VII. EMISSION CONTROL TECHNIQUES

Emissions from hazardous waste treatment, storage, and disposal facilities have been estimated to be more than 1.5 million metric tons per year [Ehrenfeld *et al.*, 1986]. Depending on the type of source, i.e., area or point source there are different types of emission and/or odor control techniques cited in the literature. The emissions can be controlled prior to treatment, during treatment or after application of a treatment method, depending on the concentration of pollutants and their properties, such as volatility. Some of the control techniques suggested for point sources of emissions are carbon adsorption, thermal incineration, catalytic oxidation and condensation. For area sources, covers are usually used to trap the VOCs for biotreatment or to vent the VOC emissions to some other control device. In this chapter, some of the control techniques, their limitations and their applications to bioremediation processes will be discussed. The control techniques applicable to control VOC emissions from various bioremediation processes are summarized in Table 7.1.

CONTROL TECHNIQUES FOR POINT SOURCE EMISSIONS

Emission control techniques for point sources include sorption onto activated carbon or resins, thermal incineration, catalytic incineration, condensers, and biofiltration. Each method has significant advantages, limitations and disadvantages.

Carbon adsorption

Carbon adsorbers have been used for solvent recovery and also as pollution control devices. VOCs are trapped on the surface of granulated activated carbon (GAC) physically or by chemical reactions with carbon. Fixed bed regenerative systems and disposable carbon canisters are two methods used to control VOC emissions. In fixed bed regenerative systems, the contaminants adsorbed to the GAC can be stripped by using hot air or steam [EPA, 1989]. When steam is not available vacuum desorption is another alternative used to desorb the bed. Regeneration of fixed bed adsorbers by applying ozone to the inlet gas stream and recycling the gases, both to desorb and destroy the adsorbed compounds, has also been attempted in a research study [San Diego APCD, 1990]. In the more conventional regeneration methods, the contaminants are commonly recovered as a liquid. With non-regenerable systems, spent carbon must still be disposed of after use. Comparing both systems, the capital cost of a fixed bed system is higher. However, when the cleanup activity takes a long time, fixed bed regenerative systems are more economical than the operating costs associated with replacement of canisters. Regenerable carbon adsorption is effective for control of VOCs with molecular weights between about 50 and 150 [EPA, 1989]. Lower molecular weight compounds tend to break through too quickly and higher molecular weight compounds tend to be difficult to desorb. The relative humidity should be less than 50% to prevent water vapor from occupying or blocking access to adsorption sites (capillary condensation) and reducing removal capacity [EPA, 1992]. The inlet stream temperature should also be less than about 150°F. If the gas temperature is greater than 150°F the adsorption properties of carbon change and the carbon may not remove the organics in the stream [EPA, 1992; EPA, 1989].

One main advantage of using carbon adsorption is its applicability at variable stream conditions (such as flow rate and VOC concentration). Carbon adsorption is often used as a control technique at soil vapor extraction sites [EPA, 1989]. To control vapors coming out of a slurry-phase treatment, carbon adsorption is used in conjunction with a vapor collection hood to capture the VOC emissions and vent these emissions to a GAC unit.

Table 7.1
Summary of recommended stream characteristics and efficiencies for regenerable carbon adsorption technique given by EPA [1989], EPA [1986] and EPA [1992].

Emission stream concentration	< 700 ppmv
Flow rate moisture	< 50%
Recommended temperature	< 150°F[a]
Molecular weight of VOC	50-150 Daltons
Actual efficiency	60-95% [b]

[a] At temperatures below 150°F, carbon adsorption works efficiently even if there are variations in the temperature.
[b] depending on the stream concentration.

Costs for carbon adsorption systems depend on process variables such as adsorption time, volumetric flow rate, pressure drop, carbon capacity and inlet and outlet contaminant concentrations. The type of carbon adsorption system, regenerative or canister, would also affect costs. Unit cost factors for utilities, operation, maintenance etc. are reported in EPA [1989]. Witherspoon *et al.* [1990] reported that for a 10,000 scfm flow rate and 100 ppmv inlet concentration (each component) the annualized capital costs are about $475,000 and operations and maintenance costs are about $250,000/yr. The capital costs consist of the cost of basic equipment, auxiliary equipment, and installation of equipment. The operation and maintenance costs are the costs of labor, maintenance, utilities, and capital related charges. The above cost estimates reported by Witherspoon *et al.*, [1990] were for a dual, fixed-bed adsorber with steam regeneration controlling a waste stream with an equal molar percentage of benzene and hexane.

Recent Adsorber Technology Advances

Kenson [1992], described a technology that uses activated carbon fibers, with the adsorbing pores at the fiber surface. Activated carbon fiber (ACF) solvent recovery systems have been applied to recover chlorinated solvents such as Freons, 1,1,1-trichloroethane (TCA), dichloromethane (DCM), trichloromethane (TCM), and trichloroethene (TCE). For GAC systems, the recovery of reactive and corrosive solvents is poor due to formation of hydrochloric acid. Whereas the use of a hot air regenerated bed avoids hydrolysis reactions. An ACF system gives a better quality solvent and is also cost effective when used for recovering corrosive chlorinated solvents like TCA. Kenson [1992, 1993] also described a system to control dilute chlorinated solvent emissions.

Robbins and Hall [1992] and Larrinaga and Hall [1993], described the application of a patented SORBATHENE unit developed by Dow Chemical Company. The SORBATHENE unit consists of adsorption/desorption steps. The authors described it as a pressure swing adsorption process. This process uses the heat generated during adsorption and reduced pressure to recover the adsorbed chemicals in the desorption process. Presently these SORBATHENE units are used to recover chlorinated organic compounds such as epichlorohydrin, monochlorobenzene, DCM, TCE, aromatics such as benzene and ketones like acetone. These units are useful for recovering various chemicals to be reused and avoid the cost of destruction in a downstream process. Skid-mounted SORBATHENE units have been developed to control volatile organic emissions produced, processed or stored in chemical processes and in waste remediation operations. Typical concentration ranges for economic recovery of solvent are between 1000 and 160,000 ppm [Larrinaga and Hall, 1993].

Another development in adsorption systems is the use of hydrophobic zeolites [Degussa, 1992] and polymeric adsorbents. At high relative humidities, the capacity of these adsorbents can be greater than activated carbon, hence they may be useful for treatment of highly humid streams. Furthermore, although zeolites may have less total adsorption capacity per unit mass of adsorbent in comparison to GAC, for low concentration VOC streams this may not be a significant drawback and some more polar compounds may actually be captured with greater efficiency by the zeolites [Crompton and Gupta, 1993]. Although not commercially demonstrated for bioremediation projects, there are plans by a number of air pollution control equipment manufacturers to apply them in the future.

Thermal Incineration

Other names for thermal incinerators are thermal oxidizers, direct-flame incinerators and afterburners. The supplemental fuel, typically natural gas, is mixed with air and the contaminated stream in a chamber at sufficient temperature and residence time to initiate combustion reactions. The combustion chambers are maintained at temperatures higher than the auto ignition temperatures of the contaminant gases. Compared to other control techniques, the destruction efficiency of thermal incineration is less sensitive to waste gas composition. Because thermal incineration operates at high temperatures, it is important to have some kind of heat recovery to make the technique cost effective. The design of thermal incinerators with heat-recovery are discussed elsewhere [Jennings *et al.*, 1984].

Thermal incineration is applicable to a broader range of compounds when compared to other control options. One main disadvantage of this technique is that it needs relatively uniform stream conditions (only minor fluctuations of about ± 10% can be accommodated) such as flow rates but VOC concentrations can vary over a wider range if supplemental fuel is provided [EPA, 1989]. The limitations on concentration range occur because variability in stream conditions cause variations in mixing and residence times from design values thus resulting in lower combustion efficiencies. The thermal incineration technique is applicable to streams containing dilute mixtures of VOC in air at constant flow rates. For dilute streams, supplemental fuel is required to maintain combustion, making the process expensive. Thus, this technique is seldom used for VOC emission control, especially if supplemental fuel is necessary.

The typical stream characteristics for application of thermal incineration are summarized in Table 7.2 below.

Table 7.2
Typical gas stream characteristics for thermal incineration

Emission stream concentration	>100 ppmv
Recommended temperature	800-1500^{o}F
Molecular weight of VOC mixture	any hydrocarbon
Efficiency	>99%[b]

[a] Sources EPA, [1992], Witherspoon, [1990]

[b] at a stream concentration above 200 ppmv this efficiency can be achieved. At a stream concentration of about 50 ppmv efficiency of 95% can be achieved.

The costs of thermal incinerator systems are governed by the method of construction, type of materials used and instrument package [Witherspoon, 1990].

Catalytic Incineration

Catalytic incineration can be described as thermal incineration with a catalyst to enhance the combustion process. An advantage of using a catalyst is that it reduces the amount of supplemental fuel required for combustion by lowering the temperatures (600-900°F) at which reactions take place. Some examples of catalyst materials are platinum, palladium, rhodium and ceramic honeycomb as pellet supports. Chromium based catalysts are also being studied for their potential to handle chlorinated waste streams [Frost, 1993].

The sensitivity of the catalyst to pollutant characteristics and process conditions has limited application of catalyst technology to waste streams having homogeneous characteristics. Contaminants may damage the catalyst and affect its performance. Therefore catalytic incinerators are not preferred when contaminants such as halogens like chlorinated hydrocarbons, lead, mercury, tin, zinc, and phosphorus are present in the stream [EPA, 1989]. Catalytic incinerators are also sensitive to fluctuations in the stream conditions. When heavy metals and halogens are not contaminants and the stream flow conditions are uniform, catalytic incineration is a better choice over thermal incineration due to its lower operation costs.

The typical stream characteristics for application of catalytic oxidation are summarized below:

Table 7.3
Typical gas stream characteristics for catalytic oxidation[a]

Emission stream concentration	>100 -3000 ppmv
Recommended temperature	600-900°F
Molecular weight of VOC mixture	any hydrocarbon
Efficiency	95 -99 %

[a] Sources EPA [1989] and EPA [1990].

The costs of catalytic incineration depend on various process variables such as VOC stream flow rate, temperature, percent LEL (lower explosive limit) and heat content. The costs also depend on the auxiliary fuel requirements and heat exchanger efficiencies. A procedure for estimating costs of catalytic incineration systems for flow rates over 5,000 scfm is given in a USEPA reference [EPA, 1989].

