during the surface emissions tests should be reported in an annual report. The concentration recorded at each location for which a high reading was recorded in the previous month should also be included in the annual report. Reports and monitoring records should be maintained for a period of five years.

11.2 Soil Gas Sampling

The Geoprobe sampling device has been accepted as a useful device for collecting soil, soil-gas, and groundwater samples at specific depths below ground surface. The Geoprobe is attached to the rear of a customized vehicle. In the field, the rear of the vehicle containing the Geoprobe is placed over the sample location. The vehicle is hydraulically raised on its base, and the probe is pushed into the ground as the weight of the vehicle is transferred to the probe. A built-in hammer mechanism allows the probe to be driven to predetermined depths, up to 50 feet.

Using the Geoprobe as the entry point into the landfill, soil gas sampling can be collected by two techniques:

- Withdrawing a sample directly from the probe rods after evacuating a sufficient volume of air to ensure that a fresh sample is being extracted.
- Collecting a sample through tubing attached by an adaptor to the bottom of the probe section. This is the preferred method because it provides more reliable results.

The internal framework of the Geoprobe is illustrated in Figure A-8. The investigator has numerous options by which to collect the sample:

- **Whole-Air Active Sampling (Compendium Method TO-15).** Using this configuration, a specially-treated whole-air canister is attached to the outlet of the sampling line which has been extended to a predetermined depth. If the canister has been previously evacuated to a pressure of -29 inches Hg, then the vacuum in the canister will withdraw the soil gas sample. Normal operation would also include an in-line flow controller and a sintered stainless steel filter to minimize particles becoming entrained in the canister atmosphere. This would allow time-integrated sampling over a given time period depending upon the selected flow rate. A normal flow rate of 1.5 mL/min would allow a 24-hour sample to be collected. The canister is then returned to the analytical laboratory where CH₄, NMOCs, and speciated organics are detected by a FID and GC/MS detectors. This approach is suited to soil gas monitoring where the contaminant concentrations are expected to be high and the vadose zone is highly permeable to vapors. If a Tedlar bag is used to collect the soil gas vapors, then an external pump is needed to move the sample from the probe tip into the Tedlar bag.
- **Solid Adsorbent Sampling (Compendium Method TO-17).** Solid adsorbent technology requires the soil gas sample to be forced from the probe tip through the adsorbent where the COPCs are trapped. This system is well suited to sites where the soil may be highly permeable to vapor and where the contaminant concentrations may be lower than required when applying whole-air active sampling. Using solid adsorbent technology allows one to collect more sample by extending the sampling period in order to reach desirable detection limits. Adsorbent technology allows one to concentrate the COPCs while allowing gas constituents that interfere with the analytical system to pass through the sampling system. Adsorbent technology allows the investigator to select a particular adsorbent for a unique list of COPCs. Common adsorbents utilized in air monitoring programs are:
 - XAD-2/Tenax/Charcoal for general medium volatile organics (C₆-C₂₀),
 - Fluorisil for chlorinated organics, and
 - Carbosieve SIII for nonpolar, very volatile organics (C₂-C₅ hydrocarbons).

Once the COPCs have been retained on the sorbent, the sorbent is returned to the laboratory for analysis by thermal desorption followed by GC/MC identification of speciated organics.

- **On-line GC Monitoring (Compendium Method TO-12/14A).** Direct on-line GC monitoring allows the investigator to obtain real-time data of COPC concentrations. From on-line data, one can plot concentration over time to study soil permeation rates. In addition, on-line sampling can be performed for other constituents (i.e., CO, CO₂, O₂, HCl, Cl₂, SO₂, NO_x, etc.).
- **FRMs 18/25.** FRMs 18 and 25, were developed for source emissions testing, are very similar to Compendium Methods TO-17 and TO-15, respectively.

