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Assessment of Airborne Emissions from Bioremediation Processes

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD
Research Division

ASSESSMENT OF AIRBORNE EMISSIONS FROM BIOREMEDIATION PROCESSES

Final Report

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SUMMARY

The report is divided into three main sections. The first section is a critical review of the literature available on bioremediation processes and the air emissions resulting from such processes. The second section includes descriptions and results of two experiments in which air emissions from bioremediation processes were monitored. The third section contains annotated abstracts of the literature cited in the first two sections and more. A separate abstract is provided at the beginning of each section.

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SECTION I

CRITICAL LITERATURE REVIEW

ABSTRACT

This report presents a critical review of the literature on bioremediation processes and air emissions from such processes. It includes an overview of microbial activities as they relate to bioremediation. A discussion of the biodegradation pathways of the major classes of contaminants (e.g., hydrocarbons, halogenated aliphatic compounds, and halogenated aromatic compounds) is included. The report includes a description of the different types of bioremediation processes in use, and a discussion of the air emissions expected from such processes. Wherever possible, quantitative examples of observed air emissions are quoted from the studies in the literature. Methods for monitoring and sampling of air emissions from bioremediation processes, and methods for controlling such emissions are also discussed in this part of the report.

I. INTRODUCTION

Polluted soils and groundwaters can be reclaimed through application of a variety of physical, chemical and biological methods. In bioremediation inorganic and/or organic materials are removed from soils and groundwater through the action of microorganisms. Target materials for bioremediation include heavy metals, such as mercury, potentially toxic ions, such as nitrate, and a wide range of organic compounds. Many polluting materials that are deposited in the soil or groundwater are transformed to a non-polluting state under normal or ambient conditions. For example if a glass of orange juice is poured onto the soil surface most of the organic components will be decomposed in a relatively short period of time by naturally occurring soil bacteria. Time required for decomposition will be a function of the soil characteristics, the temperature, and the presence of nutrients required for growth, but the organic compounds in the juice will be microbially degraded to their lowest oxidation states. In situations where bioremediation is applied the polluting materials are unlikely to be degraded naturally, or the time involved will be unacceptably long. In most cases of concern the target materials are anthropogenic and xenobiotic. Often the volatile organic compounds (VOCs) are toxic and/or hazardous and their presence prevents use of the polluted soil or groundwater.

APPLICATION OF BIOREMEDIATION

This report is focused on emissions of volatile organic compounds (VOCs) from bioremediation sites. For this reason the discussion will be limited to the presence, transformation, and emission of organic compounds. Three types of physical situations are involved in bioremediation, materials dissolved in groundwaters, materials dissolved in water held in surface impoundments, and materials in top soil and in the soil vadose zone. Landfarming, a method of waste treatment in which pollutants are added to the top soil presents a situation in which soil pollution and treatment are combined in one, intentional operation.

Groundwater Bioremediation

Methods used for groundwater bioremediation can be categorized as (1) *in situ* and (2) pump and treat. *In situ* groundwater treatment is well below the surface and should not result in significant VOC emissions. In pump and treat systems groundwater is pumped to the surface, treated and either used directly or returned to the aquifer. Emissions from pump and treat systems can be controlled by eliminating off-gases through appropriate system design [Muollo *et al.*, 1992] or treating the off-gases. In some cases the treatment is physical (e.g. stripping) and VOC emissions are the intended treatment objective [Selleck and Diyamandoglu, 1986]. Bioremediation of polluted water in pump and treat processes should not result in VOC emissions if systems are correctly designed and operated.

Surface Impoundment Bioremediation

Surface impoundments subjected to bioremediation are potential sources of VOC emissions. Such operations are relatively unusual. Discharge of contaminated liquids to surface impoundments continues at some Class I landfills (e.g., Kettleman Hills) and surface impoundments develop as drainage sumps at some landfills and result from oil well operation in some cases. Although VOCs are emitted from these surface impoundments, bioremediation is generally not involved. Use of biological methods to transform the organic materials in surface impoundments will involve some type of biological wastewater treatment. Emissions of VOCs from wastewater treatment systems have been documented elsewhere [Chang *et al.*, 1987, Montgomery, 1990].

Soil Bioremediation

Bioremediation of polluted soils presents a relatively new situation. Methods of soil bioremediation can be classified as (1) *in situ*, (2) land treatment, (also known as landfarming), (3) composting, (4) slurry-phase, (5) soil venting, and (6) soil washing.

In situ and soil venting methods require transporting oxygen, and possibly nutrients, through the contaminated volume. In some cases the microbial population is unsatisfactory and microorganisms need to be added as well. Even highly porous soils present relatively severe limitations on the transport of liquids and particles. For this reason, addition of nutrients and microorganisms is difficult. The most successful *in situ* bioremediation systems are landfarming and composting type operations in which the treatment depth is very shallow. In these cases aeration can be through mechanical mixing with plows and discs. The same operations provide transport of organisms and nutrients.

Land treatment can be divided into two types of systems: tilled and prepared pad. Tilled systems are appropriate for surface and near surface contamination where the soil can be manipulated by implements such as plows, disks and rakes. The difference between tilled land treatment and *in situ* methods is the soil working and the opportunity for emissions of volatile compounds. Prepared pad bioremediation of soils involves digging up the contaminated materials, moving them to a selected treatment location (usually on-site), and setting up a biological soil treatment operation. In most prepared pad operations, air is forced through the pile and the required soil moisture is maintained by adding water at intervals. The pile can be operated in a static fashion, with the air blown through, or the pile can be windrowed and operated as a composting system.

In slurry reactor operations a containment vessel is used and enough water is added to allow continuous mixing. Oxygen can be added as required and off-gas controls must be used to prevent loss of VOCs through stripping. Off-gas controls include gas recycling, use of the off-gases in combustion processes, and, potentially, microbial gas cleaning.

In soil venting air is drawn through the polluted soil zone and the off-gases are treated. If the off-gas treatment is biological (e.g., biofiltration) the soil venting operation becomes a type of bioremediation system. This treatment sequence has not been used in practice but appears to have considerable potential for management of VOC emissions from polluted vadose zone soils.

Soil washing involves separation of contaminated soil from uncontaminated materials such as rock, gravel, and sand. This type of process is not truly a form of bioremediation but is easily combined with biological treatment processes to form a bioremediation system.

EMISSIONS OF VOCs FROM BIOREMEDIATION SITES

Emissions of VOCs from bioremediation can result from either the deposition or the production of volatile materials in the site. Deposition can occur in land treatment systems, for example where the contaminants are mixed in with uncontaminated soil. Production of VOCs may occur as a result of breakdown of the parent compounds, particularly if local anaerobic conditions exist, or due to volatilization when the soil is agitated, such as during mixing. Production of VOCs from non-volatile compounds during biodegradation is a theoretical problem but the issue appears to have little practical significance [Lang, *et al.*, 1989], at least for aerobic processes. Microbial transformation of VOCs into more volatile compounds (e.g. trichloroethene into vinyl chloride) under anaerobic conditions, where reductive bond cleavage often occurs, has been observed. Vinyl chloride is a common component of off-gases in sanitary landfills and anaerobic sludge digesters and the source is believed to be chlorinated solvents [Lang, *et al.*, 1987, 1989].

Most bioremediation processes are designed to operate aerobically and therefore VOC emissions will be restricted to the compounds that have been identified at the site.

As noted above, compounds that are easily degraded by soil microorganisms will normally be metabolized without difficulty. For example, simple alcohols, such as ethanol, methanol, and propanol, are among the group of easily biooxidized VOCs. Sorption, biodegradation and volatilization are essentially competitive processes and would all occur. As suggested in Figure 1, VOCs sorbed onto soil particles may be volatilized or biodegraded. Emissions would occur from soil contaminated with easily metabolized compounds, but the fraction of available material biodegraded would be large. Biodegradability is related to factors such as solubility, degree of branching, degree of saturation, and the nature and extent of substitution. Solubility is important because microorganisms obtain nutrients from aqueous solution. High solubility results in high availability of a compound. Although saturated carbon-carbon bonds are not difficult for microorganisms to break, the degree of saturation is related to volatility and solubility. Saturated rings, like highly branched aliphatics, are difficult for microorganisms to degrade [Evans, *et al.*, 1988]. The effect of branching is seen in the relative degradability of isomers [Gibson, 1984, 1988]. Addition of chlorine, nitrogen sulfur, and phosphorus, to organic molecules tends to make them more stable biologically [Reinke, *et al.*, 1988; Strand *et al.*, 1991]. An exception are amino compounds, particularly α -amino acids.

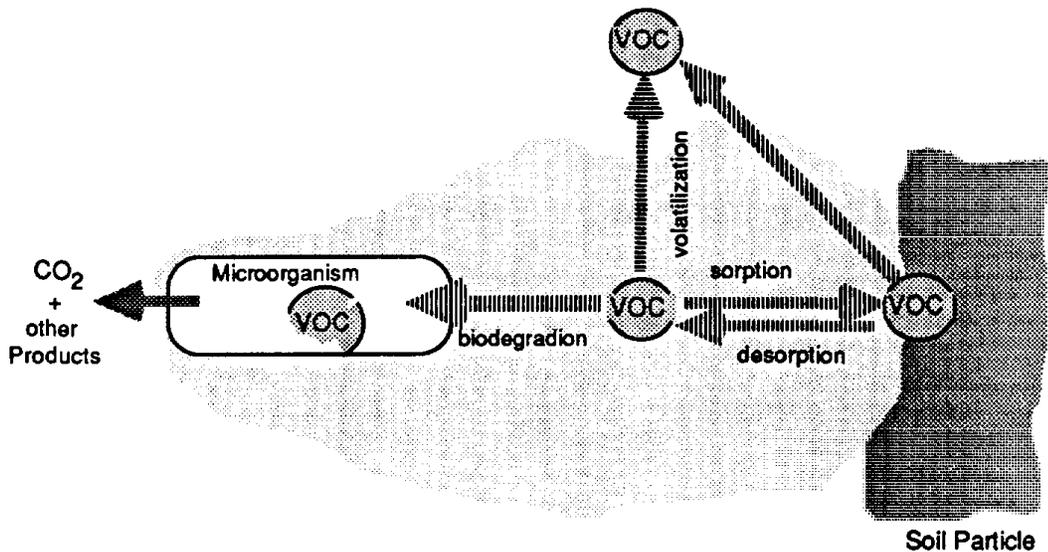


Figure 1.1
Mechanisms of removal of VOCs dissolved in bound water within the soil structure. Sorption on soil is not a terminal fate because equilibrium will be established with both the air and water.

VOCs in Bioremediation Sites

Volatile organic compounds found in bioremediation sites can be divided into three general groups: (1) petroleum hydrocarbons, particularly those from leaking buried gasoline storage tanks, (2) solvents, both chlorinated and non-chlorinated, and (3) agricultural chemicals. A partial listing of common VOCs and their physical characteristics is given in Table 1.1.

Bioremediation Sites in California

The number of bioremediation sites in California is not entirely clear at this time (May, 1992). Leaking underground storage tanks are probably the largest source of contaminated soils and groundwater in the State. Over 17,000 leaking underground storage tanks had been identified

up to January 1, 1991 [Water Resources Control Board, 1991]. In the large majority of the leaking underground storage tank sites (UST sites) petroleum products are involved. Solvents and pesticides are the material in question in a relatively small number of cases. However, because of the toxicity of many solvents and pesticides, and the resulting low allowable concentrations in soil and water, these cases present difficult problems. Remediation programs are most often under the supervision of local agencies. Reports of the type of remediation program are either not well documented or not up to date in many cases. Reported bioremediation programs are often found to be incorrect.

SCOPE AND ORGANIZATION

The purpose of this document is to provide a review of current understanding and knowledge of VOC emissions from bioremediation processes. This review is both a review of the literature and a critical review in that the information collected is discussed and compared, and conclusions are drawn about the significance of reported information and about information that is needed.

Because potential for VOC emissions is much greater from soil than from groundwater bioremediation sites, the emphasis has been placed on soil processes. The following sections deal successively with (1) biotransformation processes in general and soils in particular, (2) biotransformation of specific classes of compounds and of VOCs of particular importance, (3) bioremediation systems currently in use, (4) recorded emissions from bioremediation systems, and (5) monitoring and sampling methods used, or proposed for use in measuring emissions from bioremediation sites.

Table 1.1
Properties of selected chemicals commonly found in wastes.

Compound	Formula	Molecular Weight	Solubility mg/L	V.P. mm Hg	B.P. °C
Halogenated Volatiles					
Bromoform	CHBr ₃	253	1000	5	148
Carbon tetrachloride	CCl ₄	154	800	91	77
Chlorobenzene	C ₆ H ₅ Cl	113	1000	8.8	132
Chlorodibromomethane ¹	ClCHBr ₂	208		50	116-122
Chloroethane	C ₂ H ₅ Cl	65	6000	1064	12.2
Chloromethane	CH ₃ Cl	51		3648	-24
Chloroform	CHCl ₃	119	8000	160	61
1,1-Dichloroethane ¹	CH ₃ CHCl ₂	99	7840	297	57
1,2-Dichloroethane ¹	ClCH ₂ CH ₂ Cl	99	8690	61	83.5
1,1-Dichloroethene ¹	CH ₂ CCl ₂	97	5000	500	31.9
Dichloromethane	CH ₂ Cl ₂	85	13000	350	40
1,2-Dichloropropane ¹	CH ₃ CHClCH ₂ Cl	113	2600	41.2	96.4
Hexachloroethane	CCl ₃ CCl ₃	237	50	0.22	189
1,1,2,2-Tetrachloroethane	CHCl ₂ CHCl ₂	168	2900	8	146
Tetrachloroethene ¹	Cl ₂ CCCl ₂	166	160	15.6	121
Trans-1,3-dichloropropene ¹	ClCH ₂ CHCHCl	111	515	99.6	112
1,1,1-Trichloroethane ¹	CH ₃ CCl ₃	133	4400	100	74
1,1,2-Trichloroethane	CHCl ₂ CH ₂ Cl	133	5000	19	113
Trichloroethene ¹	ClCHCCl ₂	131.5	1.1 ^a	60	86.7
Vinyl chloride	C ₂ H ₃ Cl	62.5	-	2580	-13.9
Halogenated Semivolatiles					
Bis(2-chloroethyl)ether	(ClCH ₂ CH ₂) ₂ O	143	11000	0.4	178
2-Chlorophenol ²	C ₆ H ₅ ClO	129	miscible	1 ^b	174.5

Table 1.1. continued
Properties of selected chemicals commonly found in wastes.

Compound	Formula	Molecular Weight	Solubility mg/L	V.P. mm Hg	B.P. °C
1,2-dichlorobenzene	C ₆ H ₄ Cl ₂	147	150	1.2	180
1,4-dichlorobenzene	C ₆ H ₄ Cl ₂	147	80	0.4	174
Halogenated Volatiles continued					
Hexachlorobenzene ⁴	C ₆ Cl ₆	285	-	0.00001	323-326
Pentachlorophenol	C ₆ Cl ₅ OH	266	20	0.0002	311
1,2,4-trichlorobenzene ²	C ₆ H ₃ Cl ₃	181	-	1 ^c	213
2,4,5-trichlorophenol ²	C ₆ H ₃ Cl ₃ O	197	-	1 ^d	252
2,4,6-trichlorophenol ²	C ₆ H ₃ Cl ₃ O	197	soluble	1 ^e	244.5
Nonhalogenated Volatiles					
Acetone	CH ₃ COCH ₃	58	miscible	266 ^a	56
Benzene	C ₆ H ₆	78	1800	75	80
Carbon disulphide	CS ₂	76	2000	300	46
Ethyl acetate	CH ₃ COOC ₂ H ₅	88	87000	76	77
Ethyl benzene	C ₂ H ₅ C ₆ H ₅	106	150	7.1	136
Ethyl ether	C ₂ H ₅ OC ₂ H ₅	74	75000	442	35
2-Hexanone	CH ₃ CO(CH ₂) ₃ CH ₃	100	14000	3	128
Isobutanol	(CH ₃) ₂ CHCH ₂ OH	74	87000	9	108
Methanol	CH ₃ OH	32	miscible	97	64
Methyl isobutyl ketone	CH ₃ COCH ₂ C ₃ H ₇	100	19000	15	-84
n-Butyl alcohol	CH ₃ CH ₂ CH ₂ CH ₂ OH	74	77000	4.2	118
Styrene	C ₆ H ₅ CHCH ₂	104	300	4.5	145
Toluene	C ₆ H ₅ CH ₃	92	500	22	110.6
Nonhalogenated Semivolatiles					
Anthracene ⁵	C ₁₄ H ₁₀	178	0.045 ^a	2x10 ⁻⁴	340
Benz(a)anthracene ⁵	C ₁₈ H ₁₂	228	0.0094 ^a	1x10 ⁻⁵	400
Benzidine	C ₁₂ H ₁₂ N ₂	184	400 ^b	?	402
Benzo(a)pyrene ⁵	C ₂₀ H ₁₂	252	0.001 ^a	6x10 ^{-9a}	312
Benzo(g,h,i)perylene ⁵	C ₂₂ H ₁₂	276	0.0007 ^a	1x10 ^{-10a}	-
Chrysene ⁵	C ₁₈ H ₁₂	228	0.002 ^a	6x10 ^{-9 a}	448
Dimethylphthalate	C ₁₀ H ₁₀ O ₄	194	400	1 ^f	285
Fluoranthene ⁵	C ₁₆ H ₁₀	202	0.21 ^a	5x10 ^{-6 a}	367
Isophorone	C ₉ H ₁₄ O	138	12000	0.2	215
Naphthalene	C ₁₀ H ₈	128	30	0.05	218
Nitrobenzene	C ₆ H ₅ NO ₂	123	2000	<<1	211
Phenanthrene ⁵	C ₁₄ H ₁₀	178	1 ^a	6.8x10 ⁻⁴	339
Phenol	C ₆ H ₅ OH	94	84000	0.36	182
Pyrene ⁵	C ₆ H ₁₀	202	0.13 ^a	2.5x10 ^{-6 a}	404
Pyridine	C ₅ H ₅ N	79	miscible	18	115
Pesticides and Herbicides (sol. at 25°C)					
Alachlor ³	C ₁₄ H ₂₀ ClNO ₂	270	240	2x10 ^{-5a}	
Atrazine ³	C ₈ H ₁₄ ClN ₅	216	32	6.8x10 ^{-7 a}	
Bromacil ³	C ₉ H ₁₃ BrN ₂ O ₂	261	820	2x10 ^{-7 a}	
Carbofuran ³	C ₁₂ H ₁₅ NO ₃	221	320	8x10 ^{-6a}	

Table 1.1. continued
Properties of selected chemicals commonly found in wastes.

Compound	Formula	Molecular Weight	Solubility mg/L	V.P. mm Hg	B.P. °C
Chlorpropham ³	C ₁₀ H ₁₂ ClNO ₂	214	89	9.8x10 ^{-6a}	149 ^u
DDT	C ₁₄ H ₉ Cl ₅	355	0.00001	~0	w
Diazinon ³	C ₁₂ H ₂₁ N ₂ O ₃ PS	304	40	0.0001 ^a	w
Pesticides and Herbicides (sol. at 25°C) continued					
Dicamba ³	C ₈ H ₆ Cl ₂ O ₃	221	4500	0.00038	
Dieldrin	C ₁₂ H ₈ Cl ₆ O	381	0.02	~0	w
Diuron ³	C ₉ H ₁₀ Cl ₂ N ₂ O	233	37	1.6x10 ^{-7a}	
EPTC ³	C ₉ H ₁₉ NOS	189	370	0.008	127 ^v
Heptachlor ³	C ₁₀ H ₅ Cl ₇	373	0.0056	0.00017	w
Lindane ³		291	7.5	6x10 ^{-5a}	
Linuron ³	C ₉ H ₁₀ Cl ₂ N ₂ O ₂	249	75	8x10 ⁻⁶	
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	330	145	0.00004	w
Metolachlor ³	C ₁₅ H ₂₂ ClNO ₂	284	530	1.3x10 ⁻⁵	
Monuron ³	C ₉ H ₁₁ ClN ₂ O	199	260	1.7x10 ^{-7a}	
Parathion	(C ₂ H ₅ O) ₂ PSOC ₆ H ₄ NO ₂	291	0.00002	0.0004	707
Picloram ³	C ₆ H ₃ Cl ₃ N ₂ O ₂	241	430	5x10 ⁻⁹	
Prometon ³	C ₁₀ H ₁₉ N ₅ O	225	750	6x10 ⁻⁶	
Simazine ³	C ₇ H ₁₂ ClN ₅	202	5	1.5x10 ^{-8a}	
Triallate ³	C ₁₀ H ₁₆ Cl ₃ NOS	305	4	0.0002	
Trifluralin ³	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335	0.3	0.0001	139 ^s

Symbols

Solubility in water at 20°C unless specified otherwise.