Tichenor and Palazzolo [1987], reported on a study of the design and operation of a catalytic incinerator to destroy specific volatile organic compounds individually and in mixtures. The system on which tests were conducted, consisted of a skid-mounted catalytic incineration unit with catalyst beds consisting of ceramic honeycombs coated with platinum/palladium catalyst and a solvent vapor generation system. The operating parameters, such as catalyst inlet temperature, compound concentration, space velocity, compound type, geometry of the catalyst and catalyst volume were varied to study their effects on the incineration of the compounds. Results indicated that destruction of a specific compound or mixture of compounds was highly dependent on the catalyst inlet temperature and space velocity on an overall basis. The VOC destruction efficiency increased with decrease in space velocity and increase in temperature and increase in compound concentration. Specific results are discussed in the article by Tichenor and Palazzolo [1987]. The authors reported the relative destructibility as high to low for compound classes of alcohols, cellosolves/dioxane, aldehydes, aromatics, ketones, acetates, alkanes and chlorinated hydrocarbons in that order. All of the compound classes except chlorinated hydrocarbons were reported to be destroyed with an efficiency of 98-99% at low space velocities and high temperature [Tichenor and Palazzolo, 1987].

Condensers

Condensers are used as preliminary control devices to reduce the high concentration levels of VOCs (>5000 ppmv). The condensers work on the basis of highly variable contaminant vapor pressures. The temperature is reduced or the pressure is increased until saturation vapor pressure is attained so that the contaminant vapors condense into liquid. To obtain low temperatures for condensation, coolants such as air, chilled water, brine or refrigerants are used. The overall control efficiency (varies from 50% to 90%) of a condenser is dependent on the variability of VOC concentrations. The higher the variability in VOC mixture concentrations, the lower the control efficiency. Due to low collection efficiencies and high annual costs SVEs (soil vapor extraction) usually do not employ condensation as a control technique [EPA, 1989].

Spencer [1992], described two methods that made use of cryogenic liquids to condense specific VOCs from different types of sources such as manufacturing, automotive, aerospace and pharmaceutical industries. The two processes are termed as 1) Indirect Contact Process and 2) Direct Contact Process. In the simplest version of the indirect contact process, liquid nitrogen is used as a cryogen in the tube side of a shell-and-tube heat exchanger to condense VOCs in the air stream passed through the shell side. The indirect contact process was applied to recover methylene chloride in a pharmaceutical company. About 99.9% of recovery efficiency was achieved. In a direct contact process, the liquid nitrogen is allowed to contact the air stream with VOCs to recover the VOCs. This process has been demonstrated at a chemical company to recover chlorinated hydrocarbons. A 99% removal efficiency was reported. With streams subjected to bioremediation, high relative humidities are expected and cryogenic systems would not be favored.

Biofiltration

Biofiltration is a relatively new air pollution control technique in the U.S., though it has been applied widely for odor control in other countries. Biofiltration involves control of VOC emissions by passing off-gases with VOCs or inorganic air toxics through one or more beds of biologically active material [Leson and Winer, 1991]. Bioscrubbers and trickling filters are other processes that use biotreatment to reduce pollutant concentrations. The biofiltration technique is applicable when inlet stream concentrations are below the range of about several hundred ppmv total degradable organic carbon and bioscrubbers and trickling filters may be required for contaminant concentrations greater than several hundred ppmv to prevent fouling of the biofilter with biomass [Togna and Folsom, 1992]. Bioscrubbers and trickling filters are less preferable when compared to biofilters because they are more energy intensive, less reliable due to mass transfer limitations and more sensitive to variations in loading rates and contaminant concentrations [Witherspoon, 1990]. Nevertheless, opinions vary in that some investigators consider conditions to be better controlled in bioscrubbers [Smith *et al.*, 1993].

Biofilters utilize a biologically active material consisting of mixtures based on compost, peat or soil. Biofilter designs range from open single beds to enclosed or multi-bed systems. The choice of the system is based on factors such as space availability, environmental conditions, maintenance requirements and costs. Most applications of biofilters to date have been to control emissions from industrial facilities, waste disposal facilities and food processing industries, e.g., adhesive production, coating operations, iron foundries, waste oil recycling, pet food manufacturing, industrial and residential waste water treatment plants, composting and landfill gas extraction [Leson and Winer, 1991]. Application of biofilters to treat emissions from bioremediation processes is fairly recent. Biofiltration can be applied to control emissions from the soil vapor extraction process, *in situ* treatment, slurry-phase biotreatment and land treatment if it is possible to collect all the VOC emissions using a cover and to vent the contaminant streams into a biofilter.

Ergas *et al.*, [1992] conducted experimental studies to determine the applicability of biofilters to control POTW emissions. They found the biofilter to be an effective control of VOC emissions over a broad range of compounds. The biofilter was found to accommodate a high degree of variability in concentrations and allow fluctuations in the flow rates into the biofilter. The compounds present in the inlet stream were dichloromethane, chloroform, benzene, trichloroethene, toluene, tetrachloroethene and xylene. The removal efficiencies for chloroform, benzene, toluene and xylene varied from 30-80% (initially) to greater than 90%. The removal of chlorinated compounds was found to be inconsistent. The reasons for the inconsistent removal of chlorinated species was uncertain but was attributed to the lower degradation rates of the compounds, longer acclimation periods, requirements for cometabolism, or competitive inhibition. More recently, Ergas *et al.*, [1993] have demonstrated consistent degradation and removal efficiencies of 95^{+}% of DCM at concentrations of 3 ppmv.

Witherspoon [1990], estimated costs of a biofilter based on EPA[1985] cost data for odor control technology. For an inlet air flow rate of 10,000 cfm with an inlet H_2S concentration of 20 ppmv and an outlet concentration of <1 ppmv, the capital cost was estimated as $97,300/yr and operation and maintenance costs were estimated as $7,870/yr. The capital cost included cost of site preparation, construction of the biofilter, equipment and labor and the operations and maintenance costs included chemical, material costs, maintenance, energy and labor.

CONTROL TECHNIQUES FOR AREA SOURCE EMISSIONS

Area source emission control techniques for bioremediation systems include covers to prevent emissions from surfaces and subsurface injection in soil based treatment systems such as landfarming. Covers are really enclosure devices and often have the disadvantage of producing environmental conditions suitable for the growth of acid producing sulfur oxidizing bacteria.

Covers

Covers are a passive control device used to control air emissions and odors from area sources like hazardous waste, treatment and disposal facilities, refinery operations, and POTWs. The covers are used to trap VOCs that can be biodegraded during secondary treatment or vented to a control device [Witherspoon, 1990]. Covers come in different shapes and sizes, and are made of different materials. For land treatment, covers are used in the form of air inflated structures covering small land treatment facilities or over sections of larger facilities [Ehrenfeld *et al.*, 1986]. Usage of this type of cover is actually advantageous as it provides the operator some degree of control of temperature and moisture.

Covers provide a physical barrier to vapor transport. Examples of such covers are clean soils, synthetic covers, foams and mulch materials. The clean soil, as cover, temporarily reduces emission rates of VOCs. The effectiveness of the soil material depends on depth of the cover, mode of compaction , and the amount of contaminated soil it covers. One main disadvantage associated with soil cover is that when the cleanup takes a long time, the cover becomes less effective and may also increase the total volume of soil to be treated after a certain period of time. Suder and Schmidt [1992] reported that when a soil cover was used to cover a test pad with soil contaminated with petroleum hydrocarbons, a time-weighted control effectiveness of 98% was observed for sheepsfoot compacted soil (4-6") and a control effectiveness of greater than 99% was observed for smooth roller compacted soil (4-6").

Typically, synthetic covers are used to control VOC emissions from short-term storage piles. The synthetic cover thickness ranges from 4-6 mil to 30-40 mil [EPA, 1992]. Some examples of synthetic covers are plastic sheets and geotextile materials. The effectiveness of a synthetic cover depends on the permeability of vapors through the cover and the percentage of the soil pile effectively covered. One advantage of using synthetic covers is that unlike soil covers, they do not contribute to the weight of the waste that must be treated. Depending on the type of material, time-weighted control efficiencies ranging from 46% to 92% were reported when tested on the soil pads contaminated with petroleum hydrocarbons.

A third kind of cover material, i.e., mulch materials, may consist of sawdust, wood chips, straw and wood fibers. These materials are used to insulate the soil surface and lower the soil temperature to control the diffusion of contaminant gases. One main disadvantage of mulch materials is that if mixed with the soil, these materials increase the volume and mass of the soil to be treated. It is conceivable, however, that the materials could serve as a biofilter if provision were made to maintain aerobic conditions.

Another type of cover material is foam. Foam covers can be temporary or long duration. Typically, 1-2 inches of foam is applied on a flat surface [Suder & Schmidt, 1992]. Temporary foam covers provide coverage for an hour or two. On the other hand the long-term foams contain stabilizing additives that extend the useful life of the foam to days or even months. Gerstle [1992] demonstrated the application of vapor-suppressing foam to control emissions during a trial excavation at a site contaminated with highly acidic petroleum refinery waste within a rigid-frame PVC-covered enclosure. Foams are a highly effective mode of control technique and they can be applied directly onto the exposed contaminated soil.

One main disadvantage associated with foams is that they typically contain 90% water. The water increases the weight of the soil and makes it difficult to handle. Sometimes, depending on the types of contaminants on the surface, the foam is prone to reactions which may decrease their effectiveness. Foams are hard to apply on windy days. Foams can be applied to area sources like land-treatment facilities and slurry-phase systems.

Total enclosures are used to enclose a process completely to capture all the VOC emissions to be vented to a control device for point source emissions. The method of setting a total enclosure is described by EPA [1991]. As part of a study of the effectiveness of a foam cover, Gerstle [1992] employed a rigid frame PVC-covered enclosure over the excavation of a site contaminated with highly acidic petroleum refinery waste. A vapor suppressing foam was sprayed, to reduce the emissions. The total hydrocarbon emissions and SO_2 concentrations were monitored in the enclosure exhaust stream on both sides of the control system. The SO_2 emissions were controlled using a counterflow packed-bed wet scrubber and the VOCs were removed using a granular carbon bed adsorber. The enclosure used, captured the contaminant emissions successfully and allowed the effectiveness of the foam to be determined.

The cost of a cover includes cost of purchase, transport of the material and cost of disposal. In some cases cost of purchase and cost of disposal may not be required. Suder and Schmidt [1992] reported the approximate costs of different types of control techniques for commercial landfills and remediation projects excluding the shipping of material. The cost of temporary foam covers is about $\$0.10/ft^2$ and long-duration foams cost about $\$0.30$-$\$0.50/ft^2$. The synthetic membrane range of costs is $\$0.22/ft^2$-$\$0.32/ft^2$. The soil cover (4"-6" compacted) costs from $\$0.85/ft^2$ to $\$3.75/ft^2$ to apply at remediation sites.