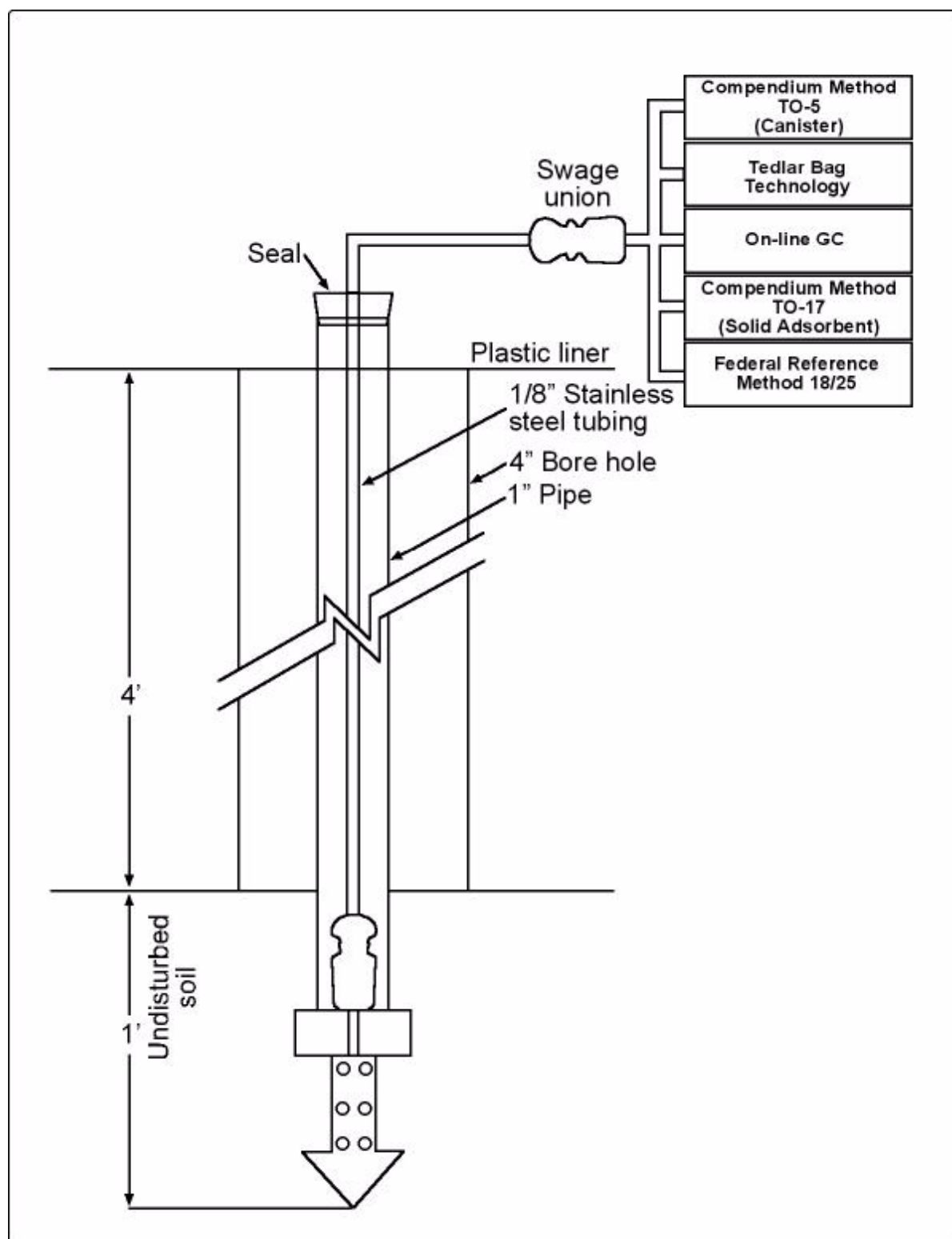


Figure A-8. Geoprobe Bore-hole Sampling Technique With Sampling Methodology.

The success of an active sampling approach to soil gas monitoring starts with the investigator driving a probe into the ground either by using the Geoprobe or by using a “slam bar.” Both of these approaches tend to destroy the natural soil permeability around the body of the probe due to soil compaction concurrent with the insertion. This is most evident in moist, heavy clay soils. Similarly, in very dry, cemented soils, driven probes can create fractures within the soil body, thus enhancing soil permeability to vapor concurrent with insertion. This can allow ambient air to mix with the contaminated soil atmosphere, thus diluting the soil gas sample. These concerns are significant when using soil probes with internal diameters greater than 3 inches. Historically, cluster wells of soil vapor probes at different depths (see Section 3.1, Figure 3-3) are used for subsurface CH₄ monitoring.

In an effort to minimize the number of sampling probes being inserted into the landfill, the use of a 1/4 inch sampling probe allows for the ability to extract a sample while minimizing the impact on the soil. Once in position, a pre-evacuated whole-air canister can be attached, as illustrated in Figure A-9, or a syringe sampling approach can be used as illustrated in Figure A-10. For semi-volatile monitoring, Figure A-11 illustrates the application of a low-volume sampling approach using EPA Compendium Method TO-10 involving PUF adsorbent sampling collocated with a whole-air canister for VOCs using Compendium Method TO-15. Once again, the sample extracted from the subsurface is regulated by an in-line flow controller along with an in-line sintered stainless steel filter to remove particles in the sample gas. This approach has many advantages:

- No power required for the monitoring system,
- One-man operation, thus minimizing labor hours,
- Ease of sampling operation and sample transport, and
- Field portable, allowing many samplers to be deployed for obtaining representative samples.

RCRA Subpart C requires monitoring of subsurface CH₄ concentrations at the landfill property boundary and within onsite structures. Subpart C does not, however, specify the number of wells or their spacing. This is determined on a site-specific basis.

Finally, the collection and concentration of soil gas contaminants can be greatly effected by the components of the sampling system. It is imperative that one use materials that are inert to the COPCs in the field investigation. Areas to which the investigator needs to pay close attention are:

- Sealing around the probe shaft at the entry point to minimize infiltration of ambient air, which can be minimized by packing the shaft with hydrated bentonite or clay, as illustrated in Figure A-8;
- Using stainless steel for the probe, with the bottom third perforated;
- Minimizing the use of porous or synthetic materials (i.e., PTFE, rubber or most plastics), which can retain sample or contribute cross-contamination;
- Purging the sample probe before attaching it to the collection system; however, purging the probe prior to sampling under conditions of low soil permeability and low contaminant concentration may actually lower contaminant levels below the analytical detection limits;
- Leak-checking the sampling system prior to sample collection to detect potential leaks and to minimize soil gas dilution; a leak-tight seal at the sampling port and leak-tight fittings in the sampling equipment helps minimize dilution of sample gas by air infiltration;
- Keeping all transfer lines short as possible to minimize trapping particulate matter and condensing extracted landfill gas in the lines.

As illustrated in Figure A-9, soil gas sampling for CH₄ and VOCs typically employs an evacuated, specially-treated canister connected to a flow controller and subsequently connected to the sampling probe. The sampling probe is first purged of at least two volumes of air using a special fitting and a purge pump. Flow is then stopped for a given time period to allow the vapor concentration in the soil pores to re-establish equilibrium conditions. Actual sampling then begins at a sampling rate low enough to prevent ambient air from infiltrating the sample. For shallow soil gas sampling, air may flow down the annulus of the probe and dilute the sample if the sampling rate is too high and the seal at the ground surface is not air-tight. Once a sufficient sample volume has been extracted, the canister is shipped to the laboratory for analysis. It should be stressed that soil gas concentrations may vary considerably over relatively small distances given the heterogeneity of the soil. Therefore, a sufficient number of samples at varying locations should be taken to establish a reasonable average value for each contaminant. If sampling is used to estimate soil gas concentrations beneath a building floor, the sampling probes should be inserted through holes drilled in the basement slab. Alternatively, the probe can be inserted at an angle under the building from outside the footprint of the building floor in contact with the soil.