VP: Vapor pressure in mmHg at 20°C unless specified otherwise.

BP: Boiling point in °C at 760 mm Hg unless specified otherwise.

^a@25 °C; ^b@12.1 °C; ^c@38.4 °C; ^d@72 °C; ^e@76.5 °C; ^f@100 °C.

^s@4.2 mm Hg; ^t@10 mm Hg; ^u@2 mm Hg; ^v@20 mm Hg; ^wdecomposes at 120 °C.

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II. BIOTRANSFORMATION PROCESSES

Biotransformation is the biologically induced structural transformation of a compound. The process can be limited to one reaction (e.g. the cleavage of a chloride from a carbon molecule or the changing of a bond between two carbons from a saturated to an unsaturated state). In most cases of engineered biotransformation the objective is biodegradation, a process that usually requires a chain of enzymatically catalyzed reactions and the transformation of the original compound to a material of higher oxidation state. Situations involving bioremediation of soils or aquifers nearly always are focused on the biodegradation of anthropogenic and xenobiotic compounds such as petroleum hydrocarbons, chlorinated solvents, herbicides and pesticides.

Approximately 1000 new chemical compounds are produced each year for use in industry, agriculture, and households [Pitter and Chudoba, 1990]. Some of these compounds pass into the water, soil, and air at or near the point of use; polluting the environment and exerting a toxic effect on microorganisms, plants, and animals. In other cases large quantities of the materials are disposed of in poorly designed or managed landfills with the result that high concentrations of the compounds accumulate in soils and groundwaters. Leaking storage tanks and illegal dumping (e.g. rinsate from vessels used in transporting chemicals) also result in high local concentrations of pollutants in soil and groundwater.

In soils and water, microorganisms are the primary, and often the sole, agents for reactions leading to the destruction of synthetic compounds. A broad range of microorganisms are normally present in the upper two to three feet of soil. Biotransformation is therefore a process that may be active naturally and in some cases pollutants undergo biodegradation without any action or intervention. However, many anthropogenic, and particularly those xenobiotic compounds are difficult for microorganisms to degrade, and are located at point where few microorganisms exist, or where other environmental requirements are lacking for biodegradation.

Compounds that are not readily biodegradable, sometimes referred to as recalcitrant or refractory compounds, accumulate in the environment. Many factors may inhibit the natural degradation of these compounds. Some degrade very slowly because of their chemical structure, their toxicity to microorganisms at the concentrations present, or their requirement for the presence of other compounds. Examples of other compounds include nutrients that are required in a fashion analogous to human requirements for amino acids, metal cofactors such as iron, cobalt, and molybdenum, which are required for certain enzymes to function, or cosubstrates which may be needed to induce enzymes for cometabolism. Environmental factors such as aeration, moisture content, temperature, pH, and salinity greatly influence biodegradability in particular environments. In other cases, microorganisms that have metabolic pathways to degrade a specific compound are either not present, or not present in sufficient numbers, to significantly degrade the pollutant.

Bioremediation makes use of indigenous or introduced microorganisms together with techniques that correct the environmental factors which inhibit natural biodegradation. In this section microbial metabolism and the various types of microorganisms, as well as the factors that influence the biodegradation of anthropogenic and xenobiotic compounds in natural and engineered systems will be discussed.

THE MICROBIAL COMMUNITY

Biological transformations are primarily the result of the activity of microorganisms. Microorganisms are ubiquitous in the environment and are responsible for most of the cycling of carbon, nitrogen, sulfur, phosphorus and other minerals. Six different groups of microorganisms are present in soils and aquatic environments: bacteria, actinomycetes, fungi, algae, protozoa, and viruses. The bacteria, actinomycetes, fungi, and algae groups have been used to degrade pollutants in bioremediation activities. Protozoa are important due to their influence on microbial populations. A discussion of viruses, which are species specific to obligate parasites, is outside the scope of this work.

Bacteria are the most abundant group of microorganisms in soil and are the primary degraders of a wide variety of natural and xenobiotic substrates. Although the numbers of these organisms are great, the size of individual organisms is small, usually between 0.2 and 2 μm , so bacteria account for less than half of the microbiological cell mass. Bacteria are a diverse group of organisms that can be classified according to their ability to grow in the presence or absence of oxygen as: aerobes, which must have oxygen; anaerobes, which grow only in the absence of oxygen; and facultative anaerobes, which grow either in the presence or absence of oxygen. Bacterial energy and carbon metabolism includes chemoheterotrophs, chemoautotrophs, photoautotrophs, and photoheterotrophs. The major morphological groupings of bacteria are bacilli, or rod-shaped bacteria, the cocci, or spherical cells, and the spirilla, or spirals. Bacteria can also be classified as eutrophs, which grow in the presence of high substrate concentrations, and oligotrophs, which grow at trace concentrations. The most common genera of bacteria in soils are *Pseudomonas*, *Arthrobacter*, *Achromobacter*, *Micrococcus*, *Vibrio*, *Acinetobacter*, *Brevibacterium*, *Corynebacterium*, and *Flavobacterium*.

Actinomycetes are a transitional group between the more primitive bacteria and the fungi. Although taxonomically these organisms are classified as bacteria, the actinomycetes are similar to fungi in that they produce slender extensively branched filaments called hyphae that develop into a mycelium. Hyphae are characteristic of fungal masses that we associate with moldy materials. Many of the actinomycetes also produce spores or chains of spores known as conidia on their hyphae similar to that of fungi. Actinomycetes are second only to bacteria in their abundance in soil and are known to tolerate a wide range of pH and temperature, grow under nutrient limiting conditions, and to be resistant to desiccation. Although their growth rate is slower than that of bacteria, their ability to thrive under adverse conditions allows them to predominate when selective pressures are great. They are chemoorganoheterotrophs and have been shown to degrade phenols, aromatics, pyridines, glycerides, steroids, chlorinated aromatics, and lignocellulose [USEPA, 1983].

Fungi and yeasts account for a large part of the total microbial mass in well aerated soils. They possess an extensive network of large diameter filaments. The mycelium may or may not be divided into individual cells by cross walls. Fungi are chemoheterotrophs; i.e. require organic carbon for cell growth and maintenance and may dominate the microbial population under dry, acidic conditions. Relatively non-specific enzymes enable fungi to utilize a broad range of energy and carbon sources (i.e. substrates) including sugars, organic acids, disaccharides, starch, pectin, cellulose, fats, and lignin [Alexander, 1991]. Because of the nonspecificity of their enzymes, fungi are able to degrade or partially degrade hydrocarbons of complex structure and long chain length, compounds ordinarily resistant to biodegradation. Recently, a great deal of interest has been shown in white rot fungus (the species of greatest interest is *Phanerochaete chrysosporium*) which is able to degrade lignin under nitrogen, sulfur, or carbohydrate limiting conditions using a peroxide-dependent extracellular enzyme system. This enzyme system has been shown to degrade PCBs, DDT, and other resistant hydrocarbons [USEPA, 1983; Glasser *et al.*, 1991; Bumpus *et al.*, 1985].

Algae can be divided up into green algae, blue-green algae (which are photosynthetic cyanobacteria), diatoms, and yellow-green algae. They are photosynthetic microorganisms which require sunlight as an energy source and carbon dioxide as a carbon source. Their presence in soil is limited to the upper few centimeters where moisture is adequate and light is accessible. Algae may be unicellular or occur in short filaments. Because of their photosynthetic capabilities, algae are tolerant of environments with low nutrient availability. Their significance to bioremediation is primarily as a source of carbon for heterotrophic bacteria. Algae have also been used in the bioremediation of aquatic systems either by bioaccumulation of hydrophobic compounds in their lipids followed by harvesting of the algal biomass, or by degradation in the presence of sunlight [Okelley and Deason, 1976; Matsumura and Esaac, 1979].

The phylum protozoa consists of the one-celled organisms, which range in size from several microns up to a centimeter. Protozoa can be divided into four main groups according to their means of locomotion: the flagellates (*Mastigophora*) which move by means of flagella, the amoebae (*Sarcodina*) which possess pseudopods, the ciliates (*Ciliophora*) which bear cilia and the spore formers (*Sporozoa*) which are vertebrate parasites [Hickman et al., 1979]. The majority of protozoa are heterotrophic, feeding on either organic matter or microorganisms. The dominant form of protozoan nutrition in soils is generally considered to be predation on bacterial cells [Alexander, 1991]. Each protozoan division requires consumption of thousands of bacteria. The primary significance of protozoans in bioremediation is due to their influence on bacterial cell numbers. Protozoans may slow down bacterial growth by grazing on bacteria or stimulate growth by synthesizing growth factors which are then taken up by the bacteria [Wiggins and Alexander, 1988]. Kaska, [1991] showed that some marine amoebae have the ability to degrade chlorinated hydrocarbons. Protozoans such as these may be partially responsible for the degradation of petroleum hydrocarbons in marine environments.

MICROBIAL METABOLISM

Microorganisms are the primary, and often the sole, agents for reactions which lead to the transformations of synthetic as well as natural carbon compounds. Typically, the microbial populations utilize carbon in organic molecules as a substrate for the manufacture of cell constituents. At the same time, energy is released and the population increases. Oxidation-reduction reactions leading to the release of energy are referred to as catabolism, and the synthesis of cell constituents is called anabolism. The combined processes of anabolism and catabolism are called metabolism. The relationship between the disappearance of a chemical and the growth of a microbial population is shown in Figure 2.1. Such multiplication of microorganisms at the expense of an organic compound typically results in the conversion, or mineralization of the organic compound into cell constituents and inorganic compounds such as carbon dioxide, water, chloride, orthophosphate, ammonium, and nitrate [Scow, 1991].

Chemoheterotrophic Metabolism

Microbial metabolism requires a carbon source, an electron donor (i.e. an energy source) an electron acceptor, and inorganic nutrients. As stated above, chemoorganoheterotrophic bacteria are the major agents of biotransformation of organic compounds in bioremediation processes. An organic carbon source, usually the pollutant, is used by these microorganisms for carbon and as an electron donor. Oxygen serves as an electron acceptor for aerobic bacteria but is frequently limiting in soils at high pollutant concentrations. Nitrate or sulfate can be used as an electron acceptor for heterotrophic reactions under anoxic conditions but these compounds can accept less energy than oxygen and a limited number of species carry out the reactions. Bacteria which carry out anoxic reactions which are those where nitrate, and nitrite are reduced are generally facultative anaerobes that preferentially use oxygen under higher redox conditions but can switch to nitrate when necessary. Sulfate reduction is carried out by an obligate anaerobic genera known as the

sulfur reducing bacteria. Anaerobic bacteria simultaneously oxidize and reduce the organic compounds they metabolize by carrying out fermentation reactions in reducing environments.

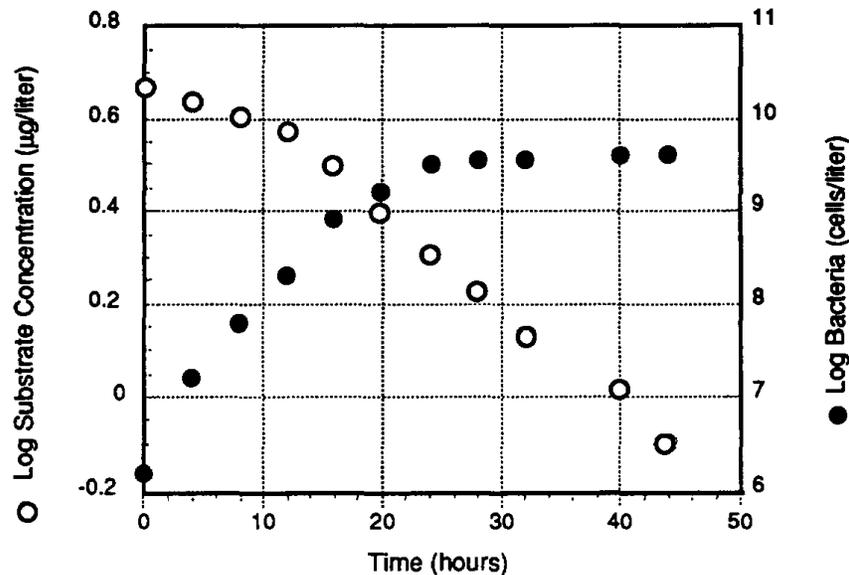


Figure 2.1
Growth of Bacteria with Corresponding Decrease in Substrate Concentration.

Autotrophic Metabolism

Autotrophic bacteria can utilize atmospheric carbon dioxide as a carbon source. Photoautotrophs obtain their energy from sunlight through the action of chlorophyll that is different from that of algae and higher plants. Only a few genera of bacteria are capable of photoautotrophic nutrition. Chemoautotrophs have the ability to fix atmospheric carbon dioxide while oxidizing inorganic compounds such as nitrite, ammonium, or reduced inorganic sulfur compounds. Only a few bacterial species carry out these reactions, yet they are of vast importance in the cycling of nitrogen and sulfur in the environment [Alexander, 1991].

Cometabolism

Microbial degradation of organic compounds is sometimes observed that does not supply energy or carbon to the cells, and so the population does not increase as a result of the compound being degraded [Alexander, 1981]. This phenomenon of gratuitous biodegradation has been termed cometabolism, cooxidation, or incidental metabolism. In cometabolism organisms use one substrate as a primary energy source and gratuitously metabolize another compound utilizing the enzymes which are synthesized to degrade the primary substrate. Cometabolism plays an important role in the biodegradation of many chlorinated and non-chlorinated molecules.

Extent of Degradation

Biotransformation processes do not always result in the complete mineralization of the organic compound [Pitter and Chudoba, 1990]. Often, the compound is only minimally degraded or transformed to the minimum extent necessary to change the identity of the compound. Although the compound may no longer be detected, a nearly identical, and sometimes more toxic compound, remains. An example of the production of a toxic product through biotransformation, a process

known as activation [Alexander, 1981], is the methylation of inorganic mercury in aquatic sediments to yield compounds which are more toxic and more readily assimilated by aquatic organisms. An environmentally acceptable level of degradation is the biological transformation of the compound to the extent that toxicity or other undesirable characteristics of the compound are removed. An example of acceptable biotransformation in bioremediation processes is provided by Claxton *et al.* [1991] who investigated the potential for activation of oil spilled in Prince William Sound, Alaska during bioremediation. In this study, a mutagenicity assay was used to determine if mutagenic products were formed during four months of biological treatment. The investigators found that mutagenicity decreased over time both in fertilizer-enhanced and natural degradation sites.

FACTORS AFFECTING BIOTRANSFORMATION

Factors which influence the density and composition of the microbial community and the rate of transformation of environmental pollutants include environmental factors, substrate factors, and microbiological factors. Primary environmental factors include moisture, aeration, temperature, pH, and nutrient availability. Properties of the substrate which can affect biotransformation include toxicity, concentration, solubility, volatility, solid phase partitioning, and chemical structure. In general, branched chain aliphatics and unsaturated rings are difficult for microbial populations to transform. The ability of microorganisms to transform compounds tends to decrease with the number of chlorine, amino and nitro substitutions, also. Biodegradation rates are important in the process as well as the ability to degrade the compounds. Microbiological factors include the presence of microorganisms with pathways for degrading compound of interest, acclimation of microbial populations, and ecological factors.

The Soil Environment

When looking at microbial processes which occur in the soil environment, it is essential to carefully consider the physical and chemical properties of soil. The term soil refers to the loose material of the earth's surface. Soil provides mechanical support and nutrients for plant growth. A broad range of bacteria, actinomycetes, fungi, algae, and protozoa are nearly always present in soil. The surface of soil granules is the site of many of the biochemical reactions in the cycling of organic matter, nitrogen, and other minerals; in the weathering of rocks; and in the nutrition of plants [Alexander, 1991]. Soil is composed of mineral matter, air, water, organic matter, and organisms. The fraction of air and water makes up the pore space and is typically about half the volume [Freeze and Cherry, 1979]. Mineral matter makes up most of the rest, with organic matter comprising from less than one percent (typical of California soils) to about six percent of the total. Small animals and microorganisms make up less than one percent of the total volume.

Properties of the soil have a profound influence on nutrient availability, aeration, and water retention and thus on biological activity. Among these are porosity, moisture content, aeration status, chemical composition, clay fraction, cation exchange capacity, and organic fraction. The amount of pore space depends on the texture, structure, and organic content of the soil. In clay soils, smaller pore sizes dominate while in sandy soils pores are larger but the total quantity of pores is less. Water moves more quickly through large pores but little is retained. Moisture content of the soil strongly influences biological activity. Water is the major component of bacterial protoplasm and an adequate supply of water is essential for microbial growth and maintenance. Too little moisture in the soil results in dry zones and loss of microbial activity. Too much moisture, however, inhibits gas exchange and results in the development of anaerobic zones with the resulting elimination of aerobic bacteria and the ascendance of anaerobes or facultative anaerobes. Aeration and moisture are directly related because the pore space in soil not filled by water is filled with gas. The soil atmosphere generally contains more carbon dioxide and less oxygen than the atmosphere above the ground as a result of the respiration of microorganisms and plant roots, and the difficulty of gas movement into small pores.

Microorganisms obtain a portion of their required nutrients from the mineral portion of the soil and so consideration must be given to its chemical composition. Nutrients required by microorganisms include nitrogen, phosphorous, potassium, magnesium, sulfur, iron, calcium, manganese, zinc, copper, and molybdenum. The dominant mineral in soil is silicon dioxide. Aluminum and iron are also plentiful, while calcium, magnesium, potassium, titanium, manganese, sodium, nitrogen, phosphorus, and sulfur are present in lesser amounts [Alexander, 1991]. Chemical composition varies greatly between soils and at different depths within the same soil. Only a small fraction of soil minerals are readily available to microorganisms. In general, the total organic carbon and total nitrogen concentrations of a soil represent a slowly utilized reservoir of these compounds rather than a readily available supply. The presence of surfaces in soil which strongly adsorb certain classes of compounds may reduce the availability of organic compounds for biodegradation. Another factor influencing the availability of nutrients is the cation exchange capacity of the soil. Clay minerals and organic matter possess sites of negative electrical charge and so attract positively charged ions such as NH_4^+ , K^+ , Ca^{++} , and Mg^{++} . Thus ammonium, which is positively charged, is less available for immediate use and is retained longer in the soil than nitrate, its oxidized and negatively charged counterpart.

The organic fraction of the soil is made up of plant debris, microbial cells, products of microbial metabolism, and humus. Humus contains a number of polymerized substances; aromatics, polysaccharides, amino-acids, uronic acid polymers, and phosphorus containing compounds [Alexander, 1991]. Much of the organic matter in soil is only slightly soluble and somewhat resistant to biodegradation. The amount of humus in soil is greatly influenced by agricultural activities.

The rate of biochemical reactions is governed by temperature as well as molecular structure. In general an increase in temperature increases the rate of reaction up to some optimal temperature above which there is a decrease in reaction rate. Each microorganism has a optimal temperature range for growth. Mesophiles can grow from about 15 to about 45° C and have optimal growth in the range of 25 to 35° C they comprise the bulk of soil bacteria. Psychrophiles develop best at temperatures below 20° C. Thermophiles grow best at temperatures between 45 and 65° C. Highly acid or alkaline conditions generally inhibit microbial activity and most bacteria favor neutral conditions. There are however, bacteria that are well adapted to acidic or basic conditions. For example, the sulfur oxidizing bacteria, an obligate aerobic, chemoautotrophic genera that produce sulfuric acid through oxidation of H_2S , function well at pH values of 1.

Substrate Factors

Chemical compounds that are difficult to remove from the environment include: synthetic polymers, chlorinated aromatic compounds, and pesticides such as DDT and chlordane. Compounds which are too large to penetrate the microbial cell and are not modified by extracellular enzymes, such as polyvinyl chloride and polyethylene, cannot be degraded. Compounds which have very low water solubilities cannot penetrate the cell rapidly enough for the organism to obtain enough energy for the growth. Molecules with certain structural properties may sterically hinder enzymatic attack. Structural factors which inhibit the degradation of compounds include the presence of amine, methoxy, sulfonate, and nitro groups; extensive halogenation; very high molecular weights or long chain lengths; benzenes substituted in the meta position; ether linkages; and branched carbon chains.

The concentration of chemicals in the environment can greatly affect the rate of their biodegradation. Compounds may be present in concentrations lower than the threshold concentration which will support growth or maintenance of the microbial population. Examples are 2,4-D and dichlorophenol: these compounds are readily degraded at concentrations in the 1-100 ppm range but may persist for years when present at concentrations in the ppb range [Alexander,

1981]. At the other end of the concentration range, compounds present in moderate to high concentration may be toxic to indigenous microorganisms in water, soil, sediment, or sewage. Oligotrophic organisms may experience toxicity and inhibition of biodegradation at lower concentrations compared to the microorganisms isolated and maintained under typical laboratory conditions such as those used in pure culture studies.