Subsurface Injection

Subsurface injection of waste is employed to reduce emissions in the landfarming treatment method. Typically in landfarming, waste is spread on the soil surface and cultivated to a depth of about six inches. In subsurface injection, the cultivation is carried on to a depth of more than ten inches and the waste is injected at the bottom of the plow slice [Vogel, 1985]. There is special equipment available to inject wastes under the surface of grasslands without much disturbance to the sod. The literature indicates that the emissions resulting due to subsurface injection are less when compared to surface application of waste immediately after application. However, the emission rates from subsurface injection are greater than those resulting due to surface application one day after application [Vogel, 1985; Thibodeaux, 1982]. Vogel [1985] reported that emissions due to subsurface injection are 70% less when compared to surface application. Vogel [1985] reported that the waste application equipment for subsurface injection cost ranges from $90,000 to $145,000 depending on the waste storage capacity, engine size and additional equipment. Usually if the basic waste equipment is available, a tool bar can be fitted to it for subsurface application. The tool bar costs from $5000 to $8000 [Vogel, 1985].

The effectiveness of subsurface injection has been demonstrated by Thibodeaux *et al.* [1982], and Coover [1990]. Coover [1990], compared the emission rates for three different waste application procedures: conventional plot application, subsurface plot application, and pre-treated plot applications. Emission rates of benzene, toluene, m,o,p-xylenes, ethyl benzene, naphthalene, hexane and the total C_5 through C_{24} hydrocarbons were measured and compared statistically in each case of waste application. Subsurface injection and pre-treated waste were found to be equally effective in reducing peak emissions of benzene, toluene, naphthalene and total C_5 to C_{24} hydrocarbons. For methyl pentane, hexane, ethylbenzene, and xylene, subsurface injection was found to be more effective in reducing the emissions. In general, application of pre-treated waste or subsurface injection was found to be more effective than surface application of untreated waste.

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GLOSSARY

anaerobic: able to live and grow where there is no free oxygen.

anoxic respiration: oxidative process similar to aerobic respiration but which utilizes nitrate or another inorganic compound as a terminal electron acceptor.

anthropogenic: material or contaminant that results from human activity. Anthropogenic pollutants are the results of discharges or spills rather than natural events such as forest fires.

aquifer: an underground layer of porous rock or sand containing water.

autotroph: organism which obtains its carbon from the reduction of inorganic compounds.

bacteriophage: virus that attacks bacteria.

biotransformation: the biologically induced structural transformation of a compound.

cometabolism: process by which a substrate is metabolized by a cell while the cell is using another substrate as its carbon or energy source.

competitive inhibitor: compound which has a similar structure to an enzyme substrate and binds to the enzyme.

consortia: mixtures of different populations.

dioxygenase: enzyme that catalyzes the addition of two atoms of molecular oxygen to a molecule.

diauxic: metabolic control which operates in such a way that enables organisms to select the substrate that allows them to grow at the highest rate.

enzyme: protein which both lowers the activation energy and directs the metabolic pathway taken by chemical reactions in an organism.

eukaryote: organism characterized by having a nucleus surrounded by a membrane.

extracellular: outside the outermost layer of the cell.

facultative anaerobe: organism which grows in the presence or absence of oxygen.

fermentation: degradative pathway in which an organic compound serves as both the electron donor and acceptor.

heterotroph: organism which requires an organic form of carbon.

hydrolysis: cleavage of a molecule by reaction with water.

hypha: a fungus thread.

lithotrophs: bacteria that use inorganic compounds as energy sources.

lyse: breaking apart the cell wall.

mesophile: organism which grows best at temperatures between 15°C to 45°C.

metabolism: processes through which living organisms grow and obtain energy.

meta position: position on an aromatic molecule separated from the point of reference by one carbon position.

mineralize: convert a molecule to inorganic ions and molecules.

monooxygenase: enzyme that catalyzes the addition of one atom of molecular oxygen to a molecule.

mutation: alteration of a genetic message.

organotroph: organism that utilizes organic compounds as an energy source for respiratory metabolism.

ortho position: position on an aromatic molecule that is adjacent to the point of reference.

para position: position on an aromatic molecule that is separated from the point of reference by two carbon positions.

phototroph: organism that obtains energy from light.

plasmid: small circle of DNA that is extrachromosomal and replicates autonomously.

prokaryote: organism characterized by lacking a nuclear membrane.

psychrophile: organism that grows best at temperatures below 20°C.

recalcitrant: (refractive) compound that does not undergo biodegradation.

substrate: compound that can be used as a carbon, energy, or nutrient source for microbial metabolism.

thermophile: organism that grows best at temperatures above 50°C.

transposon: a segment of DNA that can be moved from one area on a chromosome to another.

xenobiotic: strange to life, compound for which metabolic degradation pathways have not evolved in the natural environment.

SECTION II

PRODUCTION OF VOCs IN BIOREMEDIATION

ABSTRACT

This report includes a description of two experiments in which air emissions from bioremediation processes were monitored; a field study in which bioventing was used to bioremediate soil contaminated with jet and diesel fuels, and a laboratory scale experiment in which land farming was used to bioremediate soil contaminated with polynuclear aromatic hydrocarbons. In both studies the focus was on detecting volatile organic compounds that are products of biodegradation of the parent compounds.

I. INTRODUCTION

In this project two experimental studies of emissions of volatile organic compounds (VOCs) from bioremediation systems were conducted. The first study was run as a "tag along" project to a bioventing pilot project carried out by CH2M Hill Engineers under a contract with McClellan Air Force Base in Sacramento, CA. Soils used were taken from a site at McClellan AFB that had been contaminated with jet and diesel fuels. The second study was a laboratory scale study of VOC emissions from landfarming of the polynuclear aromatic hydrocarbons (PAHs) naphthalene, phenanthrene, and chrysene. In both experimental studies the principal focus was on detecting VOC production resulting from incomplete bioremediation. For example, chrysene has a low vapor pressure but products of chrysene degradation may be considerably more volatile. The model for such reactions is the dehalogenation of trichloroethene under anaerobic conditions that results in the production of vinyl chloride. A brief discussion of soil bioremediation, the biochemical breakdown of aromatic compounds, and the potential for increased VOC emissions resulting from soil bioremediation is given below. Details of these two experimental studies are given in Chapters 2 and 3.

Microbial degradation of organic compounds involves a series of extracellular and intracellular biochemical reactions. Large molecules are broken into smaller compounds that can be transported across cellular membranes and into the cells. Metabolism of the assimilated organic compounds provides energy and carbon structures for microbial growth. However, many compounds cannot be completely metabolized by the microbial species carrying out the initial assimilation and metabolism and the end products are excreted into the environment. In the soil, or in groundwater, the excreted compounds may be utilized by other microbial species, sorbed onto soil particles, dissolved into soil water, or volatilized and emitted to the atmosphere. These processes can be visualized with the aid of Figure 1.1.

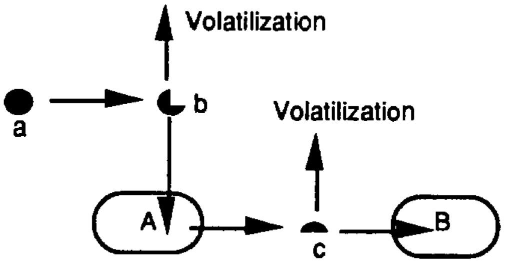

Figure 1.1
Conceptual microbial degradation sequence in which nonvolatile compound **a** is converted to semi-volatile compound **b** through a biochemical reaction catalyzed by an extracellular enzyme secreted by bacteria **A**. Semi-volatile compound **b** is assimilated and metabolized to volatile compound **c** by bacteria A. Volatile compound **c** is excreted by bacteria **A** and assimilated and metabolized completely by bacteria **B**. Both semi-volatile compound **b** and volatile compound **c** are also available for emission to the atmosphere through volatilization.

Figure 1.1 presents a very simplified scenario of the interactions that may occur in the soil. Equilibrium with the liquid phase, which must be present for biological reactions to occur, is not shown in the figure nor is adsorption onto the solid (soil) phase. However, the main point is that biochemical reaction products may be emitted to the atmosphere from bioremediation systems.

Most soil bioremediation systems are designed to operate as aerobic processes because of the more complete oxidation processes that occur, the limited number of excreted metabolic products that are observed and wider range of environmental conditions that can be tolerated relative to anaerobic microbial processes. However, aerobic bioremediation is difficult to carry out without a gas phase in close contact with the solid and liquid phases. In most cases air is passed through the reaction volume which enhances the possibility of VOC emission to the atmosphere.

Bioremediation, which generally relies on aerobic biodegradation, has considerable potential for application to soils contaminated with petroleum products and polynuclear aromatic hydrocarbons (PAHs). Most components of gasoline, diesel fuel, and jet fuel are volatile or semi-volatile. Many of these compounds are partially degraded in the extracellular environment and the potential exists for volatilization of the more volatile breakdown products. However, most products of aerobic biodegradation contain aldehyde, alcohol or carboxylic acid groups that make them less volatile than their precursors, as shown in Figure 1.2.

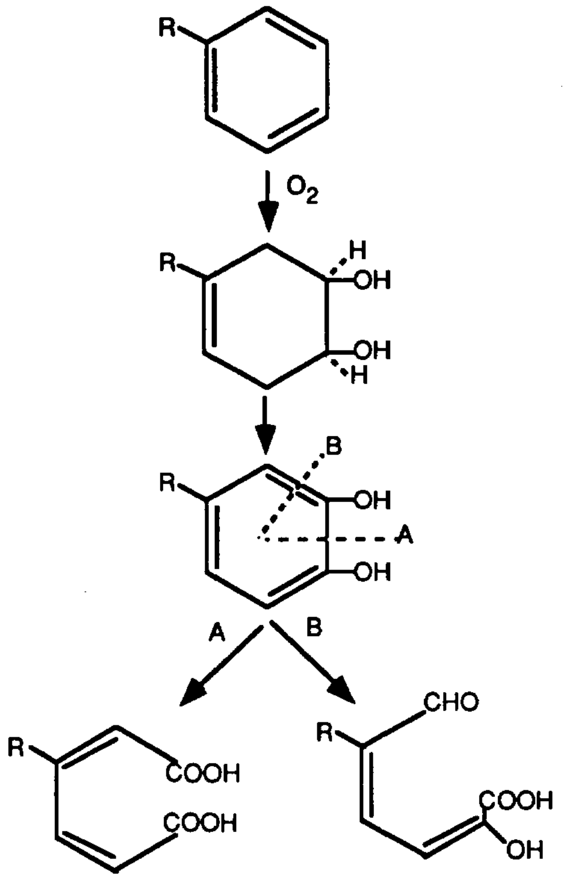

Figure 1.2
Typical aerobic biodegradation sequence of aromatic hydrocarbons

Under anaerobic conditions biodegradation sequences may result in production of products having greater volatility as explained by Castro *et al.* [1968, 1985] and Hanzlic [1981]. Nearly all of the work done in this area has been on halogenated aliphatic compounds. In soil systems anaerobic conditions are unlikely unless the moisture content is above the field capacity, adequate nutrients are available to support rapid biochemical transformations and the organic concentrations are sufficiently high to deplete oxygen.