Figure A-9. Application of EPA's Compendium Method TO-15 for VOCs at a MSW Landfill.

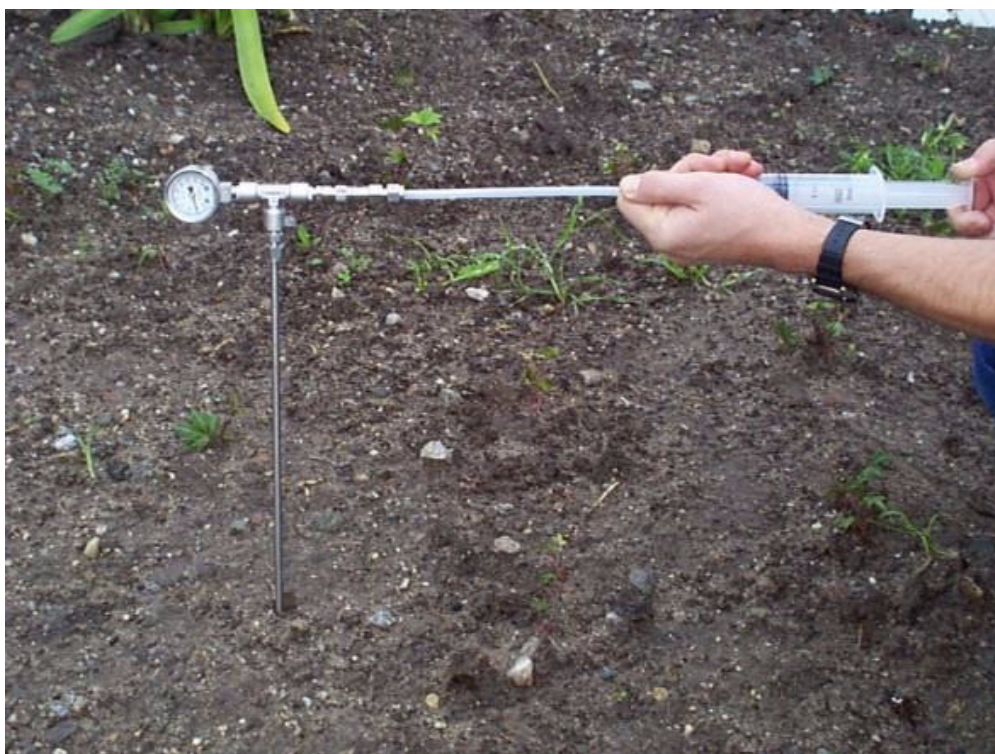


Figure A-10. Application of Syringe Monitoring for VOCs at a MSW Landfill.



Figure A-11. Application of Compendium Method TO-10A (Semi-volatiles, PCBs) and Compendium Method TO-15 (Methane, NMOCs, VOCs) Sampling at a MSW Landfill.

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11.3 Vent Monitoring

Monitoring vent tubes from MSW landfills is very similar to monitoring ambient air or LFG combustion equipment. In vent monitoring, the investigator needs to select low-volume sampling technologies so that the samples will be representative of the actual emissions from the vent. Sampling can be performed directly from the vent by inserting a probe into a small sampling port or directly down the vent. The sample is then extracted into the sampling apparatus, similar to bore-hole monitoring illustrated in Figure A-8.

If the flow of exhaust gas through the vent tube is very low, one can encapsulate the exhaust of the vent tube to retain the sample. The sampling probe is therefore inserted into the encapsulated vent. This sampling approach is illustrated in Figure A-12. This application illustrates employing Compendium Method TO-10, a low volume approach for sampling and analysis of dioxins, furans, and PCBs from the capped landfill. Figure A-13 illustrates sampling the exhaust of the landfill vent by employing samplers upwind and downwind of the emission point. Once again, a low volume sampling approach is used to capture the exhaust from the landfill vent.

11.4 Perimeter Air Monitoring

Many factors must be considered when developing a monitoring plan for the characterization of emissions leaving a MSW landfill. Such factors as target COPCs, monitoring equipment and analytical capability, cost, availability of utilities at perimeter site locations, etc. The first step in the development of a perimeter air monitoring program is the design of a monitoring strategy. The monitoring strategy helps determine the overall objectives of the monitoring program. In developing a monitoring strategy to meet sampling program objectives, several crucial items should be considered:

- Processes and sources to be characterized,
- Any relevant rules or ARARs that require the monitoring program to be conducted, and any specific regulatory requirements,
- The intended use of the monitoring data,
- A summary of DQOs and other QA concerns, and
- Any cost, physical, and time constraints.



Figure A-12. Encapsulated Vent Tube Sampling for PCBs Utilizing EPA Compendium Method TO-10A. (Note Portable Monitor to the Right of the Vent Tube for Ambient Monitoring of Emissions During Normal Vent Tube Emissions.)



Figure A-13. Upwind/Downwind Sampling for PCBs from a Landfill Vent,

The following is a brief overview of some of the important aspects when implementing and developing a perimeter air monitoring program at a MSW landfill.