Compounds that are degraded via cometabolism require specific cosubstrates which must be available as primary substrates to induce synthesis of the necessary enzymes in the cometabolizing population. If the cosubstrate is present in too high a concentration however, it competes for the enzyme sites which degrade the primary substrate and inhibits metabolism. Some schemes where the cosubstrates are pulsed into the bioremediation site are being explored in an attempt to get around this problem [McCarty, 1988].

The presence of a second substrate which is not a cosubstrate can inhibit the degradation of a pollutant due to diauxic effects. In this case, metabolic control operates in such a way that enables organisms to select the substrate that allows them to grow at the highest rate. The less desirable substrate, usually the pollutant, will only be degraded when the concentration of the more readily degraded substrate is limiting.

Microbiological Factors

Biological transformations of organic compounds are catalyzed by the action of enzymes. Most frequently, the organisms which have the enzymes to breakdown the pollutants are already present in the soil. This is often the case for petroleum hydrocarbons. However degradation of the pollutant often does not occur because of environmental limitations such as oxygen, nutrients, moisture, or pH. In such cases the goal of bioremediation is to manipulate the environmental factors to make them more favorable for degradation. Even after environmental factors have been corrected, a lag may occur before biodegradation is observed. The lag period results from the acclimation of the indigenous microbial population. Several explanations have been put forth to explain the acclimation period [Spain, 1990]. Microbial enzymes may be induced only after exposure to the chemical. Initially small populations of microorganisms capable of degrading the pollutant may be growing up to the point where significant degradation can occur. Genetic mutations or genetic exchange between indigenous populations may be occurring, also.

Some toxic organic chemicals are foreign to normal metabolic pathways of microorganisms. In these cases, the ready made enzymes for dealing with these compounds do not exist in the natural ecosystem. For the site to be successfully bioremediated, microorganisms with the catabolic pathway for the pollutant must be introduced into the soil. These organisms are most often isolated from a site where the pollutant is present. Growing the organisms in the presence of the target compounds in laboratory cultures allows the production of sufficient masses of the necessary cells and creates a selective pressure for the formation of metabolic pathways that degrade target chemicals. Sometimes the culture is also treated with ultraviolet light or chemical mutagens to increase the chances of mutation.

Another approach, *in vivo* engineering, falls somewhere between isolation of adapted populations and genetic engineering. In this case, genes for the biodegradation of pollutants are located on plasmids or transposons in a microorganism and can be exchanged among related organisms. If a microorganism known to have the degradative pathway on a plasmid or transposon exists, it can be introduced into a culture of organisms having other desirable traits and conditions can be provided which enhance genetic exchange. For instance, an organism known to be very competitive in the environment to be remediated may be given the genes to degrade a specific pollutant.

There has been a great deal of interest in the genetic engineering of organisms which have novel metabolic pathways for degrading environmental pollutants [Halvorson, *et al.*, 1985]. By adding genes for toxic compound degrading enzymes to bacteria, new strains could theoretically be tailored to degrade specific compounds in specific environments. Deliberate release of genetically engineered organisms into the environment has been stringently regulated to the point of completely restricting their use. There are both real and perceived risks to society of bacterial strains that have been given synthetic DNA sequences with no known natural counterpart. Equally significant is the fact that genetically engineered microorganisms have not been found to be competitive in "wild" environments. Maintaining plasmids requires energy and reduces the competitiveness of engineered organisms. In most cases a number of species present are capable of degrading the primary substrate, which places an engineered organism in heavy competition for growth requirements.

Ecological factors also influence bioremediation activities. Many species of microorganisms make up the microbial community at a given site. Often compounds are not acted on by a single species but a consortia of microorganisms works in concert. One species may initiate the transformation and then secondary utilizers use intermediates derived from incomplete catabolism by the primary utilizers. Or the secondary utilizers may grow on metabolic by-products of the primary utilizers which are not derived directly from the compound. These secondary utilizers also play a role in supporting the primary utilizers for example by providing certain co-factors or nutrients, or by removing toxic products [Atlas and Bartha, 1987].

Potential for Application of Genetic Engineering to Bioremediation

Interest has been shown in developing genetically engineered microorganisms (GEMs) for bioremediation. Much of this interest has been based on the assumption that better overall process performance could be achieved through designing organisms to carry out specific reactions [Olson, 1988]. Another objective has been the development of a "superbug" that would degrade recalcitrant organics such as chlorinated aliphatics, dioxins, and polychlorinated biphenyls. In general, there has been little success achieved, although efforts continue in a number of laboratories.

A number of drawbacks are associated with application of GEMs. If the required genetic sequence is encoded onto a plasmid the desired activity rapidly disappears unless a selective pressure is maintained. Competitiveness of GEMs for readily degradable substrates is low compared to "wild" organisms. Biodegradation of many of the compounds of interest (e.g. chlorinated solvents) is by cometabolic reactions that do not support growth. Ability to carry out these reactions appears to be related to consistent environmental conditions and the presence of a specific cosubstrate (e.g. toluene or methane). Some hope that stable systems can be developed is given by the work of Fujita *et al.* [1991] who reported the development of *P. putida* strains capable of simultaneous salicylate and phenol degradation with good stability over 300 generations. Fujita *et al.* also introduced the gene onto a plasmid of the floc forming bacteria *P. lemoignei* 551 with the thought that this would increase ecological stability, in mixed cultures.

Constraints on application of genetic engineering in bioremediation appear to be significant. Risks to ecosystems and human health associated with introduction of GEMs into the "wild" environment [Allbergo and Lee, 1991] are generally considered small but understanding of this issue is far from complete. Problems associated with maintaining cultures with the desired characteristics have been discussed above. Finally, problems with production of satisfactory conversions exist. The risk question appears every time proposals to use GEMs in a noncontrolled environment are made. To date, the problems associated with such uses have been quite the opposite - maintenance of the populations has been difficult. However, the irrevocability of the releases of GEMs into the environment make the concerns reasonable and the development of risk

assessment procedures prudent. Optimism that use of GEMs in uncontrolled environments will be possible is unreasonable considering that natural mutations that would carry out the desired reactions appear to be possible but have not developed. This would lead to the conclusion that long term stability in uncontrolled environments is unlikely.

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III BIODEGRADATION OF SELECTED COMPOUNDS

A discussion of the biodegradation of selected organic compounds that are known to be significant in bioremediation is presented in this section. Further information as to compound degradability and pathways of degradation, microorganisms which have been shown to degrade them, and possible biotransformation products are available in other reviews [Gibson, 1984; Rochkind *et al.*, 1986; Pitter and Chudoba, 1990; Vogel *et al.*, 1987; EPA, 1983]. Skladany [1992] identified the target compounds for bioremediation as petroleum hydrocarbons, solvents (methyl ethyl ketone, acetone, alcohols, methylene chloride), aromatics (benzene, toluene, xylene, polycyclic aromatic compounds, chlorobenzene), nitro and chloro-phenols, phthalate esters, pesticides, and chlorinated aliphatic compounds. These compounds can be roughly grouped as petroleum hydrocarbons and their oxidation products, halogenated aliphatic compounds, and halogenated aromatic compounds. Microbial degradation of only a fraction of these compounds has been studied in laboratory culture and fewer still have been studied in natural ecosystems. Biodegradation rates and pathways for biotransformation determined in laboratory cultures do not necessarily reflect biodegradation in sewage, soil, or aquatic systems. In addition, the study of metabolic pathways generally identifies only those compounds which are excreted outside the cell and accumulate long enough for the intermediate to be above the detection limit of the analytical technique [Alexander, 1981].

BIODEGRADATION OF HYDROCARBONS

Over 2 billion metric tons of petroleum are produced per year worldwide [Bartha, 1986] and large amounts of petroleum products end up polluting both marine and terrestrial environments. Low level routine discharges (urban runoff, effluents, oil treatment of roads, etc.) account for over 90% of the total petroleum hydrocarbon discharges. Accidents such as tanker disasters, pipeline breaks, and well blowouts account for less than 10% of these discharges. In general, petroleum hydrocarbons are intermediate between highly biodegradable and highly recalcitrant compounds. Petroleum compounds have entered the biosphere through seeps and erosion for millions of years and metabolic pathways for their degradation have evolved.

Hydrocarbons in crude petroleum are classified as alkanes (normal and iso), cycloalkanes, aromatics, polycyclic aromatics, asphaltines, and resins. Alkenes are generally not encountered in crude oil but may be present in small quantities in refined petroleum products due to the "cracking" process. Variations in chain length, in chain branching, in ring condensations, in interclass combinations, and the presence of oxygen, nitrogen, and sulfur containing compounds account for the wide variety of petroleum hydrocarbons. The biodegradability of these compounds is greatly affected by their physical state and toxicity. Because petroleum is such a complex mixture, its degradation is favored by a mixed population of microorganisms with broad enzyme capabilities. In addition, the initial degradation of petroleum hydrocarbons requires the action of oxygenase enzymes and so, is dependent on the presence of molecular oxygen [Atlas, 1991]. Aerobic conditions are therefore necessary for the initial breakdown of petroleum hydrocarbons. In subsequent steps nitrate or sulfate may serve as a terminal electron acceptor [Bartha, 1986] but oxygen is most commonly used.

Alkanes

The n-alkanes are the most biodegradable of the petroleum hydrocarbons. However, normal alkanes in the C₅-C₁₀ range are inhibitory to many hydrocarbon degraders because as solvents they disrupt lipid membranes. Alkanes in the C₂₀-C₄₀ range (referred to as "waxes") are

hydrophobic solids; their low solubility interferes with their biodegradation. In the degradation of alkanes, the mono-oxygenase enzyme attacks the terminal methyl group to form an alcohol as shown in Figure 3.1 [Pitter and Chudoba, 1990]. The alcohol is oxidized further to an aldehyde and then to a fatty acid. The fatty acid is degraded further by β -oxidation of the aliphatic chain.

Extensive methyl branching interferes with the β -oxidation process [Bartha, 1986] and may necessitate di-terminal attack. In general, the degradation of alkanes produces oxidized products that are less volatile than the parent compounds. However, the parent alkanes are highly volatile and may be removed from soil primarily through stripping under aerobic conditions.



Figure 3.1
Initial oxidation of Alkanes

Alkenes

Less is known about the biodegradation of alkenes than alkanes [Pitter and Chudoba, 1990]. Location of the unsaturated linkage is a factor. For example, 1-Alkenes are more degradable than alkenes with an internal double bond. There are two pathways for the metabolism of 1-alkenes [Pitter and Chudoba, 1990; Britton, 1984]. Either the double bond is oxidized, giving rise to a diol, or the saturated chain end is oxidized as shown in Figure 3.2.

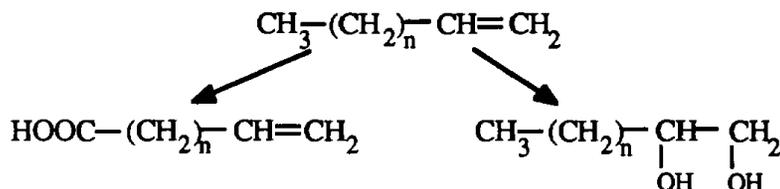


Figure 3.2
Metabolism of 1-Alkenes

Cycloalkanes

The cycloalkanes (acyclic hydrocarbons) are less degradable than alkanes but more degradable than the polycyclic aromatics [Trudgill, 1984; Pitter and Chudoba, 1990]. Their biodegradability tends to decrease with increasing numbers of ring structures. Alkyl substituted cycloalkanes are more readily degraded than non-substituted hydrocarbons and cycloalkanes with long-chain side-groups are more easily degraded than those with methyl or ethyl groups. Cycloalkanes are degraded by oxidase attack to a cyclic alcohol which is dehydrogenated to a ketone [Bartha, 1986] as shown in Figure 3.3. Alkylcycloalkanes undergo initial attack at the alkyl group giving rise to a fatty acid [Pitter and Chudoba, 1990]. Cycloketones and cycloalkane-carboxylic acids are therefore the primary products of metabolism of cycloalkanes.

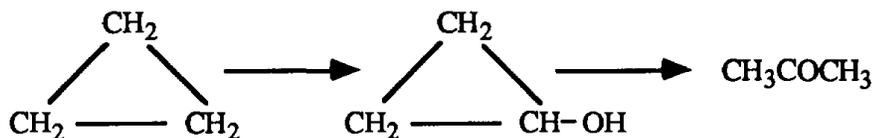


Figure 3.3
Degradation of Cycloalkanes

Aromatics

Several different aromatic compounds are present in petroleum, including 1, 2, 3, 4, and 5 ring compounds and alkyl-substituted aromatics. Aromatic compounds are more stable than other cyclic compounds due to the sharing of delocalized electrons by the pi bonds. Bacteria oxidize aromatic hydrocarbons using either two monooxygenase or one dioxygenase enzyme to trans-dihydrodiols by incorporating two oxygen atoms into the molecule (Figure 3.4) [Rochkind *et al.*, 1986]. Dihydrodiol is further oxidized to dihydroxylated derivatives (catechols). These dioxygenase reactions have been shown to occur for benzene, halogenated benzenes, toluene, p-chlorotoluene, xylenes, biphenyl, naphthalene, anthracene, phenanthrene, benzo[a]-pyrene, and 3-methylcholanthrene [Gibson, 1988]. The aromatic ring is then degraded via either the ortho-cleavage pathway (a) to yield cis-cis-muconic acid or the meta-cleavage pathway (b) to yield 2-hydroxymuconic semialdehyde [Pitter and Chudoba, 1990]. Fungi and other eukaryotes oxidize aromatic compounds using a monooxygenase enzyme to form an epoxide which can then undergo hydration to yield trans-dihydrodiols [Cerniglia, 1984; Rochkind *et al.*, 1986].

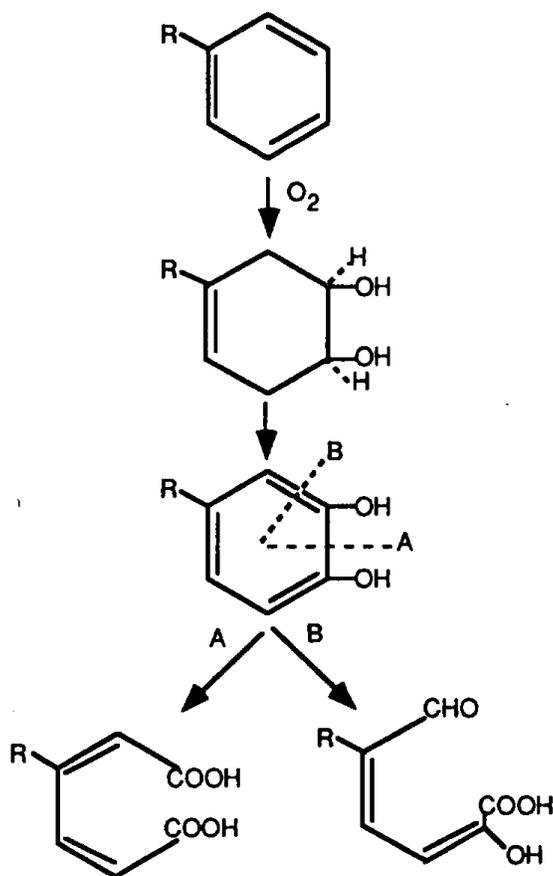


Figure 3.4
Degradation of Aromatic Compounds

Polycyclic Aromatic Hydrocarbons

Biodegradation of polycyclic aromatic hydrocarbons (PAHs, also known as polynuclear aromatics or PNAs) by bacteria, fungi, yeasts, cyanobacteria, and algae has been demonstrated [Cerniglia, 1984]. Polycyclic aromatic hydrocarbons are degraded, one ring at a time, by similar mechanisms as the ones used for aromatic compounds. Biodegradability of PAHs tends to decrease with increased numbers of rings and with increasing numbers of alkyl substituents. Atlas, [1991] reported that the enzymes required for the procaryotic degradation of PAHs are induced by the presence of lower molecular weight aromatics such as naphthalene. Thus, the high molecular weight PAHs might be resistant to microbial degradation when lower molecular weight PAHs are not present. Fungal degradation of PAHs is environmentally significant because some of the products have been implicated as toxic forms in higher organisms [Cerniglia, 1984]. Park *et al.*, [1990] showed an increase in the volatility of certain PAHs (naphthalene, and 1-methylnaphthalene) as a result of biodegradation to lower molecular weight compounds.

Asphaltines and Resins

These are high molecular weight compounds containing nitrogen, sulfur, and oxygen. Asphaltines and most resins have complex structural arrangements composed of hydrocarbon chains and nitrogen, sulfur, and oxygen atoms linking polycyclic aromatic stacks which include nickel and vanadium. Asphaltines and resins are considered to be recalcitrant compounds due to their insolubility and the presence of functional groups that are shielded from microbial attack by extensive aromatic ring structures [Atlas, 1991]. Relative and sometimes absolute amounts of asphaltines tend to increase during biodegradation of petroleum hydrocarbons because of their resistance to degradation and creation by condensation reactions. Some studies have reported removal of asphaltines by cometabolism in the presence of C₁₂-C₁₈ n-alkanes [Leahy and Colwell, 1990, Rontini *et al.*, 1985].

BIODEGRADATION OF HALOGENATED ALIPHATIC COMPOUNDS

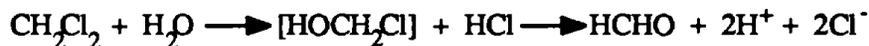
Halogenated aliphatic compounds are common contaminants of groundwater and hazardous waste sites. Industrially important halogenated aliphatics include chlorinated and brominated alkanes and alkenes in the C₁-C₃ range. Chlorinated ethanes and ethenes are commonly used as cleaning solvents and in dry cleaning operations and semiconductor manufacturing [Vogel *et al.*, 1987]. Brominated compounds are used as pesticides (EDB, DBCP) and halogenated methanes are formed during the disinfection of water. Halogenated compounds are considered to be resistant to microbial attack so they tend to persist in the environment. Physico-chemical processes such as stripping and adsorption may predominate over biological transformations for halogenated compounds due to their slow degradation rates.

Organic compounds generally act as electron donors, however because of the electronegativity of the halogen substituents, polyhalogenated compounds can act as electron acceptors in reducing environments. Therefore, the greater the number of halogens in the molecule, the less biodegradable the compound will be in aerobic systems and the more degradable it will be in anaerobic systems. The biodegradation rate is also dependent on the type of halogen in the compound. Halogens can be ordered according to their decreasing electronegativities as follows: F, Cl, Br, I. Therefore bromine which is a less electronegative compound than chlorine is more easily substituted. Cometabolism also plays an important role in the biotransformations of halogenated compounds. Trichloroethene [TCE], tetrachloroethene [PCE], and trichloromethane [TCM] (chloroform) for example, are compounds that are degraded by enzyme systems which are induced in response to a cometabolite [Strand and Shippert, 1986]. In the case of TCE, degradation occurs as a result of cometabolism by either methanotrophs [Alvarez-Cohn and McCarty, 1991], aromatic degraders [Folsom *et al.*, 1990], or ammonium oxidizers [Vannelli *et al.*, 1989] through the action of monooxygenase or dioxygenase enzymes.

Microbially mediated reactions of chlorinated aliphatic compounds include substitutions, oxidations, and reductions [Pitter and Chudoba, 1990]. Dehalogenation of the molecule is usually the first step with compounds containing a short alkyl chain. Where the alkyl chain is long, the halogen no longer influences the oxidation of the terminal carbon atom. In this case oxidation of the terminal methyl group is the first step resulting in a halogenated aliphatic alcohol. In substitution reactions, the halogen is substituted by a hydroxyl group:



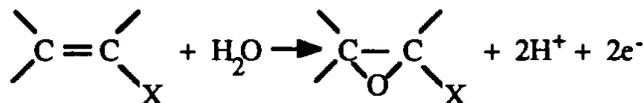
An example of this is the dehalogenation of dichloromethane:



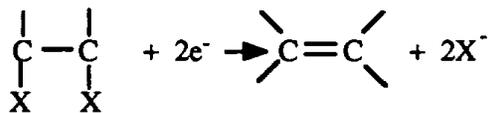
Intermediate products of the hydrolysis of dichloromethane and 1,2-dichloroethane are formaldehyde, 2-chloroethanol, and 1,2-ethanediol [Pitter and Chudoba, 1990]. In mixed cultures these are further degraded to carbon dioxide. Oxidation by alpha-hydroxylation is also a possible mechanism but is less common:



The aerobic degradation of chlorinated ethenes probably occurs by epoxidation. The epoxide is further hydrolyzed to carbon dioxide and HCl.