SOIL BIOREMEDIATION SYSTEMS

Soil Bioremediation systems can be classified according to the location of the treatment (*in situ*, on-site, and off-site) and the type of treatment process selected (bioventing, land treatment or landfarming, composting, slurry-phase, and soil washing). Although both aerobic and anaerobic bioremediation processes are theoretically possible, more complete biodegradation occurs under aerobic conditions and a number of undesirable products (e.g. H_2S, mercaptans, vinyl chloride) can be produced under anaerobic conditions. *In situ* treatment processes are carried out without significant disturbance of the soil. In most *in situ* systems, supplementary nutrients are introduced through injection wells, while oxygen and potentially ammonia, are supplied by drawing an air stream through the contaminated soil. Microbial populations in the soil utilize the nutrients and oxygen as they metabolize organic contaminants. In on-site bioremediation the contaminated soil is excavated and treated on the property. An example of on-site bioremediation might be the removal of contaminated soil surrounding a leaking underground storage tank at a gasoline service station and treating the soil on a pad located on the property. When the contaminated soil is taken to a location off of the property the treatment is referred to as off-site. The methods used for on-site and off-site bioremediation are the same. Reasons for selecting off-site treatment might include the hazardous or toxic nature of the contaminants, the length of time required for treatment, limited on-site area available for treatment, and the need for sophisticated treatment process and control.

Bioventing and land farming are two types of *in situ* treatment processes in common use. Both processes have been described in Section I of this report but brief descriptions will be given here. In Bioventing air is drawn through the contaminated soil zone. If the contaminants are biodegradable and the necessary nutrients are present aerobic biodegradation will take place in the contaminated zone. Alternatively, the contaminants may be volatilized and transported to a biologically active zone where biodegradation occurs. Where contaminants are located in the tillage zone (approximately the top one-half meter of soil) landfarming may be applied, although a more common application is for the treatment of organic slurries and wastewaters by injection into the soil. In landfarming, soil is aerated by periodic tilling. Moisture control is managed by irrigation following tilling. Because the tilling process exposes new surfaces to the atmosphere the potential for VOC emissions is high.

On-site and off-site treatment processes pose the same potential for VOC emissions as *in situ* processes. However, when soil is removed for treatment, methods to contain VOCs can be incorporated into the system design. For this reason, *in situ* soil bioremediation processes are of greater concern with respect to air pollution.

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Castro, C. E., Wade, R. S., Belser, N. O., "Biodehalogenation: Reactions of cytochrome P-450 with polyhalomethanes," *Biochemistry*, vol. 24, pp. 204-210, 1985.

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II. McCLELLAN AFB EXPERIMENTS

Measurements of VOC emissions from a pilot scale bioremediation site at McClellan Air Force Base (MAFB), Sacramento, CA were made in the summer and fall of 1992. The experimental pilot plant was designed and operated by CH2M Hill Engineers[1] and consisted of an aerated bioventing operation composed of two piles of contaminated soil seeded with compost. Air was drawn through the pile and a biofilter was used as a control device to treat exhaust air. A sampling program was conducted to estimate the potential air emissions from the soil pile. The soils were contaminated with petroleum hydrocarbons, mainly JP-4, gasoline and diesel. Techniques used for obtaining the air and soil samples, analytical techniques used to analyze those samples, and the results of the monitoring studies are described below and in the Appendixes.

The soils used in the bioremediation pilot study had been excavated and stored for a considerable period prior to beginning the project. The soils were placed on a plastic mat and covered with a plastic tarp during storage but contaminants were not characterized or monitored. Prior to construction of the pilot scale system wood chips and manure were rototilled into the soils. Wood chips were selected as a bulking agent and manure was assumed to be a good source of microorganisms with which to initiate biodegradation.

MONITORING AND SAMPLING PROGRAM

Air and soil samples collected at MAFB were analyzed on a GC/MS at University of California, Davis. The experimental objectives of collecting the air and soil samples from the site were to estimate the emission rates of VOCs from heap-type bioremediation processes. Secondary objectives were 1) to determine if biodegradation of petroleum hydrocarbons was taking place in the pile and 2) to compare the change in concentrations of groups of compounds (alkanes, cycloalkanes, etc.) in the treatment train. A surface isolation chamber technique was used to collect the samples from the surface of one of the two piles and additional samples were collected at Port 1 and Port 2 (see Figure 2.1). The materials and methods section includes the description of the bioremediation process used at McClellan Air Force Base to treat the petroleum contaminated soil, and the sampling and analytical methods used to monitor air and soil samples at the site.

SITE DESCRIPTION

Two pilot treatment piles were constructed using different contaminated soils; the B720 pile contained soil taken at building 720 and the PL pile contained soil taken from a parking lot found to be contaminated. Samples taken for this study were from the PL pile. The piles were constructed in layers, with a 6" layer of pea gravel at the base. Prior to construction the soils were mixed with wood chips (as a bulking agent) and manure (microbial seed source) and the conical piles were then put together in 1' lifts. Slotted PVC pipe, through which air was drawn, was imbedded in the pea gravel layer. Air drawn through the perforated pipes was passed through a humidification chamber followed by a biofilter.

Soils from both sources were reported to contain high percentages of clay and silt. The contaminated soil (building 720 and parking lot soils separately), wood chips and steer manure were mixed with a rotary cultivator in a volume ratio of 19:5.5:2.7 to form 27.2 yd^3 of modified soil . To reduce volatilization effects, the soil was not homogenized. Until the experiments started, the two piles were covered with plastic sheets to reduce VOC emissions.

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[1] These experiments were conducted through the generous support and cooperation of CH2M Hill Consulting Engineers.

The modified soil (contaminated soil mixed with wood chips and manure), was piled in the shape of a cone with a base diameter of 18 ft, about 5.2 ft high and a side slope of about 30°. The modified soil pile, was built on a lined treatment pad with criss-crossed 16 ft lengths of slotted, 4" schedule 40 polyvinyl chloride (PVC) pipes as shown in Figure 2.1. A 4" schedule 40 PVC header pipe carried exhaust air from the treatment pad to the edge of the pile where a 4" Konaflex® hose was used to connect the header pipe to the biofilter and finally to a blower. Each treatment pad measured 22 ft on a side and was enclosed within an earthen berm 2 ft high. A 19 mil high density polyethylene liner was used to line the pad. Leachate was collected in a 5-gallon drum sump.

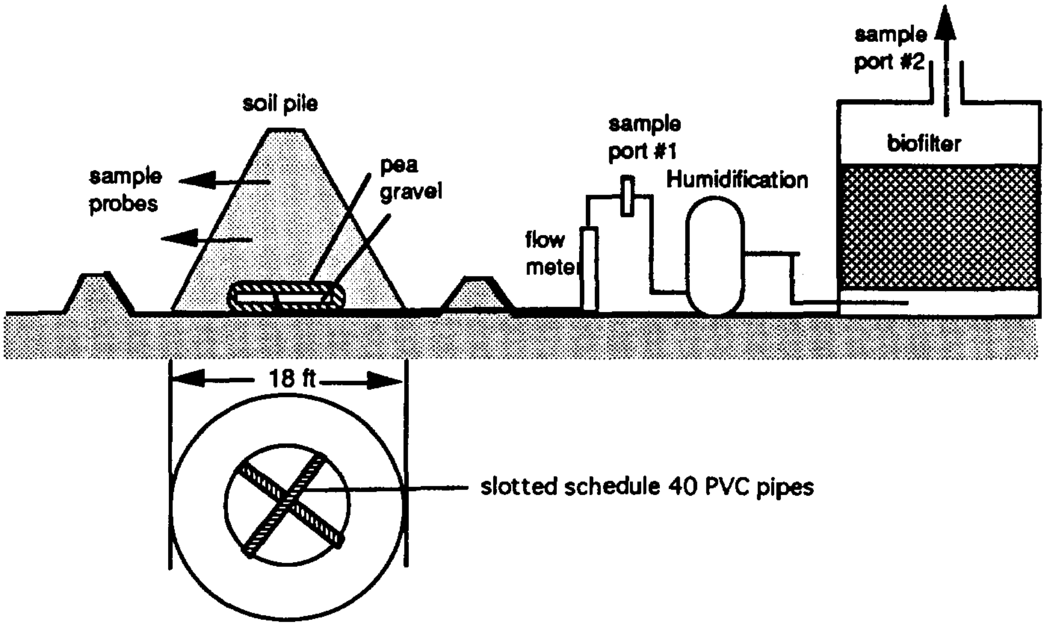

Figure 2.1
Schematic description of the aerated composting process and biofiltration unit at McClellan Air Force Base.

Water was added to each pile using a spray irrigation system, with four sprinkler heads at a 5 ft elevation placed uniformly around each pile perimeter. Because strong wind conditions resulted in frequent drying of portions of the pile, the spray irrigation system was replaced by a drip irrigation system. In the drip irrigation system, a perforated hose was placed around each pile in concentric circles so that the water was approximately uniformly distributed throughout the soil pile.

The target operating conditions for the aerated piles were a pH of 6.5 to 8.0, a temperature of 20-40°C, a soil-moisture tension of 0 to 40 mbar and an oxygen content greater than 10 percent. A temperature sensor, a tensiometer and a 1/2 inch PVC conduit were installed into the pile for temperature, soil tension and oxygen content measurements respectively.

The total number of days of operation, including the construction of the piles to the end of treatment of the piles, was 91 days. Table 2.1 lists the dates, days and operations performed by CH2M Hill.

Table 2.1.
Summary of days of operation as designated by CH2M HILL.

Date	Day	Operation
06/08/92	-3	Soil piles construction
06/11/92	0	Began B720 treatment with biofiltration
06/20/92	9	Stopped biofiltration for B720 pile. Began PL pile treatment with biofiltration.
06/28/92	17	Blower operation was changed from continuous to periodic.
06/29/92	18	Biofilter treatment system was disconnected and moved to Denver for another task.
06/31/92	20	Irrigation system was changed from spray to drip irrigation.
10/07/92	88	End of soil treatment

Although the biofilter was operated for a short period only, and was not part of this project, a description of the system is given here. Exhaust gas from a pile, was passed through a humidification column to wet the gas stream and to reduce the drying of the biofilter medium. The biofilter tank was made of 0.25" steel, had a diameter of 5.5 ft, a height of 6 ft and a volume of 1000 gallons. To distribute the exhaust from the compost pile, a criss-cross 1" PVC pipeline (4 ft across) was used. The pipeline was covered with a 6" layer of pea gravel and a 2" layer of sand in a steel ring welded to the bottom of the tank. The biofilter medium consisted of 40 ft^3 of composted yard waste, 10 ft^3 of horse manure, 10 ft^3 of peat, 10 lb of gypsum, and was seeded with 20 gallons of municipal activated sludge. The purpose of adding the above materials in the filter medium is summarized in Table 2.2. These materials were thoroughly mixed using a cultivator. The 6" diameter, 6 ft high schedule 40 PVC humidification tower operated in a counter current flow arrangement; water going downwards and the off-gas going upwards in the tower. A 4 ft depth of Flexrings™ was used as packing in the humidification bed. CH2M Hill designed this system to increase the relative humidity from 50 percent in the influent (soil pile exhaust) entering the system to > 90 percent in the effluent.