11.4.1 Site Characteristics. One of the most important aspects to consider when evaluating site characteristics is the site terrain. The geometry of the site and the contour of the location directly influence the extent and the design of the perimeter air monitoring program. Extremely complex terrain will complicate the migration of contaminants and make evaluation techniques complex with uncertain results. Fixed-point monitors may not be as effective as the application of open-path optical remote sensing devices because of the likelihood of the fixed-point monitors missing the “site plume.” To compensate, one can increase the number of fixed-point monitors as part of the perimeter air monitoring program on both the horizontal and vertical plane in an attempt to characterize the site plume. Another option is to use air dispersion modeling to map the site plume; however, air dispersion modeling is often difficult to implement and results may be inaccurate and non-representative.

Local meteorological conditions will also play a major role in the design of a perimeter air monitoring program. The placement of inlet extractive probes of a real-time or time-integrated monitoring systems must be such that the gas sample analyzed is truly representative of the site emissions regardless of wind direction. Historically, the evaluation of the 5-year wind rose (i.e., wind speed and direction distributions) is used to help locate inlet probes in an upwind/downwind scenario based upon the dominant wind direction. However, the uncertainty of the meteorological conditions at the site would require, at a minimum, four inlet probes for real-time or time-integrated monitoring systems around the site with the first system placed in the upwind quadrant based on the 5-year wind rose and the remaining systems at 90° around the site with reference to the upwind station. This placement allows appropriate coverage at a reasonable cost.

Accessibility to sampling sites is also a consideration when designing the perimeter air monitoring system. Under best conditions, the site will have an access road around the perimeter where the CH₄ sampling probes are located for ease of maintenance and auditing. The access road saves time and labor when performing inspection and audits of monitoring equipment. In addition, available utilities are important for both real-time and time-integrated networks of samplers.

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11.4.2 Evaluation of Available Information. A substantial savings in sampling time and costs can be realized by evaluating existing information. Although such information seldom satisfies the objectives of the sampling program, it can provide valuable insight into what analytes to sample, when and where sampling should be performed, and what sampling techniques are likely to be successful. For example, data from a past sampling program at a similar site may indicate which compounds are likely to be present and at what concentrations. Historical data from a nearby site might indicate the extent to which background concentrations may contribute to the on-site concentration measurements. Additionally, information may be available on contaminant phase distribution characteristics and monitoring equipment performance. The time devoted to locating and reviewing information on past test programs usually pays for itself in the development of a more efficient sampling strategy.

11.4.3 Meteorological Data. Ordinarily, the monitoring strategy will include collecting meteorological data. An important reason for evaluating these data is to determine whether the atmospheric conditions and pollutant concentrations have an impact on the surrounding community and are truly representative of conditions at the site. For example, because the volatilization of toxic compounds from contaminated soil is influenced by soil temperature and moisture, temperature and rainfall measurements may be especially important to monitoring strategies where the volatilization of contaminants from the soil is to be characterized. In this example, an effort would be made to conduct the monitoring program during periods when temperatures and rainfall are within normal ranges for the locale under study. At a minimum, the following meteorological parameters should be monitored on a continuous basis:

- Windspeed and direction,
- Temperature (at 10 m and 2 m heights),
- Relative humidity,
- Barometric pressure, and
- Precipitation.

Meteorological data are also important in determining where to site probes and monitoring equipment, and in assuring that siting decisions remain appropriate throughout the test period. The usual strategy for siting probes is to establish monitoring locations downwind of the source, with possibly one or two locations upwind of the source for background measurements. The use of an on-site meteorological station both before and during the sampling period will provide the information necessary to make intelligent decisions about monitor siting.

11.4.4 Selection of Instrumentation and Analytical Methods. An obvious factor in the selection of instrumentation and analytical sampling methods is the ability of the method to measure the compound of interest at a specified concentration, typically in the parts per million by volume to parts per billion by volume range for highly toxic compounds. The ability of a sampling method to measure low concentrations will depend on several factors, including:

- The sensitivity of the sampling method for the particular compound of interest,
- Applicability of the method for monitoring all target analytes,
- Ability of the instrumentation to collect, speciate and detect specific analytes,
- Cost constraints,
- Methodology performance and reliability,
- The detection limits of the chosen instrumentation and analytical method, and
- Ease of set-up and operation.

Other important factors to consider in the selection of sampling methods are: (1) the potential for artifact formation, (2) the minimization of erroneous data due to interfering compounds, (3) the ability of the method to achieve desired data quality objectives, (4) the ability to simultaneously measure other compounds of interest, and (5) the compatibility of the sampling method with available analytical methods. Questions that should be answered in the selection of instrumentation are:

- Can the selected instrument detect the probable target compounds?
- Does the sampling methodology sample the analyte effectively and quantitatively?
- Does the instrument transfer the analyte quantitatively from the inlet to the analytical detector?
- Can the instrumentation produce precise, accurate, and quantitative results for all of the analytes listed in the monitoring program goals?
- Does the selected instrumentation have detection limits low enough to meet the overall objectives of the sampling program?
- Would the methodology be hampered by any interfering compounds?

Typically, standardized sampling methods or Federal Register methods should be utilized in a perimeter air monitoring program. Table A-9 outlines recommended time-integrated sampling and analytical methods for traditional COPCs found at MSW landfills in order to reach health-based detection limits.

Table A-9. Recommended Sampling and Analytical Methodologies for COPCs at MSW Landfills.