The third type of reaction, reductive dehalogenation, occurs in anaerobic environments. Either a halogen is substituted by a hydrogen atom or two halogen atoms are removed giving rise to a double bond (dihalo-elimination):



Dihalo-elimination can occur in either anaerobic or aerobic environments. In the case of PCE and TCE, reductive dehalogenation results in the formation of vinylidene and vinyl chlorides [Freedman and Gossett, 1989] which are more volatile carcinogens.

BIODEGRADATION OF HALOGENATED AROMATIC COMPOUNDS

Halogenated aromatic compounds are also common contaminants of soil, groundwater, and hazardous waste sites. Industrially important halogenated aromatics include solvents, lubricants, pesticides [e.g. DDT, 2,4-D, 2,4,5-T], plasticizers, polychlorinated byphenyls [PCBs], which were widely used as insulators in electrical transformers and capacitors; and pentachlorophenol, a wood preservative [Reineke and Knackmuss, 1988, Rochkind *et al.*, 1984]. As with alkylhalides,

both the position and number of halogens are important in determining the biodegradability of halogenated aromatic compounds. Like alkylhalides, the more halogen substituents the compound has, the more likely it is to undergo reductive dehalogenation in reducing environments. Biodegradation of arylhalides may occur by dehalogenation of the ring structure by oxidation, reduction, or substitution; or ring cleavage can precede dehalogenation generating halogenated aliphatic compounds.

Haloaromatics such as chlorophenoxy herbicides and chlorobenzenes are most often degraded by oxidation to halocatechols via chlorophenol with subsequent ring cleavage [Pitter and Chudoba, 1990]. Figure 3.5 shows the ortho cleavage pathway which results in the formation of chloromuconic acid. The meta cleavage pathway results in the formation of chlorohydroxymuconic semialdehyde. Dehalogenation may proceed spontaneously after cleavage of the aromatic ring [Reineke and Knackmuss, 1988].

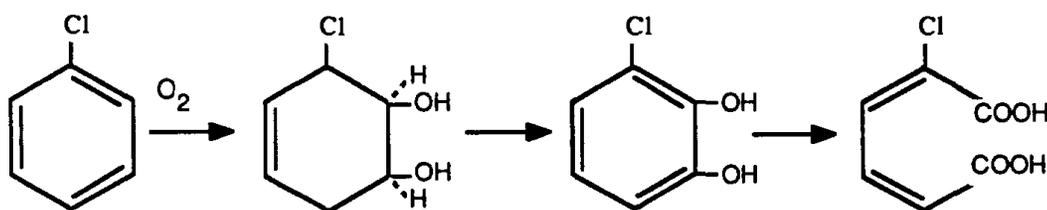


Figure 3.5:
Ring Cleavage of Chlorobenzene.

Reductive dehalogenation has been shown to occur under methanogenic conditions for chlorinated benzoates [Sufliata, *et al.*, 1982], PCBs [Thayer, 1991], PCP, the pesticide 2,4,5-T, chlorophenols, and 1,2,4-trichlorobenzene [Reineke and Knackmuss, 1988]. The result of these transformations are products containing fewer chlorines than the parent compounds. These products are unlikely to be further degraded under anaerobic conditions but can be oxidized under aerobic conditions. For example, the monochlorinated benzoates are all biodegraded to CO_2 aerobically [Levitt, Schroeder & Pfeiffer, 1985]. The reductive dechlorination of pentachlorophenol is shown in Figure 3.6. The products are 3,4,5-trichlorophenol, 3,5-dichlorophenol, and 3-chlorophenol [Reineke and Knackmuss, 1988].

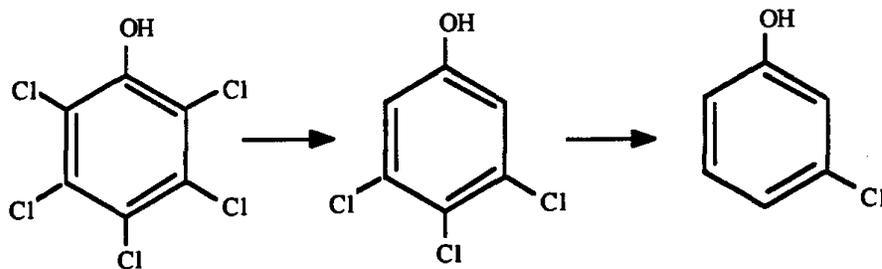


Figure 3.6
Reductive Dehalogenation of Pentachlorophenol

Substitution of the halogen by a hydroxyl group has been shown to occur for para substituted mono-halogenated benzoates, and PCP [Reineke and Knackmuss, 1988] as shown in Figure 3.7. The product of the PCP degradation is tetrachloro-p-hydroquinone which can only be degraded under anaerobic conditions.

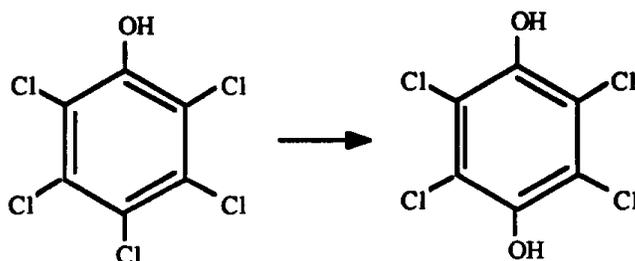


Figure 3.7
Hydrolysis of Pentachlorophenol

CONCLUSIONS

Biotransformations of organic compounds may affect both their toxicity and volatility. Biodegradation and volatilization are competing mechanisms and the more degradable a compound is the more likely it will be degraded before volatilization occurs. Highly volatile parent compounds however, such as gasoline hydrocarbons, may be preferentially stripped from the soil under certain conditions even though they are highly degradable. Some chemicals degrade to products which are more degradable than the parent compounds and so have short lives in the environment. Others degrade to recalcitrant compounds that are more persistent than the parent compounds.

In general, aerobic transformations, such as the degradation of an alkane to a fatty acid or an aromatic compound to a catechol, add oxygen to the compound making the product compounds less volatile, more soluble and more degradable. Polyaromatic hydrocarbons, however may degrade to more volatile products due to the cleaving of aromatic rings and formation of lower molecular weight compounds. This may be especially important in fungal metabolism of PAHs where extracellular enzymes are used to cleave aromatic rings. Transformation processes that make compounds more soluble can decrease their adsorption to surfaces and facilitate stripping from the liquid phase.

Some anaerobic transformations make compounds more volatile. Examples of this are the reductive dechlorination of TCE to dichloroethene and vinyl chloride or the dihaloelimination reactions which convert 1,2-dichloroethane to ethene. If kept under anaerobic conditions in soil, these compounds might diffuse slowly into aerobic zones or possibly to the atmosphere. Some bioremediation schemes have been proposed however, which would alternate anaerobic and aerobic conditions. In these treatment systems reductive dehalogenation followed by aeration and mixing might increase volatilization of volatile compounds formed in the previous stage.

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IV. BIOREMEDIATION SYSTEMS

In theory, bioremediation refers to any engineered system that utilizes microorganisms in the degradation of organic contaminants. Bioremediation systems are designed primarily to enhance the natural ability of microorganisms to degrade organics. This is achieved in two ways; (1) providing favorable conditions for the growth of the microbes for example, and (2) increasing the mass transfer or facilitating the contact between the microorganisms and the target compounds. Examples of providing more favorable growth conditions include introducing oxygen or another electron acceptor, adding required nutrients, and adjusting moisture content, temperature, and pH. Bioremediation can be applied to the treatment of soil, water or vapor. Most experiences however, have been with water and soil. This concept was first employed nearly a hundred years ago in the design of wastewater treatment systems. Its application to the field of hazardous waste is relatively new and is thus still in the experimental stages of development. Most experiences with bioremediation have been in the treatment of soils and groundwater contaminated with petroleum products from leaking underground storage tanks. There are noticeable discrepancies in the literature with respect to the classification of bioremediation processes, the nomenclature and the applications.

As noted in Chapter I, control of emissions from groundwater bioremediation systems is not a major problem, while emissions from soil bioremediation systems can be significant. For this reason, discussion in this section will focus on technologies that are used to treat the soil.

TYPES OF BIOREMEDIATION PROCESSES

Soil bioremediation processes are classified in six groups: (1) *in situ*, (2) land treatment, (also known as landfarming), (3) composting, (4) slurry-phase, (5) soil venting, and (6) soil washing. Land treatment and composting have been the most widely used bioremediation processes because they are more easily controlled and involve less capital investment. Land treatment has also been used to treat waste slurries and in this application might be considered a form of soil contamination.

In situ

In this process, the biological treatment occurs in the subsurface. The same process can be used to treat both the saturated and unsaturated zones although most applications have been in the saturated zone, i.e. to treat groundwater [EPA, 1990]. In treating the vadose (unsaturated) zone, injection wells are drilled to introduce air, nutrients, water or whatever else is needed to enhance the degrading capacity of the microbial population. Enhancing bioremediation may also involve bio-augmentation, that is the addition of non-native bacteria or microbes to degrade specific chemicals. Oxygen is often the rate limiting factor for biodegradation in the subsurface environment. It can be introduced in the form of compressed air, pure oxygen or as hydrogen peroxide in a water solution.

The inorganic nutrients required in the largest amounts by microorganisms are nitrogen, phosphorus and sulfur. Other nutrients required in small, or trace, quantities include potassium, magnesium, calcium and iron. Typical compounds that are added to supply such nutritional needs include: KNO_3 , KH_2PO_4 , MgSO_4 , MnSO_4 , CaCl_2 and FeCl_3 [Rainwater and Scholze, 1991]. Nutrients need to be added in a mobile form so that they will be transported through the medium. In most cases this means adding the nutrients in a water solution. Soils usually contain significant amounts of trace nutrients and only a few of the minerals listed above need to be added.

Laboratory analysis and batch growth experiments can be used to determine limitations. Because nutrient requirements are directly proportional to microbial growth, the greater the level of pollution, the greater the nutrient requirement.

Monitoring the moisture content of the soil during bioremediation is essential to ensure that there is enough water to facilitate microbial activity, but not too much to hinder oxygen transport. A moisture content range of 40 to 79 percent is generally recommended [EPA, 1988]. Low moisture content restricts microbial growth and transport of dissolved species. High moisture contents result in oxygen transport limitations and anaerobic zones in the medium.

In situ treatment of soils is applicable where soil excavation is expensive or difficult and with contaminants that are slightly soluble in water but are easily degradable [Ryan, *et al.*, 1991]. Performance is sensitive to high concentrations of heavy metals, chlorinated organics and some pesticides and herbicides [EPA, 1988]. High removal efficiencies should not be expected with such a system. Organics may adsorb strongly onto subsurface minerals or may penetrate into cracks and thus become inaccessible to the degrading microorganisms.

In treating the saturated zone, that is aquifers, the same design principles are applied. However, this method of bioremediation is most effective for the biodegradation of dissolved contaminants and hydrocarbons [Fiorenza, *et al.*, 1991]. Pump and treat is a variant of *in situ* bioremediation used for the clean up of groundwater. It involves the use of extraction and injection wells for circulating the water out of and back into the aquifer. At the surface, the water may be treated, aerated, or nutrients may be added. The flow of the groundwater between the wells increases the microbial degradation rate in the aquifer. Pump and treat is very effective in cleaning aquifers, but is costly because of the energy and equipment used. When treating immobile organics adsorbed to aquifer material, the injection of oxygen and nutrients may be more effective than pump and treat [EPA, 1990].

Land Treatment or Landfarming

Landfarming is a method that has been applied for centuries by agricultural farmers to decompose organic non-hazardous waste. By spreading the waste over the soil, the combined action of aerobic microbial degradation, volatilization, adsorption and photolysis (chemical reaction induced by solar radiation), decomposes and reduces the concentration of the waste. Biodegradation followed by volatilization are considered to be the primary pathways of removal of contaminants in landfarming, while the other two mechanisms are relatively insignificant [EPA, 1990]. Since about 1950 landfarming has been used in the treatment of hazardous and industrial wastes which are applied in the form of liquid, sludge or solid. Depending on the waste type, application to the soil can be in the form of sprinkler irrigation, overland flow, truck spreaders, surface application or subsurface injection with a typical injection depth of about 0.13 meters [EPA, 1983 and EPA, 1990].

Soil tilling is used to aerate the soil and to incorporate the waste into the soil matrix (increase contact between the microbes and the chemicals). To maintain optimum moisture content, water is added through different forms of irrigation, including sprinkler and trickling systems. Soil additives may also be used to control moisture content [Dupont, *et al.*, 1988]. Irrigation is also used sometimes to regulate the soil temperature. Thermal conductivity of the soil matrix is increased by adding water, thus reducing the daily variations in soil temperature. Sprinkle irrigation protects against frost formation in the winter and cools down the soil in the summer. Another method used to modify the soil temperature is the addition of mulches. Examples of mulch materials used are compost or manure, wood chips and bark, sawdust, asphalt emulsion and gravel or crushed stones [Dupont, *et al.*, 1988]. In some cases, a cover is used over the site to control the emissions of volatile compounds, thus causing the soil temperature to increase.

Since most soils are acidic, pH adjustment is often needed to enhance biodegradation. To increase and stabilize the soil pH, different calcium or calcium/magnesium-containing compounds can be added to the soil. This process is known as liming, and examples of the compounds used are calcium oxide (lime), calcium hydroxide, calcium carbonate, calcium magnesium carbonate and calcium silicate slags. Should the soil pH be high because of a high carbonate concentration or because of the presence of hazardous wastes that are high in pH, "acidification" may be necessary. Acidification, or the reduction of the soil pH can be achieved by adding elemental sulfur or sulfur-containing compounds such as sulfuric acid, liquid ammonium polysulphide and aluminum and iron sulfates [Dupont, *et al.*, 1988].

Land treatment has been successfully used particularly at petroleum refinery sites and with creosote-contaminated sludges and soils [Ryan, *et al.*, 1991, Nyer, 1992]. With enhanced landfarming, MoTec Inc. was able to reduce creosote concentrations in the soil from 6200 and 3000 ppm to 800 and 100 ppm respectively within 30 days [Bogart and League, 1988]. The enhanced treatment involved bioaugmentation with bacteria grown in high nutrient broth as well as tilling for aeration, irrigation and supply of dissolved nutrients. Land treatment has also been successfully used to treat pesticides. A reduction in the concentration of 2,4-dichlorophenoxyacetic acid (2,4-D) from about 42 ppm to 4 ppm within 77 days has been reported [Fiorenza, *et al.* 1991]. In one study, land treatment reductions of 73 percent in benzene, toluene and xylene (BTX) concentrations, 36 percent in oil and grease and 86 percent in total PAHs were achieved over a four month period were reported by [Hanstveit, 1988]. Nyer [1992] reported that pentachlorophenol [PCP] concentrations were reduced by 95 percent while PAH concentrations were reduced by about 50 to 75 percent over a five month period in a land treatment system.

Advantages of land treatment systems include low capital and operating costs and effectiveness in treating wastes with relatively high metal contents. Disadvantages of land treatment are the large land area requirements, and the fact that this degradation process takes a relatively long time and may never be complete. Because regular tilling results in high rates of contact with the ambient atmosphere, high volatilization rates can be expected. Biologically recalcitrant or refractory VOCs are very likely to be emitted.

A variant of land treatment is prepared bed systems or engineered-landfarming (Fig. 4.1): These systems employ the same principles as landfarming but are set up with engineered controls to minimize transport of contaminants and to maximize treatment efficiencies. They are used when soil is excavated from the site for one of the following purposes :

- i. To prevent contaminant transport from the site and employ bioremediation in a specially prepared area.
- ii. To prepare the contaminated site for treatment in which case the soil is temporarily removed to a storage area. Preparing the contaminated site includes placing clay or plastic liners to control the transport of contaminants from the site, or adding uncontaminated soil to provide more treatment media [Sims, *et al.*, 1990].

Composting

Composting of non-hazardous organics has been in use for many years, however, the application of composting in the field of hazardous waste treatment is relatively new and is still being researched [EPA, 1990, EPA, 1988]. In composting, the levels of moisture, pH, oxygen, temperature and nutrients can be controlled effectively thus leading to optimal degrees of biodegradation. Composting differs only slightly from land farming and prepared bed processes. The principal conceptual difference is that biodegradable organic concentrations are great enough to result in heating of the soil pile during biodegradation. Higher temperatures result in higher biodegradation rates, and of course, the potential for increased volatilization of VOCs. There are

two basic types of composting: open systems and closed systems. In an open system, the more common type, the compost is piled on a platform in long mounds, or windrows. The piles are aerated either mechanically by turning the mixture periodically, or by forcing air through perforated pipes. In a closed system, also known as an in-vessel system, the compost is placed in an enclosed reactor and aeration is achieved by stirring or forced aeration. Bulking materials such as wood chips, leaves and refuse are often mixed in with the compost to allow for higher porosity and better aeration. Advantages of composting include relatively low energy demands, low sludge and brine production, applicability to most organic compounds and tolerance to relatively high metal concentrations [EPA, 1985]. Retention time, i.e. degradation time for similar compounds is much shorter in composting than it is in *in situ* or land treatment; for example weeks rather than months [Savage, *et al.*, 1985]. Land requirements are also less for composting than they are for landfarming, and water contamination problems are minimized [EPA, 1990]. The disadvantages are high maintenance requirements and high air emissions because of the high temperatures involved. For the same reason, moisture content needs to be monitored closely to maintain optimum microbial activity.

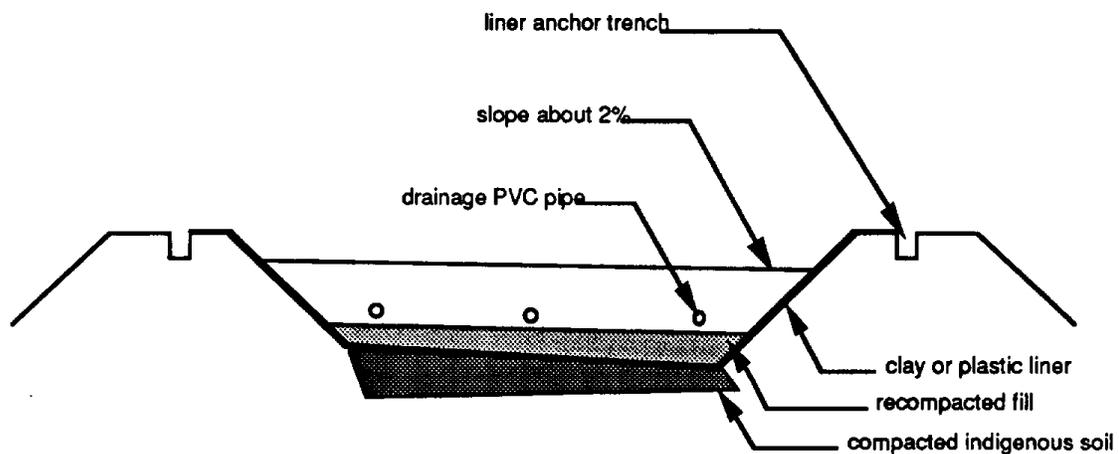


Figure 4.1
Definition sketch of a prepared bed system (adapted from Ryan, *et al.*, 1991).

Slurry-phase Biotreatment

Also known as bioreactor systems or liquid-solid contactor reactors. The treatment of contaminated soil or sludge in an aqueous medium. Water, be it contaminated groundwater, surface water or another source of water, is added to the soil to obtain an appropriate slurry density. Typically soil slurries are 50 percent solids by weight whereas sludge slurries contain less solids [EPA, 1988]. As the slurry is mixed, contact between the microbial organisms and the hazardous compounds is increased. Biodegradation is also optimized by adding nutrients (inorganic and/or organic) and oxygen and by controlling the pH and temperature to meet microbial needs. Eventually, biodegradation in such a system is relatively rapid and effective.

Slurry-phase bioremediation systems are typically operated on a batch, or semi-batch basis because of the nature and quantities of materials involved. In batch operation, a single reactor vessel is used. Contaminated soils are deposited into the reactor, nutrients, water, and microbial cultures are added, and the slurry is mixed and aerated until the conversions of the targeted compounds attain a satisfactory level. Mixing and aeration are then stopped and the solids are allowed to separate from the fluid. The solids are removed and, if appropriate, returned to their original location while the liquid may be sent to a wastewater treatment plant or allowed to evaporate. A portion of the slurry is retained in the reactor to be used as seed for the sequential

treatment runs. In semi-batch operation the treatment steps (nutrient and water addition, aeration and reaction, solids-liquid separation) are carried out in separate tanks.

Slurry-phase bioremediation is most easily carried out with relatively small batches of contaminated soil because of the difficulties inherent in mixing and aeration.