Table 2.2.
Summary of the purpose of each material in the biofilter medium.

Material in the filter medium	Purpose of the material
Horse manure	to provide nutrients
Pearlite	as bulking material
Gypsum	to prevent clumping
Municipal activated sludge	as a microbial inoculum

SAMPLING AND ANALYTICAL METHODS

In this chapter, the methods used to collect the gas and soil samples and the analysis procedure are described. A surface isolation chamber was used in conjunction with adsorbent tubes to collect gas samples coming off the pile. At the inlet and exit of the biofilter, gas samples were collected and transferred to adsorbent tubes using a syringe. Data reduction procedures and the sampling frequency descriptions are also included in this chapter.

Gas Samples

Gas samples were collected from PL pile exhaust (Port 1) and at the outlet of the surface isolation chamber. At Port 1, gas samples were drawn using 60 ml disposable plastic syringes through a three-way valve into glass sorbent tubes. The glass sorbent tubes were 4 mm I.D. and contained a mixture of Carbopak^{TM}, synthetic carbonaceous spheres and a carbon molecular sieve, Carbosieve^{TM}III. The combination of tubes, three-way valve, and nut screw are shown in Figure 2.2. Volume of gas samples collected varied from 50 ml to 400 ml, depending on the detectable concentration levels.

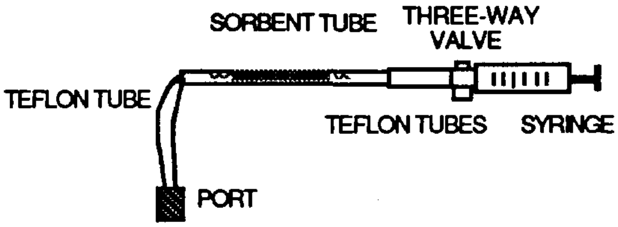

Figure 2.2.
Gas sample collection set-up at Ports 1 and 2 of the system shown in Figure 2.1.

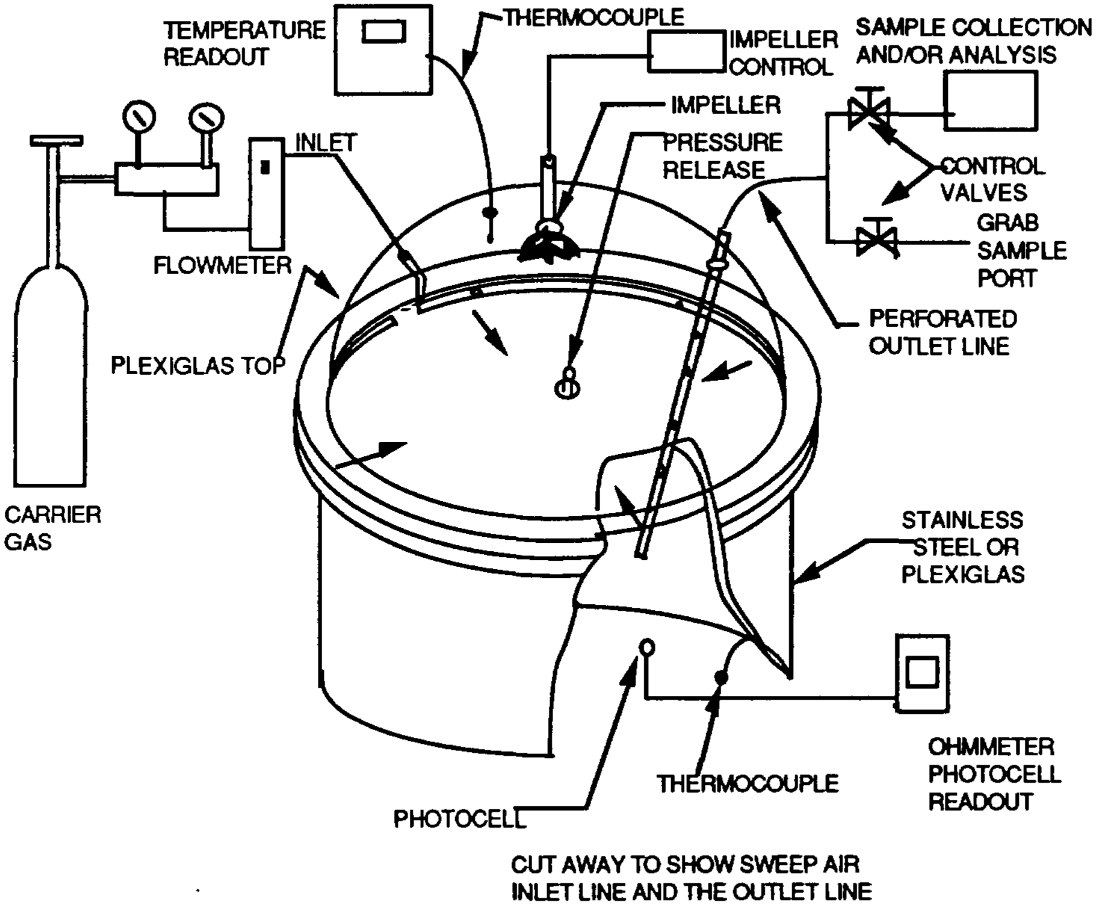

Figure 2.3
Definition sketch of typical surface isolation flux chamber (SIC).

A surface isolation chamber, of 0.41 m (approximately 16") diameter was used to collect samples of VOC emissions from the surface of the pile (see Figure 2.3). The flux chamber was placed on the pile at about 2 to 3 ft above ground level. Operation of the surface isolation chamber is described in the sampling methods section. Before taking the gas samples on the pile, two blanks were taken at the site to determine background concentration within the surface isolation chamber. For the blanks, the surface isolation chamber was placed on a clean Teflon™ sheet. Zero grade air was passed into the chamber at a flowrate of 2.45 L/min. A stainless steel manifold was attached at the outlet to allow two samples to be taken simultaneously for duplicate analysis. The blank samples were collected at the outlet of the surface isolation chamber into the sorbent tubes using a pump (SKC, model 224-PCXR7). The flow rate in the pump was calibrated to 30 ml per minute using a bubble flow meter. The samples on the surface of the pile were also collected in a similar manner as the blank samples were collected, only the surface isolation chamber was placed on the soil pile instead of a Teflon sheet. The volume of the gas samples from the surface of PL pile, collected in sorbent tubes over the days, is summarized in Table 2.3.

Table 2.3.
Summary of the sampling days and volume (mL) of gas samples taken.

	Port 1		Surface	
Day	1	2	1	2
1	100	100	120	120
3	100	50	450	450
8	100	50	120	120
16	100	50	120	120
22	300	300	240	240
36	400	400	360	360
59	400	400	360	360

Soil samples

Soil samples (25 g) were collected in glass vials with Teflon-lined caps. The vials were covered with aluminum foil and stored in a refrigerator for later analysis. The Soxhlet extraction method was used to extract the hydrocarbons with 250 ml dichloromethane from a 25 g representative soil sample. The Soxhlet extraction procedure used is described in Appendix A and the experimental set-up is shown in Figure A.1. The dichloromethane soil sample extracts were concentrated to 10 ml volume, using rotary evaporation.

Thermal desorption was also attempted to capture the volatiles and semi-volatiles from the soil samples. About 0.5 g of soil sample was introduced into an empty glass tube. The tube containing the soil was connected to a sorbent tube at one end and the contents were thermally desorbed using a tube conditioner. The experimental set-up is shown in Figure 2.4.

Sample Analysis

Gas sample analyses were carried out on a Hewlett Packard 5980A gas chromatograph with a DB-624 fused silica capillary column (J & W Scientific) and a Hewlett Packard 59970 mass spectrometer. Before analyzing the gas samples, a seven compound standard gas was analyzed for calibration. The standard mixture contained trichloromethane (chloroform), dichloromethane (methylene chloride), benzene, toluene (methylbenzene), trichloroethene (TCE), tetrachloroethene (PERC), and o-xylene. For each sample run, one calibration standard, one trip blank (blank sample collected on the travel from lab to the site) and one ambient blank were analyzed. The trip blank sample was obtained by placing a cleaned sorbent tube along with the other sorbent tubes which were used for obtaining the gas samples on site on the trip from lab to the site. All tubes were closed on both ends on a trip. No trip spike or spiked sample were taken since our experience form the past has shown that losses from the sorbent tubes are minimal once the tubes are closed tightly and since the samples were analyzed within a short period of time from sampling. The gas samples collected in the sorbent tubes were analyzed within one to three days after obtaining the samples. The temperature programs used for gas samples are summarized in Appendix B. A similar procedure was used to analyze gas samples obtained by thermal desorption of the soil samples.

Concentrated soil extract samples were analyzed on a DB-5 (J & W Scientific) column. About 1-2 µL sample volumes were injected into the column port using a 10 µL syringe. For the soil samples, deuterated PAH samples were used for calibration. The temperature program used for analysis of these soil sample extracts is summarized in Appendix B.

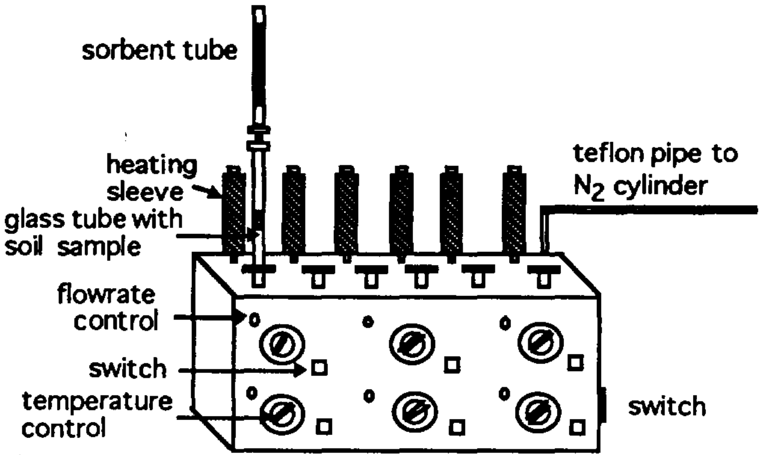

Figure 2.4.
Illustration of thermal desorption system with tube conditioner.