Pollutant	Methodology	Sampling Media
Methane/NMOC	Compendium Method TO-12 Real-time CH ₄ NMOC	Whole-air canister/FID
Speciated VOCs	Compendium Method TO-15	Specially-treated canister/GC/MS or Ion Trap
Semi-volatiles, including dioxin/furans, PCBs, Pesticides	Compendium Method TO-13A	Filter/PUF/GC/MS
Particulate Matter/Metals	Compendium Method IO-1/IO-2	Filter/ICP/MS
Mercury	Compendium Method IO-5	Adsorbent Tube/AES
Reduced Sulfur Compounds	Compendium Method TO-15	Specially-treated canister/FPD
Freons	Compendium Method TO-15	Specially-treated canister/GC/MS or Ion Trap

11.4.5 Number and Location of Sampling Sites. A variety of factors influence the number and location of sampling sites around a hazardous waste site. Factors that influence the required number and location of sites are:

- Evaluation of the 5-year wind rose for predominant wind direction; location of potential on-site emission sources (i.e., process emissions, waste handling facilities etc.);
- Location of topographic features that affect the dispersion and transport of site emissions;
- Location of sensitive receptors at the site perimeter and offsite;
- Location of offsite sources that might contribute to background concentrations; and
- The level of confidence needed to ensure that the maximum concentrations are obtained.

In determining the number and location of sampling sites, dispersion models (screening and refined) should be used to assist in estimating ground-level concentrations in the site vicinity and to determine locations of maximum concentrations for short-term (up to 24 hours) averages and long-term (monthly, seasonal, and annual) averages. Inputs into the dispersion model should include landfill waste emissions, representative meteorological data, populations close to the site, and sensitive populations. The model outputs should be plotted as concentration isopleths for each COPC.

This information will assist in siting the monitoring stations. The first priority, however, should be to locate sampling sites that:

- Provide information on possible high impacts of the emission plume on sensitive receptors (i.e., concerned citizens, downwind communities, schools, hospitals, etc.) and
- Are positioned in the plume of expected high concentrations of source constituents based upon historical meteorological data and dispersion modeling results.

Typically, programs designed for determining long-term concentration levels (e.g., annual or lifetime exposures) will require fewer sampling locations than those intended to monitor compliance with short-term action levels. The long-term prevailing wind directions are usually more predictable than day-to-day wind patterns. Sampling sites, therefore, can be more accurately situated for measuring significant long-term effects.

For determining concentration levels with respect to short-term effects, a fixed network of sampling sites should ideally be located around the perimeter of the MSW landfill, with additional samplers located near working areas and near sensitive receptors. The number of sampling sites will depend, in part, on the size of the landfill site. For large sites surrounded by nearby residences, a 12-station network would provide nearly complete spatial coverage at the fence line (i.e., one sampling station every 15 degrees), as illustrated in Figure A-14. However, cost considerations may not allow for this arrangement. Another

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example would be to determine the predominant 5-year wind rose and place one monitoring station upwind and three monitoring stations downwind. A better application of the four station arrangement must be to locate a monitoring station at the centroid of each of the 90 degree quadrants of a circle based upon the 5-year wind rose, as illustrated in Figure A-15.

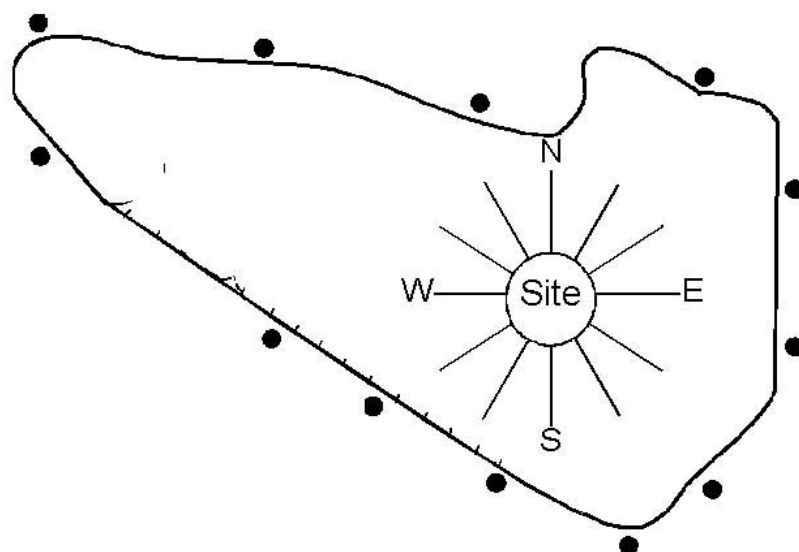


Figure A-14. Example of a 12-Point Perimeter Air Monitoring Network at a MSW Landfill site.

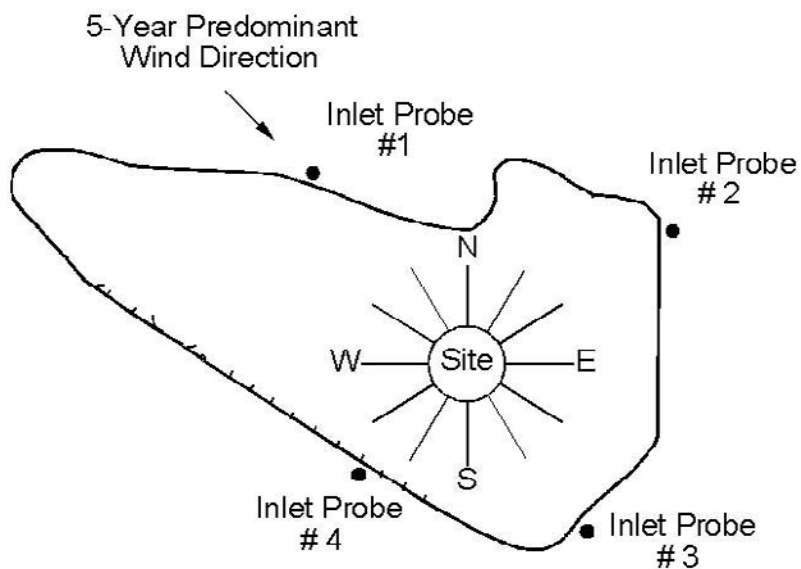


Figure A-15. Example of a 4-Point Monitoring Station Network at 90° Locations Around the Perimeter of a MSW Landfill Site.