Soil Venting

Also called bioventing or vapor extraction, soil venting, is a relatively new *in situ* technology. This method differs from *in situ* bioremediation by the fact that mainly physical processes are used to remediate the soil. One form of soil venting is the application of vacuum to the soil to induce advective transport of contaminant vapors. As vapor is extracted, more organics in the liquid phase volatilize. The more typical soil venting system however, would also involve the injection of air, through wells in the vadose zone, as shown in Figure 4.2, to supply oxygen to stimulate biodegradation of contaminants. The optimum design for bioventing considers maximum oxygenation rates for biodegradation while allowing for a sufficient retention time for the volatile organic compounds to be degraded rather than volatilized. Off-gases are usually treated (e.g., by incineration or adsorption onto activated carbon) before being released into the atmosphere but biofiltration appears to be an attractive alternative for many situations. The effectiveness of soil venting is dependent on soil permeability, moisture content and the characteristics of the contaminants. It is applicable in treating pure volatile compounds such as trichloroethene, and mixtures of chemicals such as gasoline and other petroleum products [EPA, 1990].

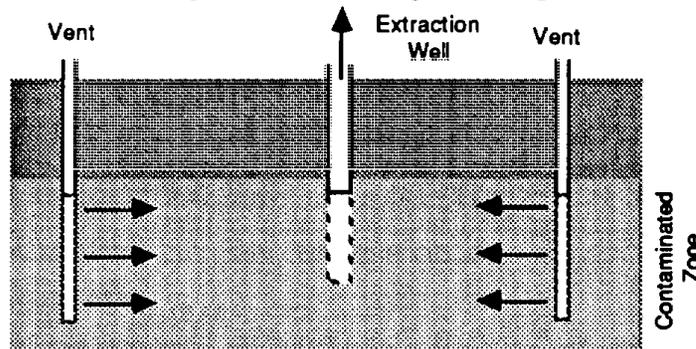


Figure 4.2
Definition sketch of a soil venting system. Biodegradation can be expected to occur in the aerated contaminated zone. Nutrients may need to be added to support a culture that is adequate to carry out significant amounts of bioremediation.

Soil Washing

A physical remediation process that can be used in conjunction with or prior to bioremediation. It is a relatively new technology in the U.S. though it is an accepted treatment method in Europe [EPA, 1990]. The purpose of soil washing is to reduce the volume of contaminated soil to be treated biologically, mainly by separating the highly contaminated fine particles (e.g., clay, silt, humus) from the larger particles such as sand and gravel. The process starts by rough-screening the soil to remove large debris, then water is mixed in to form a slurry. Intensive scrubbing of the slurry results in separation between the fine and large soil particles and the cleaning of the large particles by surface abrasion. After removing the larger particles, the remaining soil slurry is treated biologically.

SUMMARY

The choice between the different processes outlined above is very site and contaminant specific. Most often, laboratory and/or field studies are conducted to determine whether a certain process is appropriate for the existing conditions. The properties of the contaminant e.g. its solubility in water, its tendency to volatilize and its tendency to adsorb are all important factors to consider in choosing a process. For example, Fiorenza, *et al.* [1991] suggest using *in situ* bioremediation for removing soluble compounds, bioventing for removing volatile compounds and either land-farming, slurry-phase bioreactors or soil washing for removing sorbed compounds. Other factors to consider in choosing a process are: the time needed for biodegradation, the level of clean-up wanted and the expected costs [Sims, *et al.*, 1990].

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V. AIR EMISSIONS FROM BIOREMEDIATION SITES

Historically, environmental protection has focused on preventing or controlling surface and groundwater contamination. The air pathway, one of the major pathways of migration of contaminants, was not seriously considered until relatively recently. Since about 1970, with the introduction of the Clean Air Act, air pollution has become a significant issue in hazardous waste management programs [Shen, *et al.*, 1990]. Public concern over the fact that toxic air emissions from hazardous waste facilities could increase the risk of cancer and contribute to ozone formation, has grown over the last years. Estimates for total volatile organic compound (VOC) emissions in the U.S. from process and fugitive sources, including waste treatment, storage and disposal facilities are at more than 17,800 Mg/year [Shen, *et al.*, 1990].

With biological treatment systems, the goal is to destroy the contaminant rather than transport it to other media. However, based on the treatment method used, the handling operation, the site conditions and the waste characteristics, volatile organic contaminants are emitted to the atmosphere before they can be degraded. On the other hand, the biodegradation of organics in biological treatment systems is still poorly understood. Data obtained from bench-scale or laboratory studies can vary greatly from field studies. There is a need for a better understanding of the kinetics of biodegradation in multi-component heterogeneous systems. Several models have been developed to predict air emissions from bioremediation processes. These models are empirical, the data on which they were based are unknown or incomplete and the interrelationships between components and pathways are complex [EPA, 1990]. This chapter will focus on the removal pathways of the contaminants in bioremediation systems and the expected effects of these pathways on air emissions. Control measures used in bioremediation systems to limit VOCs emissions will also be considered, and case studies of observed VOC levels will be cited.

ORGANIC REMOVAL PATHWAYS

To understand how and to what extent bioremediation can induce emission of VOCs into the atmosphere, it is important to identify the mechanisms involved in VOCs emissions and define their relationship to the removal pathways of contaminants in bioremediation processes. Shen, *et al.* [1990], identified 5 major mechanisms through which VOCs can be transmitted into the air: Volatilization, biodegradation, photodecomposition, hydrolysis and incineration. Photodecomposition and hydrolysis are considered to be of minor importance in the removal of organics in bioremediation systems [EPA, 1990] and thus will not be discussed further in this section. Incineration is sometimes used as a control measure to destroy VOCs emitted from certain bioremediation systems such as soil venting. Since incineration is an add-on process and is not directly related to the removal of organics from the soil and water, it will be considered separately later in this chapter. Volatilization and biodegradation together with adsorption are the major removal pathways of contaminants in bioremediation processes and thus will be discussed in more detail.

Volatilization

At a water-air interface, volatilization describes the movement of the molecules of a chemical from the liquid phase to the gas phase. Volatilization is the result of molecular diffusion caused by a chemical potential (i.e. difference in the concentration of the contaminant) between the two media or phases. Several models have been developed to estimate the rate of volatilization, or the rate of mass transfer of a chemical from water into the atmosphere across the air-water

interface. The most commonly used volatilization description is the two-film model [EPA, 1990]. In the two-film model it is assumed that both the air and the water phases are well mixed and that the concentration of the chemical in each phase is constant. The concentration gradient near the water-air interface allows for transport of the molecules across the stagnant films in each phase by molecular diffusion. At the interface, the ratio of the concentration of the chemical in the water and in the air "is assumed to equal the Henry's law constant" (EPA, 1990) :

$$H = H_C RT = \frac{C_G}{C_L} RT \quad (5.1)$$

where:

- H = Henry's coefficient (atm-m³/mol)
- H_C = Henry's coefficient (dimensionless)
- R = universal gas constant (atm-m³/mol-K)
- T = temperature (K)
- C_L = concentration in liquid phase at edge of film (g/m³)
- C_G = concentration in gas phase at edge of film (g/m³)

The Henry's law constant is indicative of the tendency of a chemical to volatilize. EPA [1990] reported on the work of Lyman *et al.*, [1982] that for $H > 3 \times 10^{-7}$ atm-m³/mol, a chemical can be considered to be volatile, while for smaller values of H, "volatilization can be considered unimportant as a pathway for removal of the contaminant." The Henry's law constant is dependent on the type of compound considered, the activity of the compound in each phase, and the temperature. For a specific gas H can be roughly estimated from [EPA, 1990]:

$$H = \frac{P}{14.7 s} \quad (5.2)$$

where:

- P = pure component vapor pressure, psia
- s = solubility of chemical in water mol/m³
- 14.7 = conversion factor (psia to atmospheres).

At a soil-water interface, the volatilization process is more complex. As depicted in Figure 1.1, VOCs sorbed onto the soil surface may transfer into solution in the soil water or into the vapor phase in the soil air [EPA, 1990]. Transfer from the soil air to the ambient atmosphere will occur through diffusion under ordinary circumstances or by convection if ventilation is imposed on the soil. Within the soil matrix, Henry's law can be used to estimate partitioning between the soil water and the soil air. The rate of volatilization of a contaminant from soil is controlled by several factors. The most important are the contaminant concentration and the contaminant's physical properties; specifically vapor pressure and aqueous solubility. Volatilization rates increase dramatically with increasing temperature and surface turbulence. The most common source of surface turbulence is wind, but mechanical agitation is sometimes a factor [Ehrenfeld and Ong, 1985]. Other factors that influence the rate of volatilization include: soil moisture content, temperature and porosity; the organic and the clay content in the soil, soil handling and the bioremediation technique used [EPA, 1990].

Adsorption

Molecules of a compound in solution become adsorbed onto the surface of a solid through chemical reaction (chemisorption) or physical (van der Waals) forces. Chemical bonding is stronger and less reversible than physical bonding. In most cases chemisorption is essentially permanent, while physical adsorption is an equilibrium process. For this reason the discussion here will focus on physical adsorption. The rates of adsorption and desorption are dependent on the concentration of the contaminant in solution. If the concentration of the dissolved contaminant increases, adsorption increases; if the concentration decreases, desorption increases. Adsorption is controlled by several factors, the most important of which are the properties of the compound itself (e.g., molecular structure, charge, polarity and water solubility), and the properties of the soil (e.g., clay and organic content, pH, moisture content and temperature). An increase in temperature usually causes a decrease in contaminant adsorption onto the soil. An increase in moisture content usually causes a decrease in adsorption [Dupont, *et al.*, 1988]. Adsorption influences both the volatilization and biodegradation processes. Adsorption competes with biodegradation and volatilization in determining the fate of VOCs in the soil [EPA, 1990]. As for biodegradation, the strong adsorption of organics onto subsurface minerals, or their penetration into cracks that are too small for the microorganisms to reach, will render the organics inaccessible to the microbial population or their degrading enzymes [McCarty 1991].

Biodegradation

As was explained in Chapter 2, biodegradation is the biological breakdown of organics which is induced by the metabolism or cometabolism of microorganisms. Under complete mineralization, the organic chemical is transformed into harmless constituents, mainly carbon dioxide, water and cell material. Biodegradation however does not always result in mineralization. The change in the molecular structure of a contaminant during bioremediation may result in the production of a compound that is much different from the parent compound. Volatilization can become a significant pathway for the removal of a nonvolatile contaminant if the biotransformation of that contaminant results in the formation of a more volatile product. The biodegradation of several types of compounds was discussed in detail in chapter 3 and thus this topic will not be considered further in this section.

STUDIES OF REMOVAL PATHWAYS

Complete fate studies of compounds in bioremediation sites have not been performed. Much of the information published on removal pathways is a combination of field data, extrapolation from laboratory studies, and conclusions drawn from simplified models.

Laboratory Studies

Park, *et al.* [1990] conducted a laboratory study on the degradation and volatilization of 14 PAH compounds in two types of soil. The authors found that volatilization was a significant mechanism of contaminant removal only for compounds with two rings. The compounds with the higher molecular weight and ring number were non-volatile. Degradability of the PAHs tested generally decreased with increasing molecular weight and aromatic ring number as indicated in Table 5.1.

Computer Model Results on Removal Pathways

Baehr [1987] used a mathematical model to simulate the diffusive transport mechanism of specific hydrocarbons in the unsaturated zone due to partitioning of the chemicals between the aqueous and the vapor phases. The fate of residual concentrations of hydrocarbons from a gasoline spill in the absence of biodegradation was considered. The purpose of Baehr's study was to consider the potential for groundwater contamination due to the transport of gasoline

constituents over time. Composition of a leaded gasoline sample reported by Bruell and Hoag [1984] was used for the simulation. The water/air partition coefficient, H_k ($H_k = 1/H_c$) at 20°C was calculated for each of the constituents. For the composite constituents, the H_k value was computed based on the "weighted average of the properties of individual molecular species with weights proportional to the fractional composition." [Baehr, 1987]. Table 5.2 is a compilation of Baehr's results. As seen in the Table 5.1, the aromatics, mainly benzene and toluene, are the more likely to partition in the liquid phase rather than to volatilize. These compounds, though they constitute a small fraction of the total mass of gasoline, are the real threat to the groundwater. The other constituents of gasoline however, are generally very volatile. Baehr's analysis predicts that in the absence of biodegradation 50% of the initial concentration of residual gasoline in the unsaturated zone is likely to be lost to the atmosphere within about a year due to diffusive transport.

Table 5.1
Laboratory Studies on the Biotransformation of 14 PAH compounds in two types of Soil [Park, *et al.*, 1990].

Compound	Percent Volatilized (%) ^a			Degradation Rate t1/2 (days)		
	K ^b	M ^c	Mean	K	M	Mean
Two Rings						
Naphthalene	32.3	29.2	30.8	2.1	2.2	2.2
1-Methylnaphthalene	14.7	26.9	20.8	1.7	2.2	2.0
Three Rings						
Anthracene	< 0.1	< 0.1	< 0.1	134	50	92
Phenanthrene	< 0.1	< 0.1	< 0.1	16	35	25.5
Four Rings						
Fluoranthene	bd	bd	bd	377	268	322.5
Pyrene	bd	bd	bd	260	199	229.5
Chrysene	bd	bd	bd	371	387	379
Benz(a)anthracene	bd	bd	bd	261	162	211.5
7,12-Dimethylbenz(a) anthracene	bd	bd	bd	20	28	24
Five Rings						
Benzo(b)fluoranthene	bd	bd	bd	294	211	252.5
Benzo(a)pyrene	bd	bd	bd	309	229	269
Dibenz(a,h)anthracene	bd	bd	bd	361	420	390.5
Six Rings						
Dibenzo(a,i)pyrene	bd	bd	bd	371	232	301.5
Indenol(1,2,3-cd)pyrene	bd	bd	bd	288	289	288.5

Source : Park, Sims and Dupont. Journal of Environmental Engineering (1990).

a : bd= below detection

b : Kidman fine sandy loam pH= 7.9, organic carbon = 0.5%, bacterial population= 6.7×10^6 colony forming unit/g soil.

c : McLaurin sandy loam soil pH= 4.8, organic carbon 1.1%, bacterial population= 1.1×10^5 colony forming units/g soil.

Soil moisture content was about 60% of water-holding capacity, temperature was about 25°C.

Findings similar to those of Baehr were documented by Preslo, *et al.*, [1987]. By using the unsaturated zone environmental fate model SESOIL, the authors predicted the removal pathways of 13 chemicals commonly found in petroleum contaminated soils. Volatilization was predicted to be the major removal pathway for: (n) hexane, (n) heptane, (n) pentane and 1-pentene. Adsorption was the major pathway in the removal of benzo(a)pyrene, phenanthrene and benz(a)anthracene. Phenol was the compound most likely to partition in water. As for benzene,

ethylbenzene, naphthalene, toluene and (o) xylene no particular migration pathway was found to be dominant.

Table 5.2
The composition and properties of gasoline constituents used in the modeling of contaminant in unsaturated soil by Baehr [1987].

Constituent	percent by weight	molecular weight	$H_k =$ $1/H_c^a$
Benzene (C6 aromatic)	4.4%	78	5.88
Toluene (C7 aromatic)	6.3%	92	3.85
C8 aromatics	9.3%	106	3.57
C9-C11 aromatics	17.3%	132	2.94
C5 alkenes	7.2%	70	0.12
C5-C6 alkanes	25.3%	83	0.03
C6 naphthenes	3.5%	84	0.1
C7-C11 alkanes	24.2%	113	0.008
C6-C11 alkenes	1.7%	103	0.23
C7-C11 naphthenes	0.8%	98	0.25

a: H_k is the water/air partition coefficient at 20°C. It is equal to the inverse of Henry's law constant.

EXPECTED EMISSIONS FROM BIOREMEDIATION

In this section, comparisons will be made between the different bioremediation processes in terms of the expected levels of air emissions, and the control measures that can be taken to minimize their impact on the atmosphere. Case studies will be cited (wherever possible), to give the reader an idea about the volume of gas volatilized.

In Situ

In this process soil disruption is minimal. No excavation of the contaminated soil is necessary and thus no emissions are expected from soil handling. However air sparging into the unsaturated zone can lead to volatilization and gas diffusion from the soil to the surface. Volatilization at the surface due to gas diffusion (through the unsaturated zone) of volatile organics escaping from polluted groundwater has been shown to occur [EPA, 1990]. However, "data have not been located that indicate the magnitude of emissions from *in-situ* remediation sites" [EPA, 1990].

Land Treatment

Volatilization and the emission of dust particles through erosion may both be significant pathways for the migration of organics to the atmosphere during application of the waste to the soil and during tilling. Spraying the waste onto the soil or spreading it on the surface are likely to maximize air emissions whereas subsurface injection would reduce emissions significantly. Emissions of VOCs will also increase with increasing frequency of aeration or soil tilling. Other factors that influence volatilization are atmospheric conditions (e.g. wind speed and temperature), waste properties and moisture content of the soil. Dust emissions are more likely to occur when the soil is dry (especially during tilling), yet, water evaporation from soils with a high moisture

content "has been shown to increase volatile organic emissions by transporting soluble compounds to the soil surface." [EPA, 1990]. Eklund, *et al.* [1991] studied air emissions from different Superfund remediation technologies. Their estimates for typical VOC emissions from landfarming sites are at 1,500 g/hr average over 24 hours, and 188 g/hr average over 20 days.

Control of VOCs emissions from land treatment facilities can be achieved by several means [Ehrenfeld and Ong, 1985]:

- i. Reducing the waste application rate. Operators at land treatment facilities generally tend to overload the soil for economic reasons. Exceeding the design capacity may impede microbial activity and the degradation rate thus causing the volatile organics to volatilize before having the chance to be degraded.
- ii. Using subsurface injection. This method is likely to reduce the emissions of highly volatile compounds by about 20 to 40 percent, and of less volatile compounds by about 95%.
- iii. Enclosure of the treatment area. Inflatable plastic domes, generally made out of plastic are sometimes used. The size can be as large as six acres. In this case the volatile gases are collected through conduits in the dome and are treated either biologically or with incineration or adsorption.

Composting

Emissions from composting systems are primarily dependent on the aeration method used (for example, forced aeration using perforated pipes versus mechanical mixing) and the temperature within the pile. Because better control is possible, the temperature in composting piles is generally higher than that in landfarming or *in situ* systems. At the same time, the heat generated by microbial activity is more confined. Volatilization rates in composting systems are expected to be higher than those in the previous two [EPA, 1990]. No data however, has been located that documents the magnitude of VOC emissions from this type of treatment. No material was found in the literature that describes control measures for reducing VOC emissions in open windrow systems.

Slurry-Phase Biotreatment

The mixing and agitation involved in the slurry-phase bioreactor treatment systems is likely to produce significant amounts of volatilization. However, because slurry-phase systems can be enclosed vapor phase control measures can be installed relatively easily. Off-gas treatment by biofiltration or GAC adsorption is possible in most cases. An alternative would be to use membrane aeration systems and eliminate the off-gas stream altogether [Muollo, *et al.*, 1992].

Soil Venting

As was mentioned before, soil venting is primarily a physical treatment process that relies largely on using vacuum to extract vapors from soil. Hinchee, *et al.* [1991] reported on the use of soil venting to volatilize and stimulate *in situ* biodegradation of JP-4 jet fuel from a spill at Hill Air Force Base in Utah. An estimated 27,000 gallons (100,000 liters) of fuel were released, contaminating approximately 20,000 cubic yards (15,000 m³) of unsaturated soil. The water table was about 600 ft (190 m) deep. Hydrocarbon concentrations in the soil were up to 15,000 mg/kg. Fifteen vent wells were drilled to a depth of about 50 ft (15 m). The soil was initially vented at a rate of 26 acfm (44 m³/h) and as the hydrocarbon concentration levels dropped, the venting rate was gradually increased to about 1,500 acfm (2,500 m³/h). Oxygen was the only stimulant for biodegradation, since no nutrients or moisture were added. The off-gas was treated by catalytic incineration. Initially, the off-gas had to be diluted in order to bring the hydrocarbon concentrations below explosive levels and within the incinerator's hydrocarbon operating limits. Based on the air volume introduced and the carbon dioxide produced, versus the oxygen

consumed, rough calculations were made to obtain the mass of JP-4 volatilized (11,300 kg) versus JP-4 degraded (2,100 to 2,200 kg). JP-4 converted to cells and JP-4 partially degraded to intermediate products were not accounted for. Soil venting was carried out for a period of about 6 months. The conclusion was that volatilization was the primary mechanism of removal accounting for about 75 to 85 percent of total removal.