Data Reduction

Data from the GC/MS analysis were downloaded onto a Hewlett Packard Chem Station-59970. Identification of compounds were obtained using a mass spectral library, Wiley.L and the best matches are reported. The species in the various peaks were classified as alkanes, cycloalkanes, small aromatics, alcohols, acids, or naphthalenes based on some characteristic ions. When a compound was classified as belonging to a particular group by identification of characteristic ions, e.g., alkane, cycloalkane, etc., it was also identified by searching in the library. Results were usually found to be consistent. For example, if a search of Wiley.L identified a compound as being n-hexane, then classification according to characteristic ions would usually identify the compound as an alkane. Generally, the error in identifying a compound by the library match is reported to be about 20 percent. Ketones and aldehydes could not be classified based on primary ions and were identified based on the library identification of the compounds. Table 2.4 summarizes the classification of compounds based on detection of characteristic ions [McLafferty, 1966]. If ions corresponding to more than one group of compounds were found in a peak, the compound representing the peak was classified under a group whose characteristic ions were greater in magnitude (abundance) when compared to the magnitude of other ions. In a spectrum where such ambiguity existed the compound classification was checked with the library identification and was generally found to belong to the same group of compounds.

Standards were not available for most of the components appearing in the gas samples collected at MAFB. Therefore, an alternative means of quantifying the concentration of components in the samples was needed. The areas under the peaks representing different compounds were converted into concentration in ppbv (parts per billion by volume) on the basis of the concentration of dichloro-methane and toluene in the standard samples (see section 3 for description of a standard sample). Dichloromethane and toluene were chosen to estimate the concentrations, because their peaks in the chromatogram were prominent (narrow and consistent) with respect to the other compound peaks. This enabled a relative comparison of the quantities of compounds and trends of concentration of the compounds present in the gas samples to be performed. Also by estimating two concentration values for each group of compounds based on the concentrations of dichloromethane and toluene, it was possible to observe the trend shown by the compound concentrations over time and to be able to give a range of concentrations of components present in the gas samples. The results are shown in the form of graphs in the results and discussion section below. In estimating the concentrations an assumption was made that the total ion chromatograph (TIC) area was linearly proportional to the mass of compound present. It is recognized that this is a crude assumption, but has some value in an order-of-magnitude analysis.

Table 2.4.
Summary of the characteristic ions corresponding to different type of compounds.

Type of Compound	Mass per charge (m/z)
Alkane	57, 71
Cycloalkane	55, 69
Small aromatics	51
Alcohols, oxygen	59, 73, 87
Acids (aliphatic)	60, 73
Naphthalenes	128, 142, 156

Compound concentrations were estimated based on the concentration of dichloromethane in the standard as indicated in Equation 2.1. The concentrations of compounds in the samples based on toluene concentration in the standard, were also estimated in a similar manner.

$$\frac{\text{Mass of dichloromethane in standard}}{\text{Peak area of dichloromethane}} = \frac{\text{Mass of compound in sample}}{\text{Peak area of compound in sample}} \qquad (2.1)$$

Mass of a compound = (concentration of a compound) x (volume of a compound)

Therefore, concentration of a compound on the basis of dichloromethane concentration,

$$C_i = \frac{(C_{mc})x(V_{mc})x(P_a)}{(P_{mc})x(V_a)} \qquad (2.2)$$

Where C_{mc} = Concentration of dichloromethane in standard

V_{mc} = Volume of standard in the sorbent tube

P_a = Peak area of a compound in the gas sample

P_{mc} = Peak area of dichloromethane in the standard sample

V_a = Volume of the gas sample collected in the sorbent tube for analysis

Sampling Frequency

Frequency of the gas sampling from the parking lot pile is summarized in Table 2.3. The gas samples were taken on the 1, 3, 8, 16, 22, 36 and 59th days after starting the treatment on day 1. On the 45th day, gas samples were taken on the surface of the pile using surface isolation chamber with the vacuum pump on and off, to observe the difference in the air emissions on the pile due to aeration. The soil samples were taken only on the first day and last day of the treatment.

RESULTS AND DISCUSSION

Gas samples were taken at selected time periods, as indicated in Table 2.5 and soil samples were taken on the day of pile construction and on the last day of treatment of piles (see Table 2.1).

Emissions of all compounds in each group (alkanes, cycloalkanes, alcohols, aldehydes, acids and ketones) are presented for each sampling day in Tables 2.5 through 2.8. The procedure used for estimating the concentrations of compounds based on dichloromethane and toluene was described in the previous section.

Surface Isolation Flux Chamber Testing

The surface isolation chamber was checked for leaks by immersing the chamber in water and leaks were detected at two locations on the rim where the dome and the cylinder were attached. At a 2.5 L/min. purge gas flow rate, loss through the leaks was 0.25 L/min. Because the sampling period at MAFB was short (15 to 20 min.), and since the flux chamber would be under positive pressure during sampling (flow rate going in is 2.5 L/min, compared to 0.03 L/min leaving the chamber), the effect of leakage on sampling was expected to be minimal.

A test was conducted to determine if the surface isolation chamber was kept air tight on the soil pile during sampling. For the test, all openings on the surface isolation chamber were covered except the outlet port, which was connected to a bubble flow meter, and the inlet port, which was connected to the purge gas air cylinder. When the purge gas was passed through the chamber, initially no air flow was detected by the bubble flow meter. The position of the flux chamber was adjusted and air flow could be detected. This test was done under field conditions where the soil pile surface was under vacuum, but an uneven one, and quantification of the flows was difficult. However, the results can be interpreted to mean that estimated emissions from the pile surface reported in Tables 2.5 and 2.6 are minimum values.

Table 2.5.
Emissions fluxes of classes of compounds on the surface of the PL pile[a] in µmol/m^2-sec.

Day	Alkanes	Acids	Alcohols	Aldehydes	Ketones
1	0.000	0.000	1.626	0.118	1.412
3	1.051	0.000	0.978	0.000	0.996
8	0.000	0.943	0.136	0.428	0.000
16	0.000	0.100	0.021	0.035	0.000
22	0.000	0.065	0.051	0.009	0.018
36	0.000	0.015	0.001	0.005	0.000
59	0.000	0.039	0.002	0.000	0.000

[a] The columns contain emission fluxes estimated based on toluene (or dichloromethane) in the standards.
The concentrations of compounds obtained in ppbv were converted to moles/m^3 based on the volume of air (1 mole of gas contains 24.5 L of volume @ 25 °C). Emission fluxes were then obtained using equation (D.2).

Table 2.6
Estimated total emission rates of compound groupings from the surface of the PL pile[a], µmol/min.

Day	Alkanes	Acids	Alcohols	Aldehydes	Ketones	Approx. Total
1	0.00	0.00	37.90	2.75	32.91	73.6
3	24.50	0.00	22.80	0.00	23.22	70.5
8	0.00	21.98	3.17	9.98	0.00	35.1
16	0.00	2.33	0.49	0.82	0.00	3.6
22	0.00	1.52	1.19	0.21	0.42	3.3
36	0.00	0.35	0.02	0.12	0.00	0.5
59	0.00	0.91	0.05	0.00	0.00	1.0

[a] The total emission rates are obtained by multiplying the emission fluxes in Table 2.5 by the surface area of the PL pile (see Appendix D).
Note: The emission rates estimated are based on the toluene based concentrations.

Table 2.7
Emissions of compounds at Port 1 due to application of vacuum suction, µmol/min.

Day	Alkanes	Alcohols	Cycloalkanes	Aldehydes	Ketones	Acids	Approx. Total
1	35.55	0.00	50.15	26.31	0.00	0.00	112.0
3	98.03	0.00	304.87	95.14	198.73	0.00	696.8
8	3.79	3.46	5.34	13.29	6.52	10.01	42.4
16	0.00	0.04	0.00	0.00	0.00	1.27	1.3
22	0.00	0.00	0.00	0.11	0.00	0.00	0.1
36	0.00	0.07	0.05	0.24	0.00	0.02	0.4
59	0.00	0.04	0.00	0.00	0.00	0.00	0.04

Table 2.8
Maximum and minimum estimated emission rate from the surface of the pile and Port 1 over the duration of test.

	Emission rate, µmol/day	
Source	Maximum	Minimum
Surface	1.06X10^5	700
Port 1	1.0 X 10^6	61

Soil Sample Extracts

The primary compounds found in the initial soil samples were long-chain alkanes and cycloalkanes. Aromatic acids and aliphatic acids were not detected by the GC/MS in the initial soil samples. In the final day soil samples, there were fewer alkanes and more of alcohols, aldehydes, and ketones when compared to initial day samples. Acids may have been lost in the thermal desorption process . It is also important to note that four soil samples of 0.5 g mass are not totally representative, particularly considering the very heterogeneous nature of the material.

Results from analysis of soil sample extracts obtained by Soxhlet extraction indicated that PAHs were present below detection limits. However, the final soil sample analysis by thermal desorption indicated the presence of naphthalenone, which is a possible product of aerobic biodegradation.

Vapor Phase Emissions

Estimated VOC emission rates from the PL pile surface were initially lower than the exhaust rates but of same order of magnitude. The pattern of surface emissions was also similar to the exhaust rates, with emission rates dropping sharply after the first week. The pattern of emissions for acids and alcohols is consistent with these compounds being products of aerobic biodegradation reactions. Aldehydes would be expected to be low initially and appear as products. Aldehydes may have been produced during the period following excavation and prior to pile construction.

The higher VOC concentrations in the exhaust gas may have been the result of short-circuiting in the pile. The fact that the total surface emission rates were initially lower than those at Port 1, but later became higher, is indicative of incomplete capture of volatile compounds by the induced flow. Attempts to measure air flux into the pile with a soap film method were unsuccessful. Our impression was that the flux over the surface was not uniform. When CH2M HILL was using a spray irrigation system, constant dry patches were observed on the pile in spite of periodic watering. This may be due to the high winds and sunlight and also the soil characteristics. However, the dry patches were not so prominent when the irrigation system was changed to a drip irrigation system.

Cycloalkanes were detected in the exhaust (Port 1) samples but not in the surface emissions. Because the sampling and analysis procedures were essentially identical and because of the number of samples taken this result appears to be valid. The alkanes found in the initial soil samples were long chain and the cycloalkanes may have been of low volatility.

Acids observed were mainly acetic acid, benzoic acids and carboxylic acids from the spectrum of the compounds and library matches. The aromatic and aliphatic acids are the fastest degradation products and the aromatic acids are more volatile than the parent compounds [Perry and Green, 1984] which may be the reason for observing higher concentrations at the surface of the pile.

Emission rates of alcohols and volatile acids were greater from the surface of the PL pile than in the exhaust gas stream. The reason for this situation is unknown. Production of these compounds may have varied spatially within the pile. For example, if the surface was more aerobic than the interior, production of these biodegradation products may have been limited to the near-surface region.