Guidance for Evaluating Landfill Gas

Each of the stations illustrated in Figure A-15 serves specific objectives as part of the MSW landfill perimeter air monitoring program:

- Station #1 is the predominant upwind site based upon the previous 5-year wind rose; this station should identify specific constituents entering and impacting the site;
- Station #2 is the second station that provides data on the impact of emissions from the site;
- Station #3 is the predominant downwind site based upon the previous 5-year wind rose; it should be approximately 180° from Station #1; working with Station #1, a predominant upwind/downwind concentration of the emissions from the site can be instantaneously calculated; and
- Station #4 monitors the impact of emissions from the site.

After the number of stations has been determined, the placement of samplers must be considered. In many cases, constraints on placing samplers can be encountered because of wind flow obstructions caused by nearby buildings, trees, hills, or other obstacles. Other constraints might be related to security, the accessibility of electrical power, and the proximity to roadways or other pollution sources that might affect the representativeness of the sample. Specific guidelines for siting samplers for representative conditions are given in Table A-10.

Table A-10. Example of Summary of Key Probe Siting Criteria for Perimeter Air Monitoring Programs at MSW Landfills.

Factor	Criteria
Vertical spacing	• Representative of the ground breathing zone and avoiding effects of obstructions, obstacles, and on-site traffic. Height of probe intake above ground in general: 2–3 m above ground and 2–15 m above ground in the case of nearby roadways. • 1 m or more above the structure that supports the inlet probe.
Horizontal spacing	• Minimum horizontal separation from trees acting as an obstruction must be >10 m from the dripline. • Optimum horizontal separation from trees should be >20 m from the dripline. • Distance from probe inlet to an obstacle such as a building must be at least twice the height the obstacle protrudes above the inlet probe. • If the inlet probe is located on a roof or other structures, there must be a minimum of 2 m separation from walls, parapets, penthouses, etc. • There must be a sufficient separation between the inlet probe and a furnace or incinerator flue. The separation distance depends on the height and the nature of the emissions involved.
Unrestricted airflow	• Unrestricted airflow must exist in an arc of at least 270° around the inlet probe, and the predominant wind direction for the monitoring period must be included in the 270° arc.
Spacing from roads	• A sufficient separation must exist between the inlet probe and nearby on-site roadways to avoid the effect of dust and vehicular emissions on the inlet. • Inlet probe should be placed at a distance of 5–25 m from the edge of the nearest on-site roadway depending on the vertical placement of the probe inlet, which could be 2–15 m above ground.

11.4.6 Cost Factors. A number of issues affect the cost of establishing and conducting a perimeter air monitoring program at a MSW landfill:

- Objectives of the perimeter air monitoring program,
- Analytes to be monitored and the program required detection limits,
- Frequency and duration of the monitoring program,
- Accessibility for installation of the perimeter system, and
- Contingency monitoring.

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The objectives of the perimeter air monitoring program will most certainly be affected by costs. Whether the program is established to monitor risk-based concentrations of COPCs, evaluate or document off-site exposure for protection of the surrounding community, or monitor on-site workers as part of an industrial hygiene program, overall costs are affected. The primary objectives will dictate the type of sampling equipment and analytical requirements to meet the DQOs of the program. Even the level at which emissions are to be monitored will affect cost. For example, if the alert level at the perimeter is measured in terms of CH₄ and NMOCs rather than speciated organics, then the analytical equipment is less complicated, thus less costly. If, however, the purpose is to monitor individual COPCs at the risk level of 1-in-1 million, the analytical system must be far more sensitive, thus increasing the cost of the perimeter air monitoring program substantially.

The number and type of analytes to be monitored will also affect the cost of the program. If the requirements are to monitor on a real-time basis for a large group of speciated organics rather than monitoring for CH₄ and NMOCs, the program cost will increase. A larger analytical system will be required to give a full chromatogram of the analytes to be monitored. On the other hand, if one is able to select an appropriate subset of the compounds to be monitored and limit their number to less than five, cost savings can be achieved.

The frequency of sample collection will have a significant cost effect on the perimeter air monitoring program. Although real-time, on-site automated monitoring helps reduce the cost because analysis is on-site, the implementation of concurrent quality assurance monitoring using time-integrated systems must be taken into account, which brings into issue data turnaround and laboratory responsiveness as a factor in the decision for the implementation of the time-integrated monitoring techniques. Moreover, capital equipment, maintenance, and operational costs must be considered.

All of the above factors play an important role in establishing a real-time or time-integrated perimeter air monitoring system at a MSW landfill. Figure A-16 illustrates a full complement of monitoring systems located at the perimeter of a MSW landfill. Figure A-16 includes sampling techniques for VOCs (center sampler with canister); for TSP (far-field sampler); and for dioxins, furans, semi-volatiles, and PCBs (near-field sampler). Some sampling stations at the perimeter of the MSW landfill site can be as simple as a VOC sampler at the property line or perimeter of the site, as illustrated in Figure A-17.



Figure A-16. Time-Integrated perimeter Air Monitoring System at a MSW Landfill.



Figure A-17. Compendium Method TO-15A Application for Monitoring VOCs at the perimeter of a MSW Landfill.