Soil washing

Soil washing is physical remediation process that can be used in conjunction with, or prior to, bioremediation. The agitation, mixing and scrubbing involved in soil washing are expected to produce significant amounts of volatile compounds. So far there are no data on the magnitude of such emissions [EPA Available Models 1990].

EMISSIONS FROM SOIL HANDLING PROCESSES

At sites contaminated with VOCs, any treatment process that involves excavation or venting will be a significant source of air emissions [Fiorenza, *et al*, 1991]. Other soil handling practices such as dumping, grading, storage and transport, which are often part of bioremediation operations, can contribute largely to air emissions. Eklund, *et al*. [1990] used the transect technique to measure emissions caused by such practices. Two sites (identified as A and B) were considered. The primary contaminants in site A were xylenes and ethylbenzene whereas site B contained mainly oil-separator waste, diesel and aviation fuels, cleaning solvents and other fluids. Remedial activities at site A included mainly excavation and storage. Site B was not undergoing remediation at the time, so excavation, grading and storage were simulated for the purpose of measuring emissions. Sampling was done 80 ft and 30 ft downwind of the emissions source at sites A and B respectively. Measurements were taken over 3 transect runs at site A and 4 at site B. Air emissions from the storage piles were monitored using a flux chamber to measure the change in the rate of emissions over time. Wind speed and direction were monitored constantly. Measurements were taken when the 20-minute wind speed exceeded 4 mph. No sampling was done when the wind speed exceeded three times the mean speed. The results of the transect runs are summarized in Table 5.3. Total non-methane hydrocarbon (TNMHC) concentrations were found to be larger than the sum of emissions of individual compounds. This was explained by the presence of unidentified peaks representative of "relatively heavy volatile compounds (C₈ to C₁₂)."

Table 5.3
Summary of air emission measurements from soil handling practices [Eklund, *et al.*, 1990]

Measurement	Type of operation	Site A	Site B
Average TNMHC (ppb)	Baseline	0	0
	Excavation	500	500
	Grading	n/a	500
Estimated VOCs (ppb)	Baseline	5-50	0-2
	Excavation	5-50	1-10
	Grading	n/a	1-10
Starting TNMHC emission rate ($\mu\text{g}/\text{m}^2\cdot\text{min}$)	Storage	3500	920
TNMHC emission rate at 24 hrs ($\mu\text{g}/\text{m}^2\cdot\text{min}$)	Storage	370	120

CHAPTER 5 REFERENCES

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VI. MONITORING AND SAMPLING OF BIOREMEDIATION SITES

The objective of this chapter is to identify suitable methods of estimating VOC emissions from bioremediation sites. Sampling methodologies discussed in this chapter are standard vapor phase techniques and the focus is on the applicability of these techniques to monitoring emissions at bioremediation sites. Applicability of a given technique will be related to a number of factors, one of which is the type of bioremediation system used.

Sampling approaches, both direct and indirect, that could be used to obtain emission rates at hazardous waste sites are reported in the literature. A recent review has been completed by Shen et al., (1990) and much of the material presented below has been drawn from that article.

Table 6.1
VOC Sampling Methodologies' Applicability to Measuring Emissions From Bioremediation Sites

Sampling technique	Type of source	Limitations and comments
1. Surface isolation flux chamber	Active landfills	Limited to small cells with uniform composition.
	Inactive landfills	Can be used on surface and for vents at inactive landfills.
	Surface impoundments	Required to float equipment
	Land treatment	subject to treatment cycle variabilities
2. Head space samplers	Applications similar to the surface isolation flux chamber	Typical use is for concentration measurements, data used for relative comparison purposes.
3. Wind tunnels	Inactive controlled and uncontrolled landfills surface impoundments	Used to estimate emissions under simulated wind flow. Can be difficult to perform sampling because of air supply needs.
	Waste piles	Provides estimates of particulate matter emissions.
4. Subsurface direct emission measurement technologies	Inactive controlled and uncontrolled landfills	Used to measure soil concentration or emission rates at subsurface locations.
	subsurface contamination	Typically used to identify and map subsurface contaminants via soil gas concentration; can be used to estimate emissions from disturbed waste conditions.
5. Concentration profile technique	Surface impoundments, land treatment	Requires complex equipment; Meteorological conditions must meet criteria; not suited for small impoundments or land treatment plots.

Table 6.1 continued

VOC Sampling Methodologies Applicability to Measuring Emissions From Bioremediation Sites

Sampling technique	Type of source	Limitations and comments
6. Transect technique	Active landfills, surface impoundments, land treatment drum storage	Meteorological conditions must meet criteria; requires minimal interferences from other upwind sources.
7. Upwind/downwind technique	All TSDF facilities and uncontrolled waste sites	Emission estimate limited, technique typically used as survey technique in the development of a program to more accurately represent emissions.
8. Mass balance technique.	Most TSDF facilities	Must identify and be capable of measuring all streams.
9. Air monitoring/ modeling technologies	TSDF or hazardous waste site	Meteorological conditions terrain, and upwind interferences will affect utility; analytical sensitivity is usually a limiting factor.
10. Predictive modeling	Most TSDFs uncontrolled uncontrolled landfills/lagoons	Models require site-specific input data to be representative.

DIRECT EMISSION MEASUREMENT TECHNIQUES

Measurement of the gas concentration, flow rate and area of the emitting surface before the gases diffuse into atmosphere is termed direct emission measurement. Typically in direct emissions measurements, air is purged into an enclosed chamber to simulate wind conditions. Shen, Nelson and Schmidt [1990] summarized the following direct emission methods:

1. Surface emissions isolation flux chamber [Eklund *et al.*, 1985; Dupont, 1987; Schmidt and Balfour, 1983].
2. Head space samplers [Kapling *et al.*, 1986].
3. Wind tunnel [Astle *et al.*, 1982].

and for subsurface soil fluxes the direct emission measurement techniques suggested were,

4. Downhole isolation flux chamber [Schmidt and Balfour, 1983].
5. Soil probes [Kerfoot, 1987].
6. Vapor monitoring wells [Schmidt *et al.*, 1986].

Surface Isolation Flux Chamber (SIC)

The surface isolation flux chamber (SIC) method is an enclosure method that has been used to make direct emission measurements from surface impoundments, landfills and contaminated soils. A chamber is used to isolate a known surface area for emission measurement. Clean dry purge gas (gas that is organic compound free) is introduced into the chamber at a known controlled rate. Within the chamber the purge gas is mixed with emitted vapors and gases by the physical design of the purge gas inlet. The concentration of the exhaust gas is measured at the chamber outlet for specific pollutants by a real-time analyzer and/or is collected and stored as a sample for laboratory analysis.

Emission flux is given by

$$E_i = \frac{C_i Q}{A} \quad (6.1)$$

where E_i = emission rate of component i , $\mu\text{g}/\text{m}^2 \text{ sec}$.

C_i = concentration of component i in the exhaust gas, $\mu\text{g}/\text{m}^3$.

Q = purge gas flow rate into chamber, m^3/sec .

A = surface area enclosed by chamber, m^2 .

To determine the emission rate for a source of much greater area than that isolated by the flux chamber, a sufficient number of measurements must be taken at different locations to provide statistical confidence limits for the mean emission rate [Shen *et al.*, 1990; Balfour and Schmidt, 1984].

Surface Isolation Chamber Construction: A SIC consists of an isolation chamber, typically stainless-steel or acrylic, with an inlet for purge gas (pure nitrogen or pure sweep air, free of organics) and an outlet for exhaust gases. A pressure release valve is provided to avoid pressure build up inside the chamber and an impeller is installed to ensure complete mixing. A rotameter can be used to measure the flow into the chamber. The SIC equipment also includes a sampling manifold for monitoring and/or collecting the species of interest. Samples are collected for subsequent analysis after steady-state emission rate is approached. Concentration of total hydrocarbons can be monitored continuously using flame ionization detector (FID) and/or photoionization detector (PID) based analyzers. Samples can be collected for detailed gas chromatographic analysis using gas tight syringes (on site analysis), evacuated canisters or sorbent tubes (off-site analysis).

Potential SIC Operational Problems: Operation of a surface isolation flux chamber depends on the environmental and site conditions. The influence of wind speed, temperature, atmospheric pressure and relative humidity on emission rates are not well defined. Because of the isolation of the emitting surface, the SIC technique measures emission rates under a virtually no wind speed condition [Balfour and Schmidt, 1984]. The extent to which the emission rate measured with a SIC is biased due to isolation from environmental factors is not known, although some field experiments have been performed to determine the variation of emission rates with environmental factors [Balfour *et al.*, 1983]. SICs are most useful for homogeneous area sources where the emission rate is independent of the gas phase pollutant concentration. But for some area sources an increased gas phase pollutant concentration may reduce the pollutant emission rate from the isolated portion. High winds, large and heterogeneous landfills and highly agitated/dynamic surfaces may result in highly variable and inaccurate flux measurements. To mitigate the problem of high winds, SICs can be improvised so that the wind speed can be simulated by adjusting the flow of purge gas into the chamber or alternate methods such as concentration profile technique or wind tunnel method can be used. For heterogeneous area sources, a boundary layer technique or transect technique can be used.

SIC Impact on Emissions: Flow regime within the SIC is of critical importance as component emission rate calculations are based on the assumption that emission measurements from the chamber effluent are representative of a completely-mixed chamber volume [Balfour *et al.*, 1983; Dupont, 1987]. The surface isolation flux chamber must be operated at low purge flow rates or a purge pump should be used to limit excessive pressure build-up and potential emission suppression during sampling. But if the purge flow is too low, the emission rate measured is also significantly reduced as there could be component accumulation within the chamber affecting the

component's flux into the lower atmosphere [Hwang, 1985]. Pressure effects are particularly important when there is no forced ventilation from the source, e.g. measurement of soil emissions.

Previous studies [Gholson 1989, 1991] indicate that there could be significant differences in the measured emission rates when the incoming sunlight was shielded from the chamber. Internal air temperature could lower; however change in air temperature alone should not affect the emission rates. The soil temperatures affect the emissions. Therefore soil temperature is one of the important factors to be considered.

The relative humidity of the air inside the SIC will vary depending upon soil conditions. Condensation can form in the chamber at high relative humidities (70 - 100%). The relative humidity is an other important factor to be monitored because the sorbed VOCs can be liberated (desorbed) by water vapor competing for sites.

Surface isolation flux chambers are relatively easy to handle and do not require a highly qualified operator. Emission rates can be measured in the field without modeling, and the field personnel can control the testing conditions. This technology can be used for volatile materials, such as vapors and gases, and is generally independent of the sampling medium used for sample collection [Shen *et al.*, 1990].

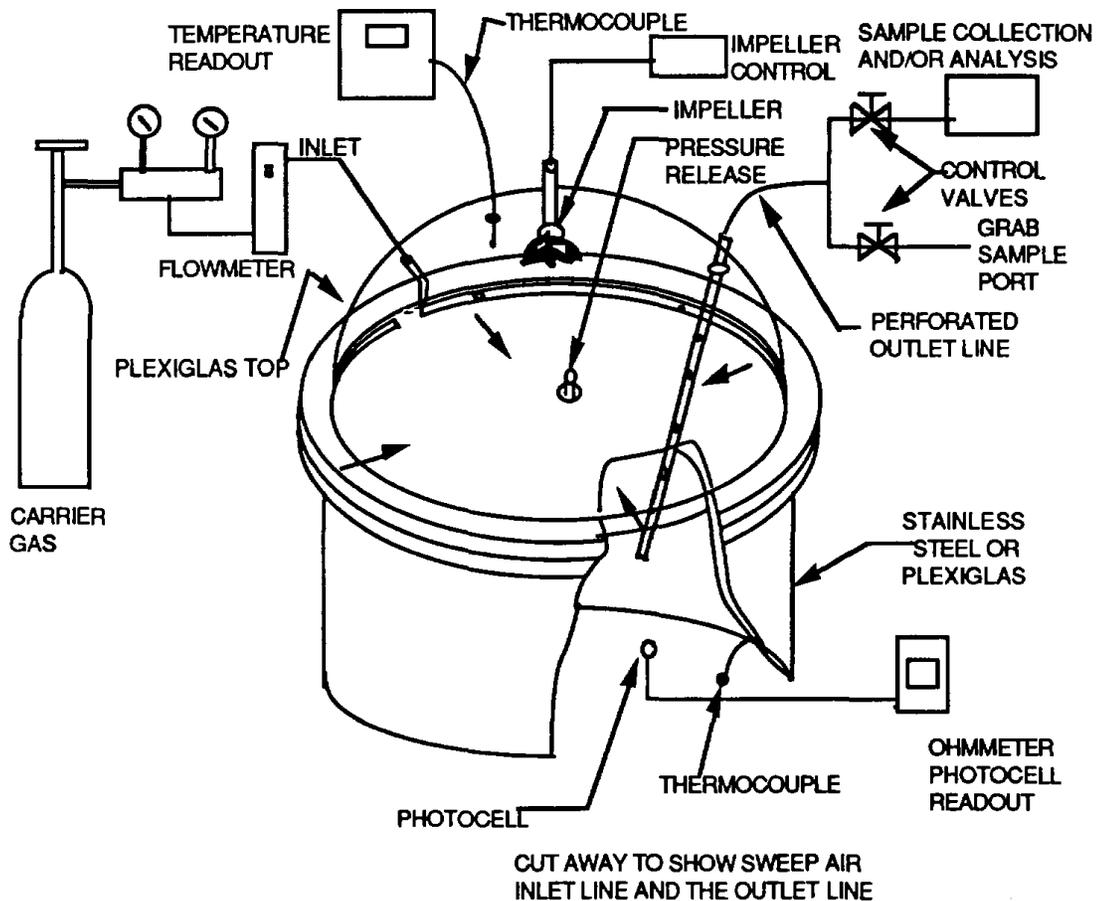


Figure 6.1
Definition sketch of typical surface isolation flux chamber (adapted from Shen *et al.*, 1990)

Review of Applications Balfour *et al.*, [1983] performed direct emission measurement using the SIC technique at a Marine Corps helicopter facility in Tustin, California. A statistical analysis of the data was performed to investigate the effect of the variables (chamber geometry, impeller rate, chamber opacity, relative humidity, sweep air flow rate and temperature) on the VOC emission rates measured in the field. The field tests were performed using two different geometries of the SIC, flat and dome shaped acrylic tops. Balfour *et al.* [1983] found that the variations in chamber geometry and relative humidity did not affect the measured emission rates. The measured emission rates decreased and internal air temperatures were lowered when sunlight was shielded from the chamber. Measured emission rates decreased when the sweep air flow was decreased. They suggested the possibility of adjusting the emission rates based on an average temperature to lower the variability associated with measurements. The sampling and analytical variability associated with the SIC measurements were estimated to be at 33 percent.

Balfour and Schmidt [1984], sampled active and inactive landfills, land treatment facilities, surface impoundments, drum storage tanks and solvent recovery systems using a SIC. Balfour and Schmidt [1984] found that the statistical approach (gridding) was suitable for sampling surface impoundments, land treatment plots and landfill cells with homogeneous waste. However, for landfills with large cells and heterogeneous wastes, sampling resulted in highly variable data. Based on experience and information gained, Balfour and Schmidt [1984] concluded that whenever possible, the SIC should be used to measure the emission rates from sites which have homogeneous composition due to their inherently greater sensitivity and lower variability. They also concluded that the isolation flux chamber is not suitable to sample extremely large waste bodies having large spatial variability or highly agitated liquid surfaces.

Balfour, Whetherold and Lewis [1984], used a SIC to sample large landfarm, landfill solids from the manufacturing processes of acrylonitrile, acetone cyanohydrin, lactic acid, tertiary butylamine, iminodiacetic acid and a commercial hazardous waste management facility which consisted of a wastewater facility, drum transfer and processing operations, active and inactive chemical landfills, a sludge disposal facility, and also a landfill with heavy metals, flammable solids, general organics and PCBs/pesticides. Balfour *et al.* [1984], used two types of sampling/analytical techniques. One technique consisted of collecting samples in evacuated stainless steel canisters for a GC analysis in a lab and the other technique involved collecting samples in a gas syringe for an on-site GC-FID analysis. Balfour *et al.* [1984] found the effect of the SIC upon sample integrity to be minimal. For active landfills the precision of SIC measurements was found to be considerably better than that associated with transect technique.

Hwang [1985], used the concentration profile (C-P), transect, and SIC techniques to measure emission rates and compare them with estimated rates obtained by theoretical predictions. The measurements using a SIC were performed on a reduced lagoon (waste water treatment influent), active landfill (drums and bulk materials) and a land treatment facility (oily refinery sludge). Hwang [1985], found that the theoretically predicted results were mostly within the confidence intervals of the measured results, given the wide variations of experimental conditions.

Eklund, Balfour and Schmidt [1985], presented procedures for the use of an emission isolation flux chamber and the results of volatile species rate measurements at two spill sites, three landfills, several surface impoundments, a landfarm operation and a remedial action site. They concluded that the SIC method was suitable for determining VOC emission rates from a variety of sources. They reported the theoretical range of hydrocarbon emissions that can be measured to be 5.4 to 5.4×10^5 $\mu\text{g-C/m}^2\text{-sec}$ with the analytical methods available at that time. The SIC method was found to be more sensitive and less affected by environmental factors as compared to the indirect techniques. They also concluded that the SIC method may alter the environment at the sampling location and as such may have an effect on the true emission rate.

Dupont and Reineman [1986], performed laboratory and field experiments to determine the volatilization of hazardous organics. Field experiments were conducted at an active petroleum refinery hazardous land treatment site using SICs and a split Tenax sorbent tube concentration system for sampling. The compounds of interest were benzene, toluene, ethylbenzene, p-, m-, o-xylene, and naphthalene. Six SICs were used to perform the field sampling. Mean recoveries from chamber/Tenax™ sorbent collection system for the seven compounds of interest ranged from 61 percent to 94 percent. Dupont and Reineman [1986], concluded that the sampling systems must be operated at purge flow rates less than 1 L/min or in conjunction with a down stream purge pump to minimize chamber internal pressures and potential soil emission suppression.

Dupont [1987], presented a laboratory evaluation of a sampling system for quantification of specific volatile compounds from land treatment facilities. The system consisted of a SIC and Tenax tube. The compounds of interest in the study were benzene, toluene, p-, m-, o-xylene and naphthalene. Dupont [1987] recommended the Tenax™ solid sorbent material for volatile contaminant collection and concentration due to its effectiveness for the compounds of interest in the study and its performance within the SIC. Compound recovery data obtained using the chamber/Tenax sampling system indicated that the recovery efficiency was independent of mass level over a range of injected masses from 0.09 to 250 µg/tube. Dupont [1987] recommended the quantification of recovery efficiency for systems as applied in field use to account for system losses occurring during sampling. It was also recommended that the breakthrough volumes be critically evaluated for the mass loading and operating conditions expected in laboratory and field emission estimations while using Tenax. At purge flow rates of ≤ 1 L/min into the SIC when no impeller was used, complete mixing was ensured within the chamber, allowing for representative grab sampling of a uniform air space under the chamber. To provide optimal collection/concentration efficiency, air phase mixing, and minimal disturbance to soil surface flux activity, Dupont [1987] recommended the use of a constant flow purge pump down stream of the SIC, along a constant volume split stream Tenax sampling manifold.

Gholson, Albritton and Jayanty [1989], performed field experiments on two hazardous waste treatment, storage and disposal facilities. One was a wastewater treatment facility at a chemical plant and the other was a waste stabilization facility. The results obtained by Gholson *et al.*, [1989] in their laboratory and field experiments indicated that the liquid surface emission measurements can be made with very good precision. They also found that operational and environmental parameters have only a minor effect on the precision and accuracy. During the laboratory studies a compound dependent negative bias ranging from 40 to 80 percent was observed. The negative bias during the laboratory studies was thought to be caused by changes in the liquid turbulence caused by the SIC. Little change in the bias was detected over the range of wind velocities and solar intensities in these studies. Precision estimated for the field evaluations were higher than those for the laboratory study. Gholson *et al.*, [1989] suggested quantitative studies to compare the effects of the SIC on surface turbulence in the field to those in the simulated surface impoundment to determine the existence of negative bias in the field as found in the laboratory. They also emphasized the need to improve the measurement method so that the emission rates of reactive VOCs such as nitrobenzene and aniline can be measured.

Gholson *et al.*, [1991] performed laboratory and field experiments to determine the precision and accuracy of an enclosure method and integrated canister sampling on surface impoundments (quiescent liquid surfaces). They found that the SIC method of measuring the emission rate enables the measurements to be made with good precision and also that the environmental parameters have only a minor effect on the precision and accuracy of the method. In the laboratory studies, consistent compound dependent negative biases ranging from 40 to 80% were found. Gholson *et al.*, [1991] concluded that this negative bias was a worst case and that the real measurements would be closer to the true values of emission rates. They also concluded that the

negative bias in the measurements was due to the chamber's influence on the surface turbulence in the surface impoundment simulator and therefore may be less significant on a larger open surface. They recommended sweep flow rates above 2 L/min to prevent concentration buildup in the chamber. Gholson *et al.*, [1991] found a precision of the 3% relative standard deviation attained by the chamber method under ideal conditions of a single compound, steady solar conditions, and emission rates above 0.5 mg/m(2)-min.