The order of relative biodegradability of hydrocarbons has been listed as follows by Bartha and Atlas [1977]:

1. n-alkanes, C_{10}-C_{25}
2. iso-alkanes, increase in degree of branching decreases the biodegradability
3. olefins
4. low molecular weight aromatic hydrocarbons
5. polynuclear aromatic hydrocarbons (PAHs)
6. cycloalkanes

Following the above findings, the cycloalkanes would be the slowest to be biodegraded and should be present in the soil for a longer time relative to other groups. Emission rates obtained at Port 1 do suggest that initially cycloalkanes are present in large concentrations. However, there were no cycloalkanes seen in samples obtained on any sampling day on the surface, and emissions should have been detected from the PL pile surface.

A possibility exists that through channeling and short-circuiting the exhaust gas measurements were not representative of the pile. If a significant fraction of the exhaust air passed through a small volume of the pile, uncharacteristically high in cycloalkanes, the results given in Tables 2.5 through 2.7 would have been obtained.

In the absence of gas standards, estimation of the absolute quantities of contaminants emitted from the surface and in the PL pile exhaust were based upon dichloromethane and toluene standards. The order of magnitudes of compounds being volatilized on the surface of the pile and the compounds in Port 1 samples were similar. Estimation of the concentration of contaminants based on the concentrations of two different compounds in a standard showed that the concentrations over time showed similar trends except for cycloalkanes and aldehydes. However, the concentrations based on toluene standards were more than double the concentrations based on dichloromethane standards. The data are believed to be acceptable in a qualitative but not a quantitative sense.

Summary

The results of this experiment can be summarized as follows:

1. The compounds appearing in the GC/MS analysis of the gas samples collected at MAFB could not be identified or quantified individually due to the lack of matching standards. Based on the characteristic ions appearing in the ion chromatograph and the computer library match of the ion spectrum, the species in the various peaks were classified as being: alkanes, cycloalkanes, alcohols, aldehydes, and ketones. The emission of alcohols and acids is consistent with these compounds being products of aerobic biodegradation.
2. In the absence of matching gas standards, toluene and dichloromethane standards were used as alternatives in estimating the concentrations of the above contaminants. This method did not prove to be satisfactory.
3. Total surface emissions from the soil pile were initially lower than emissions in the exhaust gas, but later became higher. This is believed to be the result of short-circuiting in the pile. The volatile compounds were not completely captured by the induced flow.
4. The initial analysis of the soil samples indicated the presence of long-chain alkanes and cycloalkanes. In later analysis, more alcohols (possible products of biodegradation) could be seen compared to the alkanes. No acids were detected during analysis, which could have been the result of acids being lost during the thermal desorption process.

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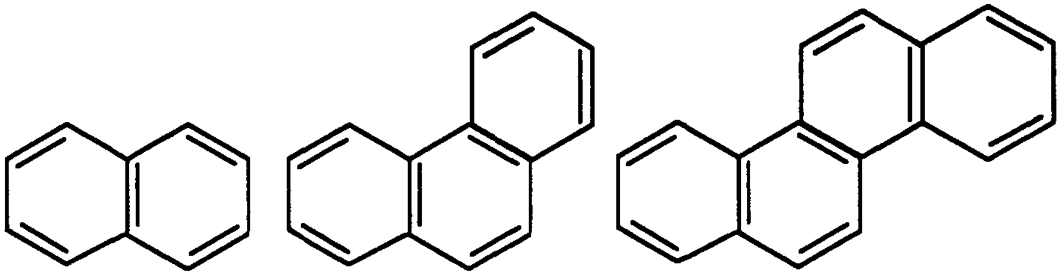
McLafferty, F.W.,*Interpretation of Mass Spectra An Introduction*, W.A.Benjamin, Inc., New York, Amsterdam, 1966.

Perry, R. H., Green, D., *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw Hill Book Company, New York, 1984.

III. LABORATORY SCALE LANDFARM EXPERIMENT

A two-cell laboratory scale landfarm was constructed of polyurethane coated plywood sheets and a soil mixture composed of Yolo silt loam. Three PAHs, naphthalene, phenanthrene, and chrysene (shown below) and a microbial culture were added to the soil at the beginning of the experiment. Soil extracts and vapor phase samples were taken at selected time intervals and analyzed using GC/MS.



Naphthalene Phenanthrene Chrysene

Figure 3.1
Chemical structure of naphthalene, phenanthrene, and chrysene, the three PAHs used in the laboratory landfarm experiment.

LANDFARM DESIGN AND OPERATION

The laboratory scale landfarm was composed of a two-cell box with soil in one of the two cells. Tilling was achieved by transferring the soil from one cell to the other cell on a weekly basis.

Soil Box

The soil box was constructed of 3/4 inch thick plywood sheets. Outside dimensions of the box were 4 ft x 4 ft x 10 inches. Two cells, each 4 ft x 2 ft x 8 inches deep were created by placing an eight inch wide plywood strip down the center of the box, as shown in Figure 3.2. The box was set on a 1% grade, leading into drainage holes in the corner of each cell. The purpose of the slope and drains was to collect excess water for recycle. However, through the duration of the experiment, the moisture content of the soil was maintained below field capacity and excess water was not collected at the drains. The box seams were sealed with silicone sealant and all surfaces were given five coats of Flecto Varathane® 92 clear gloss exterior wood finish, a polyurethane plastic coating. The box was then allowed to dry for 3 months to minimize contributions of VOCs from the coating chemicals during the experiment.

Soil Characteristics

Yolo silt loam was collected in December, 1992 from the UC Davis student experimental farms located on Hutchinson Road, west of State Highway 113. Two soil samples were analyzed at the DANR analytical laboratory on the UC Davis campus and results of the analyses are given in Table 3.1.

The soil was initially at field capacity with respect to water content and was dried in the laboratory for approximately two weeks prior to being passed through a 2 mm sieve to provide homogeneity. Sand (Lone Star™, 30 mesh sand) was added to the soil to improve workability and structure. Addition of the sand was accomplished by dividing the dried Yolo silt loam into 10 batches of equal weight and mixing each batch with the appropriate amount of sand in a concrete mixer. The soil mixture characteristics after addition of the sand are given in Table 3.1.

Table 3.1
Characteristics of soil used in laboratory landfarm experiment

		Content, % by weight				
Sample	pH	Nitrogen	Organic	Sand	Silt	Clay
1	6.9	0.143	2.33	25	51	24
2	6.9	0.128	2.26	23	53	24
Mixture	6.9	0.116[a]	1.96[a]	35	43	22

[a]calculated

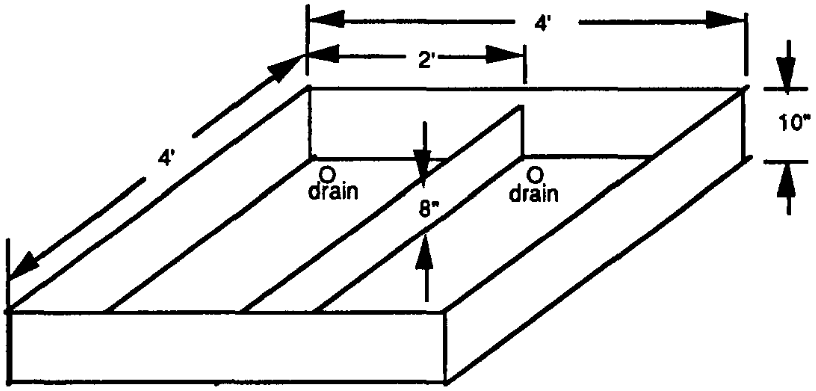


Figure 3.2
Soil-box used in laboratory scale landfarm experiment

PAH Characteristics

The three PAHs used in this experiment were selected to provide a range of volatility and biodegradability. Physical characteristics of the compounds are given in Table 3.2. The source of the compounds was Aldrich Chemical Company and purities of the compounds were 98%. Only naphthalene is considered to be volatile enough to produce significant emissions from contaminated soils.

Initial concentrations of the three PAHs was 130 mg naphthalene per kg soil and 100 mg phenanthrene per kg soil and 100 mg chrysene per kg soil. The greater initial concentration of naphthalene was selected because of the compounds higher relative volatility.

Microbial Culture

Because the purpose of the experiment was to identify volatile biodegradation products, it was important to ensure that biodegradation began in the laboratory scale system without a long lag period. Microbial cultures capable of degrading each of the three PAHs were developed using activated sludge from the UC Davis wastewater treatment plant and soil taken from a bioremediation site at Coalinga, CA Class I that had been undergoing treatment for PAH contamination.

Microbial cultures were developed by inoculating 40 mL volumes of BOD dilution water [American Public Health Association, 1985] containing 100 mg/L of the target PAHs with activated sludge and Coalinga soil microorganisms. Three sets of three 40 mL volumes were made up containing 100 mg/L of one of the three compounds, naphthalene, phenanthrene, or chrysene. One 40 mL volume in each set was set aside as a blank, 1 mL of activated sludge was added to one of the 40 mL volumes, and 1 mL of supernatant from washed Coalinga soil was added to the remaining 40 mL volume. The nine samples were placed on a shaker and incubated at 37 °C for two weeks. At the end of the two week incubation period growth in the samples was measured by relative turbidity. Turbidity values of the blanks were greater than 0 due to the insolubility of the PAHs. Results of the turbidity measurements are given in Table 3.3.

Table 3.2
Physical Properties of Target PAHs

Compound	Formula	Molecular weight	Solubility[a] @ 25°C mg/L	Vap. pres. @ 25°C mm Hg	Boiling point °C
Naphthalene	$C_{10}H_8$	128	30	0.05	218
Phenanthrene	$C_{14}H_{10}$	178	1	6.8×10^{-4}	339
Chrysene	$C_{18}H_{12}$	228	0.002	6×10^{-9}	448

[a]solubility in water

Table 3.3
Microbial growth using naphthalene, phenanthrene, and chrysene as substrates and activated sludge and a culture taken from a hazardous waste landfill as inoculants

		Turbidity	
Compound	Blank	Activated Sludge	Coalinga Soil
Naphthalene	3.1	4.5	5.7
Phenanthrene	4.2	12	22
Chrysene	84	98	120

The samples were incubated at 37 °C for 3 additional weeks and aliquots from each bottle were plated in duplicate on triptocase soy agar (TSA) media. The plates were incubated for 3 days at 37 °C. Plates from the blanks showed no bacterial growth, whereas the plates from all other bottles had a significant number of colonies.