In summary, this appendix has provided the RPM and other stake holders with information associated with the monitoring techniques and instrumentation needed to quantify landfill gas constituents. It has also discussed the nature of landfill gas, the development of a landfill target compound list (TCL), and technologies for monitoring landfill gas, including time-integrated and real-time techniques for inorganics, organics, and suspended particulate matter (SPM). Additionally, this appendix has provided guidance on the use and application of Federal Reference Methods (FRMs) and Compendia methods for quantifying COPC concentrations found in landfill gas.

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Appendix B

Testing for Homogeneity Using The Wilcoxon Rank Sum Test

In order to properly characterize the emissions from a landfill and to determine how many and where subsurface samples should be collected, it is necessary to identify those areas of the landfill that are nearly homogeneous. This determination is performed by using the results of the surface screening procedures. Through the application of statistical methods on these screening data it is possible to determine if the landfill must be subdivided into near homogeneous areas. For the purpose of this guidance it was decided to use the statistical method referred to as the Wilcoxon two-sample, rank-sum test. The Wilcoxon Rank-Sum Test is a non-parametric procedure for comparing two independent samples of sizes n_1 and n_2 , after the samples are combined and the observations are ordered from smallest to largest. Generally, non-parametric tests replace assumptions about normality with less stringent assumptions, such as symmetry and continuity of distributions. This method is used to determine if two independent sample populations are statistically similar (i.e., same mean and median). For this application, statistically similar populations refer to areas within the landfill that have methane or NMOC emission profiles that are nearly homogeneous.

B.1 Procedures

The Wilcoxon statistical procedure can be broken into a six step procedure.

Step 1 Define Hypothesis

The purpose of hypothesis testing is not to question the computed value of the sample statistic but to make judgments about the difference between the sample statistic and a hypothesized population parameter.

- Null hypothesis (H_0 : x_1 is equal to x_2) – There is no difference between the two populations, and they have the same mean concentration.
- Alternative hypothesis (H_a : x_1 is not equal to x_2) – There is a difference between the two populations and they have different mean concentrations.

A level of significance (α) must also be established at this point for testing the hypothesis. There is no single standard or universal level of significance for testing a hypothesis. If the hypothesis is correct, the significance level indicates the percentage of sample means that is outside the desired level of confidence. The higher the significance level, the greater the probability of rejecting a hypothesis when it is actually correct. Whether a null hypothesis is accepted or rejected depends largely on the chosen level of significance. The significance level (also known as the alpha-level) of a statistical test is the pre-selected probability of rejecting the null hypothesis when it is, in fact, true. Usually a small value such as one percent or five percent is chosen. If the P value calculated for a statistical comparison is smaller than the significance level, the null hypothesis is rejected. A five percent significance level has been used in this guidance document.

Step 2 Tabulate Data and Assign Populations

To use the selected statistical methodology, the landfill surface screening data that was collected to identify methane or NMOC hot spots must be assigned into two populations (e.g., east landfill and west landfill). The following methodology and criteria is recommended:

$$N = n_1 + n_2$$

Where:

- N = Total population of concentration data,
- n_1 = Population of size n_1 from area 1 of the landfill,
- n_2 = Population of size n_2 from area 2 of the landfill,
- $n_1 \leq n_2$, and
- $n_1 \geq 4$.

The available data should be listed in a sequential manner in terms of spatial relation between sampled grid locations. The sample sets should have a spatial relationship that is continuous and inclusive. The interface between populations sets n_1 and n_2 should have practical meaning. Figure B-1 illustrates acceptable and unacceptable population assignments. Since the goal is to determine if the landfill is a homogeneous emitter, the initial effort is to subdivide the data into two populations of size n_1 and n_2 such that the average concentration and the distribution of the emission data is approximately equal. Graphical

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contouring and mapping of the concentration data will allow one to quickly determine how to subdivide the data. Absent graphical contouring, a trial and error method is used to assign the concentration data to one or the other data sets.

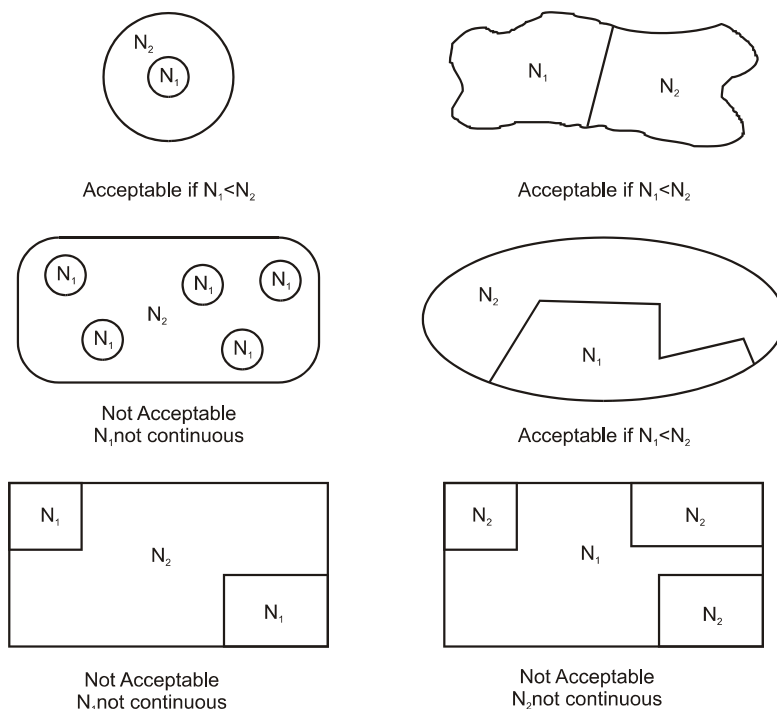


Figure B-1. Illustrated Data Population Assignments and Spatial Relationships.