Wind Tunnels

Shen *et al.*, [1990] suggested the applicability of wind tunnels to VOC emission measurement, based on development of portable wind tunnel by Astle *et al.*, [1982] for odor source strength measurement. The wind tunnel method is valid for estimating volatile emissions when the mass transfer coefficient of air is greater than the mass transfer coefficients of soil and waste [Murphy, 1982].

Emission flux is given by:

$$E_i = \frac{C_i Q}{A} \quad (6.2)$$

where E_i = emission rate of component i, $\mu\text{g}/\text{m}^2\text{-sec}$.

C_i = concentration of component i in the exhaust gas, $\mu\text{g}/\text{m}^3$.

Q = purge gas flow rate through the tunnel, m^3/sec .

A = surface area enclosed by chamber, m^2 .

Wind Tunnel Sampler Construction: Wind tunnel samplers are open-bottomed enclosures that isolate the area being measured from emissions from the other areas. They provide a constant flow of air at typical wind speeds (1 to 15 mph). This air, along with the emitted VOCs, is collected at the outlet by adsorption onto Tenax, other adsorbents, canisters or Tedlar™ bags for subsequent analysis. The samples collected are analyzed using a GC/FID system or GC/MS or another suitable method of analysis. The wind tunnel developed by Astle *et al.*, [1982] made use of a blower to deliver the desired tunnel velocity and the samples were drawn from the tunnel at various distances downwind, using a rigid container/flexible bag technique.

Potential Operational Problems of Wind Tunnels: The principal problem in operating the wind tunnel is maintenance of a constant flow of clean air into the chamber at typical wind speeds.

Review of Applications:

Astle, Duffee and Stankunas [1982], developed a methodology which included a wind tunnel technique for sampling to estimate vapor and odor emission sampling. Peterson and Steinberg [1990] applied wind tunnel modeling to evaluate the accidental spills of toxic chemicals. McFarland, Wong, Anand, and Ortiz [1991] used a wind tunnel to obtain comparable data for numerical predictions of aerosol penetration through a model transport system.

Head Space Samplers

Head Space Samplers (HSS) are similar to surface isolation chambers except the exposure time component is used to estimate rate instead of flow rate measurement. The quantity or concentration of emitted vapors and gases which builds up in the chamber over a period of time are measured in these units.

There are two modes of operation in head space sampling: (1) static and (2) dynamic. In static mode, a sampling enclosure is placed over the emitting surface for a given period of time. Therefore it is useful for relative evaluation purposes. The enclosure may be purged initially with clean air or nitrogen. Emissions are then allowed to concentrate in the chamber for later withdrawal to sampling media such as a sorbent tube, gas tight syringe or evacuated canister.

The main disadvantage with static mode operation is that the emission flux may decrease as the concentration within the enclosure increases because the concentration gradient from the soil gas to the air interface is reduced.

Emission flux is given by,

$$E_i = \frac{C_i V_e}{tA} \quad (6.3)$$

where E_i = emission rate of component i, $\mu\text{g}/\text{m}^2$.

C_i = concentration of component i, $\mu\text{g}/\text{m}^3$.

V_e = volume of the enclosure, m^3 .

t = length of time enclosure is in place, sec.

A = surface area enclosed by chamber, m^2 .

In dynamic mode operation, the sampling enclosure is placed over the emitting surface, and the sample is continuously withdrawn from the enclosure. The emitted species is concentrated on sampling media to increase the ability of the analytical method to detect air contaminants or may be operated continuously and monitored as is done for SIC sampling. The disadvantage in dynamic mode operation is that as the atmosphere within the enclosure is withdrawn, the emission rate value may be affected by the addition of bulk flow of the soil gas into the chamber or air entrainment occurring within the enclosure because of leakage at the enclosure's bottom edge or by sweeping through the soil at the enclosure's bottom edge.

Emission flux for dynamic mode operation is given by:

$$E_i = \frac{C_i V_s}{At} \quad (6.4)$$

Where E_i = emission rate of component i, $\mu\text{g}/\text{m}^2\text{-sec}$.

V_s = total volume of sample withdrawn, m^3 .

t = length of sampling interval, sec.

A = surface area enclosed by chamber, m^2 .

Potential Operational Problems: There is a possibility of concentration gradients building up during the measurement using HSS. Therefore the gases inside the chamber should be well-mixed. In small chambers, this mixing is usually accomplished by diffusion. For large chambers a small fan within the chamber may be required to avoid concentration build-up [Rolston, 1986]. Another important factor to be considered is the possibility of underestimation of

the gas flux due to increase in concentration with time. A technique for correcting the flux due to the concentration build-up that involved sampling at one depth within the soil has been proposed by Rolston *et al.*, [1978]. Hutchinson and Mosier [1981] developed a correction method that involved sampling the concentration within the chamber at three times separated by equal time intervals. Errors in emission estimation could result if the chamber materials adsorb the any of the VOCs. This problem could be avoided using materials which do not adsorb VOCs for chamber body under given environmental conditions. However, at very low concentrations (ppbv levels), complete avoidance of adsorption is difficult.

The impacts on emissions by a headspace sampler are more or less similar to those by a surface isolation flux chamber. One main factor is the change in the soil environment. The headspace sampler could decrease the evaporation on the soil surface it isolates. Also the temperature within the chamber could change causing change in pressure and remedial activity in case of a waste treatment source.

Headspace sampling is simple to understand and perform. Similar to SIC sampling, emission rates can be measured in the field without modeling, and the field personnel can control the testing conditions. Also highly trained personnel are not required to do headspace sampling.

SUBSURFACE DIRECT EMISSION MEASUREMENT TECHNOLOGIES

Subsurface measurement technique involves measuring emission rate or gas concentration at some depth below the land surface by placing an enclosed chamber within the soil or on an exposed surface at depth. Some of the methods are:

- down hole isolation flux chamber.
- soil probes.
- vapor monitoring wells.

All three methods are operated using sweep air as in the surface isolation flux chamber. They can provide a direct measurement of a subsurface soil's emission rate potential. Another way is to sample without sweep air, like HSS samplers, to measure the soil's pore gas concentration.

The main advantage in subsurface emission measurement is that the emission concentration within soil pores is higher than in the atmosphere above the site. Therefore these technologies can provide lower detection limits than the other technologies [Shen *et al.*, 1990]. The soil pore space concentration data can be used as an input to the predictive modeling.

Downhole Isolation Flux Chambers

A diagram of a downhole isolation flux chamber is shown in Figure 6.2. The downhole isolation flux chamber consists of a chamber fabricated from plexiglas pipe. A plexiglas flat is cemented on the tube top. The chamber output manifold consists of a stainless steel Swage bulkhead fitting and Teflon tubing leading to the instrument manifold. The input and output lines are constructed in such a way that it is possible to make flux measurements below land surface. The exposed chamber is placed on the soil/waste surface. Clean sweep air is introduced near the bottom of the chamber, close to the core hole surface. Schmidt *et al.*, [1982] used sweep flow rates ranging from 1.5 to 12 L/min in their field sampling using a downhole flux chamber. The top of the chamber is weighted to reduce raising and lowering difficulties in the sample source. The chamber is supported by a cable as shown in the schematic.

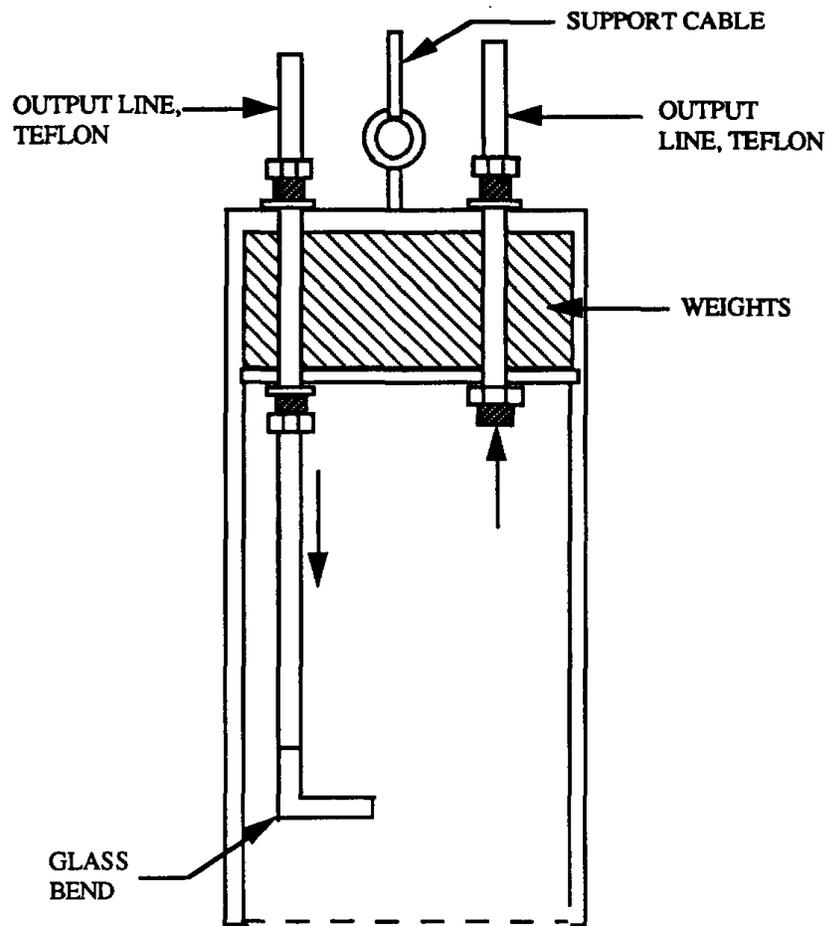


Figure 6.2
Definition sketch of down hole flux sampler (adapted from Shen et al., 1990).

Soil Probe Samplers

Soil probes are used to measure subsurface emissions at shallow depths [Schmidt *et al.*, 1982]. Ground probes are fabricated Teflon-coated galvanized steel pipe. Iron drive heads with support cables to enable probe installation. The probes are fit with drive heads, capped and driven into the soil/waste manually. A Teflon input line is used to introduce sweep air close to the exposed surface. Sweep air flow can be controlled with the help of a regulator and can be monitored using a rotameter. The output line consists of a long Teflon tube connecting the probe and the output manifold.

INDIRECT EMISSION MEASUREMENT

The indirect emission measurement techniques consist of measuring the atmospheric concentration of the emitted species and then determining the emission rate by modeling. For these techniques, the emission source is considered to be a point source. An overall emission rate for a given area source is produced. The indirect technologies require meteorological monitoring to properly align the sampling systems and to reduce data following sample analysis.

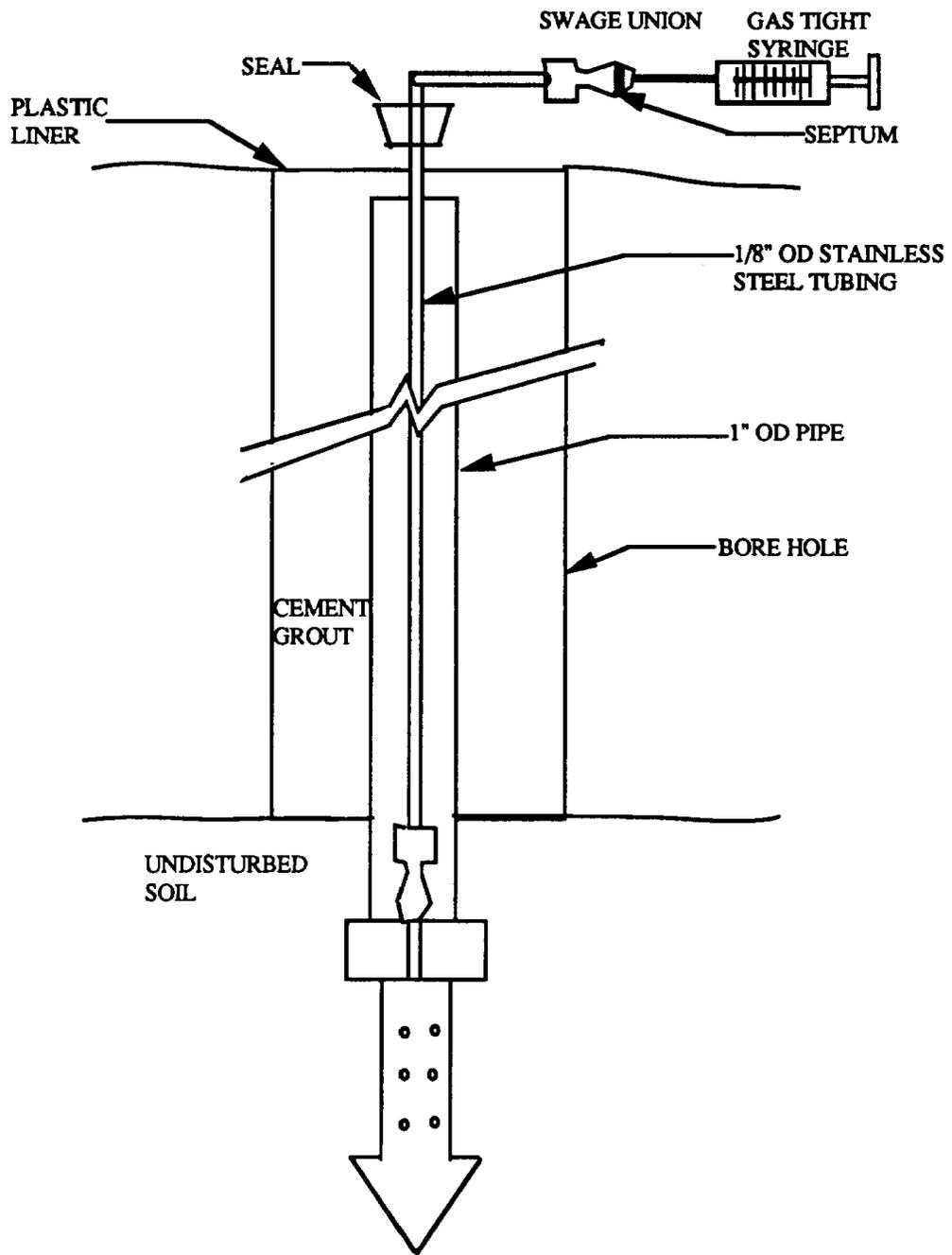


Figure 6.3
 Definition sketch of soil probe sampler (adapted from Shen et al., 1990).

The main disadvantage with indirect emission measurements are their dependence upon meteorological conditions. Changes in the meteorological conditions will significantly affect the ability to collect useful data. Also these technologies may not be applicable at some sites where the source area is excessively large or where the upwind concentrations of the contaminants of interest are high. Some of the indirect emission measurements summarized by Shen *et al.*, [1990] are as follows:

1. Concentration profile technique (C-P technique) [Thibodeaux, *et al.*, 1982].
2. Transect technique [Kapling *et al.*, 1986; Farmer *et al.*, 1980].
3. Boundary-layer emission monitoring [Epslin, 1988].
4. Upwind/Downwind technique.
5. Cross-wind sampling.
6. Mass balance

CONCENTRATION-PROFILE

The concentration-profile (C-P) method was developed by L.J. Thibodeaux and co-workers at the University of Arkansas. It builds upon earlier studies of moisture and pesticide volatilization from soil and liquid surfaces. Use of the C-P technique requires the measurement of the emitted species concentration profile at logarithmically spaced heights at a point above the emission source. The method is based on measurements of wind velocity, volatile species concentration and temperature profiles in the boundary layer above the waste body. An explicit dependence upon the molecular diffusivity of water vapor and the VOC of interest arises from boundary layer analogies for momentum and mass transfer and an expression for water vapor flux above a crop surface used by Thibodeaux *et al.* These measurements are used to estimate vertical flux of the volatile species as:

$$E_i = \left(\frac{D_i}{D_{H_2O}} \right)^{2/3} \frac{S_v S_i k^2}{\Phi_m^2 S_c} \quad (6.5)$$

Where E_i = emission flux rate of organic species, i g/cm²-sec.

D_i = molecular diffusivity of organic species, i in air, cm²/sec.

D_{H_2O} = molecular diffusivity of water vapor in air, cm²/sec.

k = Von Karman's constant.

S_v = logarithmic slope of the air velocity profile, cm/sec.

S_i = logarithmic slope of the air concentration-profile for organic species, i , g/cm³.

Φ_m = Businger wind shear parameter.

S_c = turbulent Schmidt number for air and water vapor.

n = exponent for diffusivity ratio taken to be 2/3.

$1/(\Phi_m S_c)$ = atmospheric stability correction factor expressed as a function of Richardson number. The stability correction factor corrects the estimated emission rate for water vapor to measured values under various atmospheric stabilities. This correction factor is valid only under specific meteorological conditions.

Concentration Profile Methodology

The C-P method sampling equipment typically would consist of a 4-m mast with a wind direction indicator, wind speed sensors, temperature sensors and air collection probes at six logarithmically spaced heights above the area source. Also a continuous real-time data collection system and thermocouples for measuring temperature. During sample collection, wind speed, air temperature and relative humidity are measured.

Potential Operational Problems: The C-P technique depends upon accurately measuring the velocity and concentration profile immediately above the surface. For a heterogeneous area source, the C-P technique is not suitable as it yields the flux at a point. The C-P technique is not applicable during periods of low wind speeds (less than 5mph) or very high wind speeds (greater than 20mph) [Balfour and Schmidt, 1984]. This technique will be affected by natural atmospheric fluctuations in wind speed, wind direction and atmospheric stability. When components are present in low concentrations there may also be a difficulty in obtaining accurate logarithmic concentration profiles.

Impacts on Emissions: The C-P method does not have a significant impact on the rate of emissions from a source. This is a significant advantage over most direct emission measurement techniques which may alter the emissions locally. Skilled operators are required to sample using concentration profile technique. More personnel are required to apply the method as compared to a surface isolation flux chamber [Balfour and Schmidt, 1984].

Adaptability: The C-P technique can be used only on sites with extensive aerial emissions because of its dependence on fully developed turbulent velocity and concentration boundary layers. Also, the species being emitted must be detectable with sufficient precision that the concentration profile can be determined.

Review of Applications: Balfour and Schmidt [1984], applied the C-P method to surface impoundments and a land treatment facility. Balfour and Schmidt [1984] found that the C-P technique provided valid data for some compounds, but not for others when compared to the volatile components in the waste at both surface impoundment and land treatment plots. There was a difficulty in obtaining valid logarithmic concentration profiles due to low concentrations of components and associated variability at such low detection levels for some compounds. The variability associated with the C-P technique was found to be less than with the transect technique. Balfour and Schmidt [1984] suggested use of the C-P technique rather than the transect technique for waste bodies where the SIC technique is not suitable. However the C-P or transect technique should be selected as a mode of sampling based on the type of site, environmental factors and other relevant factors.

Balfour, Wetherold and Lewis [1984], applied the C-P technique to a land treatment facility and also a surface impoundment. In comparison of measured emissions rates with predicted emission rates, the predicted emission rates compared favorably with the measured emission rates for specific compounds. But for some compound classes, predicted emission rates were much greater than the measured rates. Balfour *et al.*, [1984], reasoned that the possible contributing factor to the higher rates measured by the concentration profile method was the tilling of the land treatment site. In general both for land treatment facility and surface impoundments the emission rates estimated using the C-P technique were lower than those measured with the SIC. Both the individual and overall variability of the measured emission rates were greater for C-P technique when compared to the chamber technique.

Thibodeaux [1982], used the C-P technique to assess air emissions from two surface impoundments of a hazardous waste disposal facility.

Hwang [1985], presented a comparison between measured and estimated rates. The sampling techniques used were the C-P, transect and SIC techniques. The C-P technique was applied on a land treatment facility with oily refinery sludge as waste. The conclusions were that the predicted results were mostly within the confidence intervals of the measured results and agreed reasonably well given the wide variations of experimental conditions as mentioned earlier in the review of the SIC method.

Thibodeaux *et al.*, [1984], used the C-P method to determine the volatile chemical emission rates from wastewater-treatment facilities for the pulp and paper industry. The flux rates of methanol, acetone and total hydrocarbon were measured during field tests with the C-P technique. Acetaldehyde was detected in very low concentrations.