Step 3 Rank Data

The Wilcoxon test is based on ranking the data of the combined population ($N = n_1 + n_2$). The Wilcoxon rank-sum test statistic is the sum of the ranks for observations from the smallest (n_1) data sets. All the data must be placed in ascending order, regardless of which population set it was derived, and ranked from 1 to N . In order to account for ties, all tied values should be assigned an average ranking. For example, if you have 2 values that are tied for the second lowest value they would all be assigned a ranking of 2.5. This is done because the tied pair would occupy the second and third ranking spots, and the average between 2 and 3 is 2.5. Similarly, if you have 5 values tied for the fifth ranking spot you would assign a rank of 7 because the average value between ranking 5 and ranking 9 is 7 $[(5+6+7+8+9) / 5 = 7]$.

Step 4 Calculate Statistics

The sum the ranks (W) is calculated by summing the average rank values of the associated sample set, which in this case corresponds to population 1. When the combined population is less than 20, W is compared with the values found in a Wilcoxon Rank-Sum Table. When the combined population is 20 or greater, the distribution of W can be treated as if it were normal and utilize the following test statistic (Z):

$$Z = \frac{W - \frac{n_1(n_1 + n_2 + 1)}{2}}{\sqrt{\frac{n_1 n_2 (n_1 + n_2 + 1)}{12}}}$$

Step 5 Apply Decision Criteria

For small sample sets, the two populations can be considered statistically similar and, therefore, one homogeneous area if $W_\alpha < W < W_{1-\alpha}$. For large sample sets the value Z can then be compared to a specific level of significance on a distribution table. Again if $Z_\alpha < Z < Z_{1-\alpha}$, then the two population sets can be considered to be near homogeneous. Steps 2 through 5 should be repeated until the landfill has been completely subdivided into homogeneous areas.

B.2 Wilcoxon Rank-Sum Spreadsheet

A Microsoft Excel workbook has been developed to assist the practitioner in implementing the Wilcoxon Rank-Sum Statistical Procedure. This workbook is divided into several spreadsheets that require the practitioner to input their data set, assign the appropriate populations, and establish an appropriate confidence interval. The following spreadsheets are included within the workbook.

Sheet 1: Intro

This worksheet provides disclaimer and contact information.

Sheet 2: Step 1 – Enter Data

This worksheet is setup to allow the practitioner to input sampling location coordinates, concentration data, and assigning of population sets. Each data point should be assigned to either population set one or two. A graphical chart has been setup on Sheet 5 to assist in determining how to best divide the data sets; however, it requires sample location coordinates be entered. A filtering function has been positioned at the top of the “Population Set” column; this can be used to condense the data to show only data assigned to population 1, 2, or all. A button can also be found on this worksheet called “Clear Data”. This button will completely erase all data entered on this worksheet.

Sheet 3: Step 2a – Check Results

This worksheet is used to check the results for large data sets ($N > 20$ and $n_1 \geq 4$). The appropriate confidence interval for a given situation can be put into this worksheet. Several error messages are embedded within this worksheet to assist in troubleshooting and ensure proper application of these methods. This sheet will also indicate whether the two sample sets are considered homogenous by comparing the calculated Z statistic to the Z_α and $Z_{1-\alpha}$ associated with the designated level of confidence.

Sheet 4: Step 2b – Check Results

This worksheet is used to check the results for small data sets ($N < 21$). On this worksheet, an appropriate confidence interval for a given situation can be selected from a drop down menu. This sheet will look up the appropriate W_α and $W_{1-\alpha}$ values based on the values found in the Wilcoxon Rank Sum Table found later in this workbook. Several error messages are embedded within this worksheet to assist in troubleshooting and ensure proper application of these methods. This sheet will also indicate whether the two sample sets are considered homogenous by comparing the calculated W_{rs} value with the W_α and $W_{1-\alpha}$ values.

Sheet 5: Verify Locations

This sheet plots the input coordinate data for use in determining how to best divide the sample sets.

Sheet 6: Wilcoxon Rank-Sum Tables

This sheet contains the Wilcoxon Rank-Sum Tables. These tables are provided for information purposes only and as a reference for extracting and comparing W_α and $W_{1-\alpha}$ values with W_{rs} when dealing with small sample sets on Sheet 4.

B.3 Spreadsheet Access

The complete useable form of these spreadsheets can be found on the Environmental Quality Management, Inc. web site, as Wilcoxon.xls. To access and download this file, go to <http://www.eqm.com/lfg/> (accessed August 2005). Then click on the link to download the file.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT The report provides guidance to superfund remedial project managers, on-scene coordinators, facility owners, and potentially responsible parties for conducting an air pathway analysis for landfill gas emissions under the Comprehensive Environmental Response, Compensation, and Liability Act, Superfund Amendments and Reauthorization Act, and the Resource Conservation and Recovery Act. The document provides procedures and a set of tools for evaluating LFG emissions to ambient air, subsurface vapor migration due to landfill gas pressure gradients, and subsurface vapor intrusion into buildings. The air pathway analysis is used to evaluate the inhalation risks to offsite receptors as well as the hazards of both onsite and offsite methane explosions and landfill fires. Summary examples of the application of these procedures and tools to three Superfund sites are included.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Landfills Emissions Methane Organic Compounds Toxic Chemicals Measurement Superfund Sites	Pollution Control Stationary Sources	13B 13C 14G 07C 07D
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (<i>This Report</i>) Unclassified	21. NO. OF PAGES 214
	20. SECURITY CLASS (<i>This Page</i>) Unclassified	22. PRICE