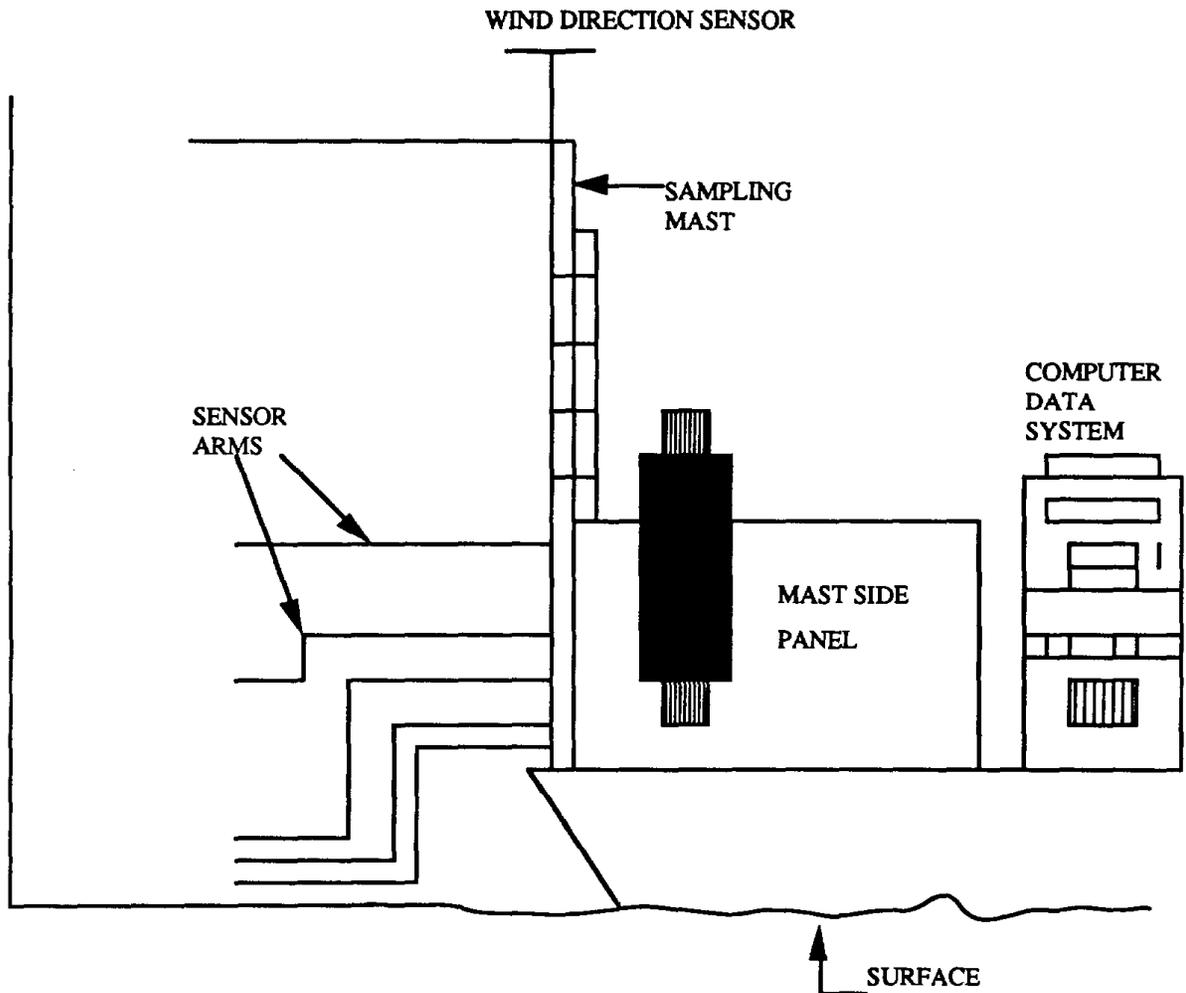


FIGURE 4
Mast sample collection system for C-P sampling (adapted from Shen *et al.*, 1990).

TRANSECT TECHNIQUE

The Transect technique is used to measure emission rates of fugitive particulate and gaseous emissions from area and line sources [Shen *et al.*, 1990]. This method can be applied to landfills, surface impoundments and waste handling operations. The transect technique is used to measure the concentration of VOCs at a number of locations perpendicular to the plume center line. Horizontal and vertical arrays of samplers are used to measure concentrations of volatile species within the effective cross-section of the fugitive emission plume [Balfour and Schmidt, 1984].

The emission rate can be estimated as follows [Balfour and Schmidt, 1984]:

$$E_i = \frac{u}{A_s} \int_{A_p} C_i(h,w) dh dw \quad (6.6)$$

Where E_i = emission rate of component i , $\mu\text{g}/\text{m}^3\text{-sec}$.

u = wind speed, m/sec .

C_i = concentration of component i at point (h, w) for upwind background, $\mu\text{g}/\text{m}^3$.

h = vertical distance co-ordinate, m .

w = horizontal distance co-ordinate, m .

A_s = surface area of emitting source, m^2 .

A_p = effective cross-sectional area of plume, m^2 .

Description: The sampling equipment typically consists of a central mast having three equally spaced air sampling probes in the vertical direction, a wind direction sensor, wind speed and temperature sensors at the top of the central mast. The central mast is located along the expected plume centerline. Two additional shorter masts with single air sampling probes are placed with equal spacing to either side of the central mast. One sampler is used to collect air samples at an upwind location. The associated masts are spaced in a manner that the spacing selected covers the expected horizontal plume cross-section. The samples can be collected in evacuated canisters. The meteorological observations and/or profiling are obtained by real-time analyzers. Meteorological parameters are also monitored prior to sampling in order to determine if acceptable sampling conditions exist.

The advantage of a transect technique as compared to the C-P technique is that the transect technique is less susceptible to changing meteorological conditions and is easier to implement. When direct numerical integration across the plume is carried out, errors can result from a lack of sufficient information on vertical dispersion. In principle the transect method can be used in conjunction with a dispersion model to estimate total emissions from a source, allowing the dispersion model to estimate the vertical dispersion. A method for rationally inverting downwind concentration measurements to predict emission source strength has recently been described by Lehning *et al.*, [1993].

Potential Operational Problems The transect method depends upon the wind blowing towards the sampling system. Therefore under unfavorable meteorological conditions the method may not work [Esplin, 1988]. Like the C-P technique this method is not applicable during periods of low wind speeds (less than 5 mph) or very high wind speeds (greater than 20 mph) [Balfour and Schmidt, 1984]. The transect technique also experiences difficulty because it may not be able

to detect low concentration components, however, it is less sensitive than the C-P to problems of precision. The location of the samplers could greatly affect accuracy.

The problems associated with the cross-wind sampling method are entrainment of road dust and vehicle emissions which are not related to the fugitive source.

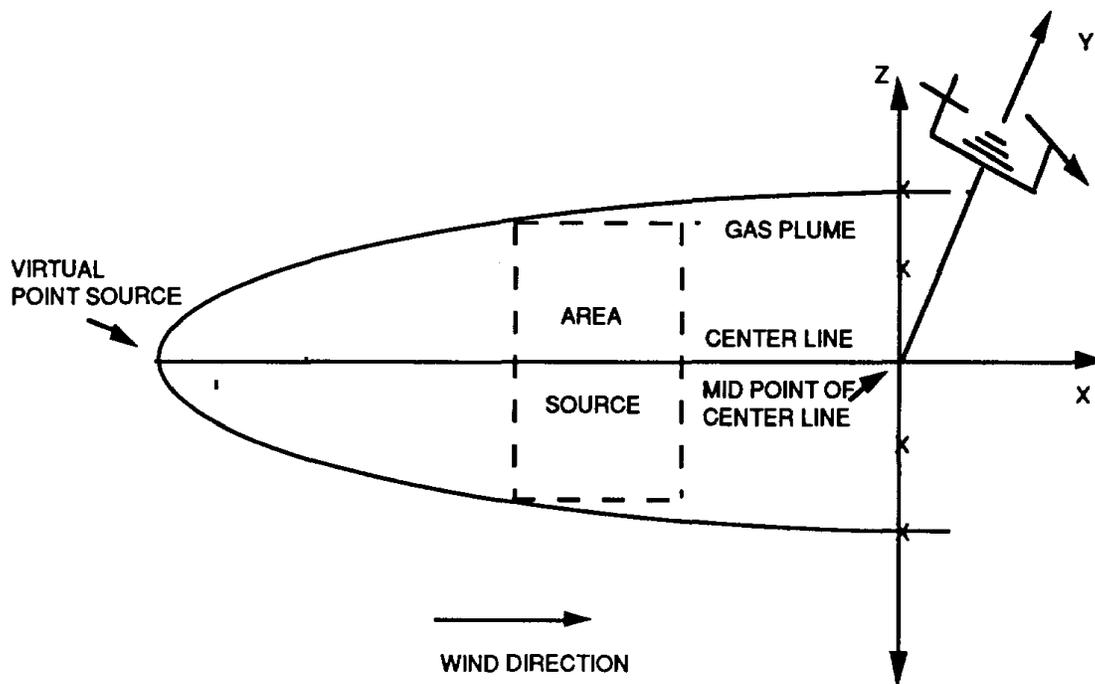


Figure 6.4
Definition sketch of transect technique.

Complexity and Adaptability of Transect Technique: The transect technique requires a skilled operator to sample the chemical species from the source site. As with the case of the flux-profile method, an on-site meteorological survey needs to be undertaken in advance to know where to place the samplers and samples cannot be drawn until the expected wind direction materializes.

The transect technique is not suitable under unfavorable meteorological conditions. Also it is not possible to account for the vertical dispersion of the emitted species without application of a dispersion model. There are two techniques that are modifications of the transect technique, the boundary layer emission monitoring and the crosswind sampling methods. Epslin [1988] proposed a boundary layer monitoring technique for determining the atmospheric emission rate of pollutants from large heterogeneous area sources, such as hazardous waste sites. The boundary layer technique is like the transect technique, but instead of sampling and analyzing continuously, a tethered balloon is used to collect samples continuously at three or more different elevations while traversing the boundary layer of the plume. Plume air is drawn down Teflon sampling lines and pumped through Nafion dryers to large Teflon bags. After the plume traverse has been completed, the samples are then transported to an analyzer where the pollutant concentration in each bag is

determined. The advantage of using tethered balloons is that the vertical concentration profile can be measured more accurately and direct numerical integration across the plume can be carried out. Cross-wind sampling is an indirect emission measurement technique [Shen *et al.*, 1990]. Integrated air samples are taken with the help of a mobile sampling station traversing the plume in the cross wind direction [Wisner and Davis, 1989]. The emission rate from the fugitive source is estimated using a simple Gaussian plume model based on the meteorological conditions and the type of site. The advantage of using this method is that fewer sampling stations are required to characterize a fugitive source as compared to other indirect techniques. This method is reported to be insensitive to complex source configurations, changes in the wind direction and the horizontal dispersion rate. Nevertheless, from a fundamental perspective, if a Gaussian model is used to estimate emission, an assumption must typically be made regarding stationarity of the atmospheric conditions and location of emission points for heterogeneous sources. More typically, the assumption is made that the sources are homogeneously distributed.

Review of Applications: Balfour and Schmidt [1984], applied the transect technique to active landfills and surface impoundments. They found the transect technique to be the only appropriate method of sampling during placement of waste at an active landfill. Also they found that the concentrations of some components approximated a normal distribution across the sampling array, allowing the plume area to be estimated and concentration flux to be calculated. Transect measurements at active landfill and surface impoundments resulted in highly variable component concentrations across the sampling array. Balfour and Schmidt [1984] found that for all applications of the transect technique, low component concentrations, upwind backgrounds and variability in the plume location/concentrations contributed to the difficulty in obtaining a valid plume definition.

Eklund, Ranun and Orr [1990], used the transect technique to sample two sites which had soil or waste containing measurable amounts of volatile organic compounds together with ongoing site cleanup activities. Measurements were made during excavation periods and grading periods. Measurements were also made for small scale storage piles constructed at each site. Total emissions at each twenty minute period was determined using a dispersion model technique applied to the array of ambient air concentration data.

Balfour, Wetherold and Lewis [1984], used the transect technique to sample an active landfill, chemical landfill, and drum storage and handling. They used two methods to estimate the emission rates. One method was direct integration of the concentration over the entire cross-section of the plume. Another method involved use of a dispersion model to estimate the emission rates. Emission rates calculated by using the dispersion model were found to be consistently higher than the first method. However the authors could not conclude which of the two methods provided the most accurate estimate. The transect technique was found to be very sensitive to ambient weather conditions and localized physical parameters. For the active landfill the transect data obtained were widely scattered. The concentration profiles were very irregular, and normal curves could not be easily fitted to these data.

Hwang [1985], in a comparison of measured emission and predicted emission rates from a variety of sources, used a transect technique to estimate emission rates from an evaporation pond (solvent wastewater) and an active landfill (oily refinery sludge). His findings were that the scatter of data in constructing the plumes for the transect method resulted in large confidence intervals. The predicted results were found to be within the confidence intervals of the measured results as mentioned earlier (see reviews of SIC method).

UPWIND/DOWNWIND TECHNIQUE

Measuring the VOCs at single upwind and downwind locations is termed as the upwind/downwind technology [Hwang, 1985]. In this method there are a limited number of

sampling points and there is no specific sampling model applied. This results in a higher degree of uncertainty as compared to C-P and transect techniques. The advantages of using the upwind/downwind technique are that it is simpler to implement and that data may be acquired more rapidly and at lower cost compared to many other techniques. The greatest disadvantage associated with this technique is the uncertainty of emission rates due to limited sampling points. An air dispersion model is required to estimate the emissions using this technique and they have inherent assumptions. Owing to its disadvantages, the upwind/downwind technique is generally used for screening and not for emission rate estimation.

PSEUDO-MASS BALANCE:

Mass balance is an indirect method of determining emission rate [Balfour and Schmidt, 1984]. A mass closure is estimated as mass losses or emissions at steady state, i.e., all unaccounted losses are assumed to have been emitted. The expression for estimating emissions is given by:

$$\text{Mass losses} = \text{Emissions} = \text{Mass in} - \text{Mass out}$$

Typically most of the flow rates and material rates in chemical processing industries are measured in terms of volumes. Therefore the fluid densities can be used to convert volumetric measurements to mass flows. The above expression can be modified as:

$$E_i = \sum L_j W_{i,j} P_j - \sum L_k W_{i,k} P_k \quad (6.7)$$

Where: E_i = emission of component i, kg.
 L_j = volume of inlet stream j, m³.
 L_k = volume of outlet stream i, m³.
 $W_{i,j}$ = weight fraction of component i in inlet stream j.
 $W_{i,k}$ = weight fraction of component i in the outlet stream i.
 P_j, P_k = density of liquid stream j and k, respectively, kg/m³.

All the above parameters must be measured.

Potential Operating Problems: The mass balance method's use is limited in application to an actively controlled system with documented and metered inflows and outflows. There is a considerable amount of time required for measurable material losses to occur and small losses are difficult to measure due to precision of analytical methods available. For an uncontrolled site, due to the complexity of the waste present, in order to estimate emission losses it is necessary to collect and analyze a large number of samples. This process could be very expensive [Shen *et al.*, 1990]. Thus the mass balance technique is highly influenced by the ability to obtain homogeneous samples of the process waste. The emission rate estimated by this technique is typically a small difference between two large values. The resulting emission rate will typically have a large variability. Therefore whenever possible, the mass balance method should not be the only means of determining the emission rate from the source [Balfour and Schmidt, 1984].

OPTICAL REMOTE SENSING (OSR)

Spectroscopic techniques using laser light sources are used for characterizing the emission of contaminants from a source and characterizing the impact from contaminant release from a source on downwind receptors.

Various advantages of optical remote sensing over point monitoring/sampling techniques were noted by Grant *et al.*, [1992]:

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1. ORS techniques can probe regions inaccessible or otherwise difficult to sample such as plumes from smoke stacks and hazardous waste landfills.
 2. Optical remote sensing provides path-averaged measurements which are useful for continuous perimeter monitoring and locating gas leaks.
 3. Concentrations can be estimated by ORS technique in seconds or minutes.
 4. No sampling of air is required so that concerns about sample integrity are not relevant as they are with the point sample.
 5. For some instruments several gases can be measured simultaneously.
 6. Open-path measurements combined with on-site meteorological data may possibly be used to estimate emission rates from a variety of source types.
 7. Measurement programs using point monitors or point samplers with an associated analytical procedure can be very expensive if one tried to match the spatial and temporal coverage that is easily achieved by optical sensors.

Disadvantages associated with optical remote sensing are:

1. Cost of instruments and training of the personnel to reach the stage where reliable measurements are made may be very high.
2. There is a possibility of spectral interference from atmospheric trace gases other than the target gases, e.g. water vapor, carbon dioxide, ozone and other pollutants.
3. The spectral database required as part of ORS measurement strategy is not yet complete.
4. The method minimum detectable concentrations and spatial resolution may or may not be adequate for the desired application.
5. The process of establishing equivalency for ORS has not yet been approved by the EPA.

Description of Optical Remote Sensing Technology: The optical remote sensor is generally set up to transmit a beam of radiation across a parcel of air to be measured. There are two types of configurations. One is the bistatic configuration and the other is monostatic configuration. In the bistatic configuration, a radiation source (transmitter) is placed at one location, with a sensor (receiver) at another location. The two locations define the optical path. The spectrally selective analyzer can be at either end. In the monostatic configuration, the transmitter and receiver are collocated and either a topographic target (building wall, ground vegetation etc.) atmospheric aerosols and molecules or a retroreflector is used to reflect the transmitted radiation back to the receiver. The monostatic method potentially permits movement of the sensors line of sight more readily, but it is also subject to greater uncertainty because the path length may not be as well defined.

Three types of open path monitoring (OPM) technologies, a subset of ORS, have the ability to meet the requirements of sampling at bioremediation sites. The three types of open-path

systems are Fourier Transform Infrared (FTIR), Ultraviolet-Differential Optical Absorbance (UV-DOAS) and Gas Filter Correlation (GFC). Draves, Eklund and Padgett [1992] describe the applicability of the methods to various air contaminants. Table 6.2 extracted from that paper illustrates detection limits for various compounds over a 200 m pathlength. A comparison with short and long term action levels is provided as well. Although detection limits for grab sampling devices such as canisters are considerably lower than for OPMs, OPMs have been usefully applied to establish maximum concentrations to which downwind receptors have been exposed [Solinski et al., 1992]. As the technology improves and costs come down, OPMs may be more widely applied.

Table 6.2
Comparison of open path monitoring technology detection limits and action levels of compounds most commonly found at superfund sites, ppb [Draves, Eklund and Padgett, 1992].

Compound	Canister GC/MD	FTIR ¹	GFG ¹	UV-DOAS ¹	Action Levels	
					Short-term ²	Long-term ²
Trichloroethene	0.47	12.5	NA	ND	498	0.109
Chloroform	0.37	15	180	ND	19.6	0.009
Tetrachloroethene	0.57	150	NA	ND	250	0.279
1,1,1-Trichloroethane	0.41*	10-45	NA	ND	1830	183
Methylene chloride	0.38*	35	NA	ND	502	0.606
t-1,2-dichloroethene	0.52*	10-45	NA	ND	2000	17.72
Vinyl chloride	0.42	10-120	210	ND	10.2	0.005
1,2-dichloroethane	0.39	100	NA	ND	9.90	0.009
Chlorobenzene	0.48	53	NA	ND	100	4.36
1,1-dichloroethane	0.92*	10-45	100	ND	990	124
Carbon tetrachloride	0.41	10	NA	ND	20.4	0.011
PCBs	NA	a	a	a	b	b
Benzene	0.53	130	300	3.75	0.940	0.038
Toluene	0.17*	120	300	3.75	1000	533
m-Xylene	0.15*	50	300	3.75	998	161
o-Xylene	0.15*	75	300	15	998	161
p-Xylene	0.15*	80	300	3.75	998	69.0
Ethylbenzene	0.67*	80	300	7.5	998	230
Phenol	a	a	a	3.75	49.0	516
Cyanides	ND	d	d	d	b	b
Arsenic compounds	ND	d	d	d	b	b
Cadmium compounds	ND	d	d	d	b	b
Chromium compounds	ND	d	d	d	b	b
Copper compounds	ND	d	d	d	b	b
Lead compounds	ND	d	d	d	b	b
Mercury compounds	ND	d	d	0.025	b	b
Zinc Compounds	ND	d	d	d	b	b

a = potential to detect these compounds.

b = compound specific.

c = for atomic mercury.

d = potential to detect certain compounds.

¹ assumes 200 m pathlength.

² Short-term action levels are on an hourly basis and long term action levels are on an annual basis. The various measurement techniques may yield multiple data points over a one-hour period comparison to the action levels.

* = provided by vendor.

NA = not available.

ND = not detectable.

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