Addition of Water, Microorganisms, and Chemicals

Water, PAHs, microbial inoculum and nutrients were added to the soil and mixed by hand using a trowel for 30 minutes. The final mixture was placed in one of the two cells of the soil-box at the beginning of the experiment. Addition of water, PAHs, microbial inoculum and nutrients to the soil was based on an estimate of 230 kg of dry soil required to fill one compartment of the soil-box. To bring the soil to a water content of 13 % (dry weight basis), 30 liters of water was required (3 liters for each of the 10 batches of soil). Because aqueous solubilities of the three PAHs were low, the compounds were initially dissolved in 200 mL of toluene. The toluene was expected to volatilize quickly after application to the soil. Initial concentrations of the three PAHs were 130 mg naphthalene per kg soil and 100 mg phenanthrene per kg soil and 100 mg chrysene per kg soil. As stated above, the greater initial concentration of naphthalene was selected because of the compound's higher relative volatility. Twenty milliliters of the toluene-PAH mixture was then added to 3 liters of water and the mixture was continuously mixed with a magnetic stirrer. The microbial inoculum (described below) was then added to the water-toluene-PAH mixture and the suspension was mixed into 23 kg of soil.

Temperature Control

Microbial processes are highly temperature sensitive and under optimal environmental conditions microbial growth rates and biodegradation rates approximately double with each 10 °C increase in temperature. Conditions in soil are usually quite far from optimal with respect to availability of limiting nutrients, temperature, and moisture content. However, the impact of environmental temperature should be significant. At the beginning of the landfarm experiments soil temperature was 16 °C. Four heating lamps were placed 18" above the soil surface and controlled using a thermocouple at mean soil depth and a thermostat set turn the lights off at 21°C. The lamps were removed after two weeks and during the remaining period of the experiment the soil temperature ranged between 18 °C and 23 °C.

Landfarm Operation

Soil was tilled once each week using a hand trowel to mix and move the soil from one compartment to the other compartment of the soil-box. Water was added to the soil on a daily, or alternate day basis, based on visual observation of surface dryness. Moisture content of the soil never exceeded field capacity, which is typically about 23% for Yolo silt loam and would have been somewhat less for the mixture used in this study. Measured values of the soil moisture ranged between 13 and 18 percent, as shown in Table 3.4. Although moisture conditions in the soil were not closely controlled good removals of all three PAHs occurred and based on this fact biodegradation was satisfactory, if not optimal.

Table 3.4
Soil Moisture Content

Date	Moisture content, % dry weight
4/1/93	13.3
4/14/93	13.2
4/21/93	16.2
4/28/93	16.9
5/5/93	18.3
5/14/93	17.7

SAMPLING PROTOCOL

Vapor phase samples were taken with the same surface isolation flux chamber (SIC) used for the McClellan AFB studies. Zero grade air was used as the carrier gas, with an inlet flow of about 2.5 L/min. The air samples were pulled out at a flow rate of 30 to 40 mL/min. Samples were taken once a week, or once every 10 days, at the time of soil tilling. Sampling for the volatile air emissions started one week after the experiment started, while sampling for the semi-volatiles started two weeks after the experiment started.

Volatile Air Emissions

Duplicate volatile compound samples were taken before and after tilling. Initially, blanks were taken by placing the SIC on a tedlar sheet in the soil box. Because of the appearance of unexpected compounds, later blanks were taken in the soil box without the tedlar sheet. The purpose of the blank samples was to identify any background emissions from the room, the soil box and the paint that is on it, and the SIC itself. All samples were taken on custom made Supelco glass sorbent tubes, 4 mm ID, containing a mixture of Carbopak^{TM} and Carbosieve^{TM}III. The sampling time ranged between 10 and 30 minutes, thus making the volume of air sampled range between 400 and 1200 mL. After sampling, the sorbent tubes were kept in a refrigerator for about 6 days prior to analysis. Unfortunately, other chemicals stored in the refrigerator were later found to have possibly affected the original samples.

The VOC samples were analyzed on a Hewlett Packard 5980A gas chromatograph and a Hewlett Packard 59970 mass spectrometer.. A glass capillary column, J & W Scientific DB624, was used. The temperature program was such that the initial time was zero minutes, and the initial temperature was 40°C, increasing at a rate of 7°C per minute, to reach a maximum of 250°C, with a final time of 5 minutes, thus adding to a total run time of 35 minutes.

Table 3.5
Sampling for volatile air emissions:

	Blank		Before Tilling		After Tilling	
Date	# of samples	Volume mL	# of samples	Volume mL	# of samples	Volume mL
4/7/93	2	450	2	600	2	450
4/14/93	2	600	2	600	2	400
4/21/93	1	600	1	600	1	600
4/28/93	2	450	-	-	2	450
5/14/93	1	800	2	1200	2	1200

Semi-volatile Air Emissions

Semi-volatile air emission samples were taken after tilling the soil. Glass tubes, 6 mm OD, filled with Carbotrap C (graphitized carbon) 20/40 mesh from Supelco (surface area 12 m^2/g), were used for sampling. Three tubes were used each time. The sampling time ranged between 5 and 6 hours, to ensure a volume of air sampled, within the three tubes, of 30 liters or more (Table 3.6). During sampling, the SIC was moved from one spot on the soil to another every hour.

Table 3.6
Sampling for semi-volatile air emissions

Date	Volume liters
4/14/93	36.0
4/21/93	55.0
5/5/93	29.9
5/14/93	37.6
5/21/93	44.2
6/4/93	43.1

After sampling, the Carbotrap material in the glass tubes was emptied into a cellulose extraction thimble, and Soxhlet extraction with dichloromethane (see Appendix A) was used to extract the semi-volatiles from the Carbotrap. The dichloromethane solution was then concentrated using a rotary evaporator, to a volume of about 1 to 3 mL. A few microliters of the concentrate was then injected into the GC/MS using a DB-5.625 column. The temperature program was such that the initial time was 4 minutes, the initial temperature was 50°C, increasing at a rate of

8°C/min, to a maximum of 310°C, and a final time of 20 minutes, resulting in a total run time of 56.5 minutes. A standard solution with known concentrations of PAHs was used for comparison.

Soil Samples

Samples were taken during soil tilling. To achieve a representative sample, the soil was collected from different spots within the box. A 25 g aliquot of each sample was then analyzed, first by carrying out a Soxhlet extraction with dichloromethane, as described above and in Appendix A. After concentrating the solution, the sample was fractionated (as described in Chapter II), to separate the polar and nonpolar compounds . The fractionate was then concentrated again to a volume of about 1 to 3 mL. A few microliters of the concentrate were then injected into the GC/MS, using the same column and the same temperature program used for the semi-volatile samples.

RESULTS

The results of the laboratory scale landfarm experiment are presented below. There is good evidence that the three target PAHs were biologically degraded. Production of VOCs as metabolic end products is less clear. Of the three target PAHs only naphthalene was identified in the vapor phase samples and none of the three were identified in the semi-volatile samples. However, all three target compounds, naphthalene, phenanthrene, and chrysene were identified in the soil extracts. Compounds identified in the soil extracts that could be products of biodegradation included ethyl benzene, and 1,3-dimethyl benzene. A number of larger compounds ($> C_{18}$) were also identified and these may be normal humic substances in the soil. Similar results were recorded for the semi-volatile and volatile analyses. Although quantification of the vapor phase samples was not possible, the relative abundance of the compounds was low.

Vapor Phase Samples

The analysis of the volatile compound samples taken with the SIC, indicated the presence of a considerable number of contaminants, most of which are believed to have been present due to problems in sampling and storage. Contaminants that appeared in the blanks, or in the quality control tests were ruled out as being degradation products. As an example, toluene and styrene were chemicals that were identified in the volatile compound samples. Toluene and styrene are highly biodegradable compounds that are possible PAH degradation products. However, neither toluene nor styrene are likely to have been produced under aerobic conditions. The compounds were found in the sample blanks as well as the refrigerator blanks. Because these tubes may have been used previously in studies involving toluene, hexane (methyl pentane) and styrene, it is more likely that the tubes were insufficiently cleaned prior to use. Our experience with sorbent tubes indicates that when they are stored for periods of several weeks, material deep within the pore structure of the sorbent can diffuse out. Although the tubes may appear to be clean immediately after use, or for a few days, they will "bleed" compounds after several weeks. Therefore the presence of these two compounds is assumed to have resulted from contamination. There is also a possibility of contamination from the Varathane™ coating of the soil box. This possibility was investigated but the results were indeterminate.

Two conclusions can be made about the volatile compounds samples:

1. Naphthalene is the only one of the three target compounds that appeared in the volatile samples. The fact that naphthalene gradually disappears with time fits well with the literature information on the compound's volatility and biodegradability. Naphthalene also disappeared with time from the soil extracts, as shown in Table 3.7.

Table 3.7
Naphthalene disappearance with time, based on area (in millions) under peak in the total ion chromatograph (TIC)

Date	Blank Samples			Samples Before Tilling			Samples After Tilling		
	1	2	average	1	2	average	1	2	average
4/7/93	0	62	31	2897	3067	2982	1527	754	1141
4/14/93	-	-	-	-	-	-	-	-	-
4/21/93	-	-	-	-	-	-	-	-	-
4/28/93	-	-	-	-	-	-	-	-	-
5/14/93	-	-	-	-	-	-	-	-	-

2. Butanoic acid, butyl ester ($C_8H_{16}O_2$) was identified in the volatile compounds samples at the end of the sampling period, as shown below in Table 3.8, and also appeared in the semi-volatile compounds samples.

Table 3.8
Butanoic acid, butyl ester appearance with time, based on area (in millions) under peak in the total ion chromatograph (TIC)

Date	Blank Samples			Samples Before Tilling			Samples After Tilling		
	1	2	average	1	2	average	1	2	average
4/7/93	-	-	-	-	-	-	-	-	-
4/14/93	-	-	-	-	-	-	-	-	-
4/21/93	-	-	-	-	-	-	-	-	-
4/28/93	-	-	-	-	-	-	-	-	-
5/14/93	0	0	0	3.66	9.83	6.75	9.04	6.19	7.61

Qualitative analysis of the semivolatile compounds was done using a PAH semi-volatile standard. Identification of the standard compounds was satisfactory, as indicated in Table 3.9 and the compounds identified in sampling program that could be degradation products are listed in Table 3.10. The elution times of the standards were used to identify semivolatile compounds in the vapor phase samples. Semi-volatile compounds identified in the SIC sampling program are listed in Tables 3.11 through 3.16.

Table 3.9
Semi-volatile compound PAH standard[*].

Time (min)	Peak	Mol. Formula	Mol. Weight	% Match
13.23	azulene	$C_{10}H_8$	128	94
	naphthalene	$C_{10}H_8$	128	94
18.29	biphelylene	$C_{12}H_8$	152	86
	acenaphthylene	$C_{12}H_8$	152	70
18.83	acenaphthylene, 1,2-dihydro-	$C_{12}H_{10}$	154	95
20.44	9-H fluorene	$C_{13}H_{10}$	166	93
23.43	phenanthrene	$C_{14}H_{10}$	178	96
	anthracene	$C_{14}H_{10}$	178	93
23.59	phenanthrene	$C_{14}H_{10}$	178	95
	anthracene	$C_{14}H_{10}$	178	94
27.18	fluoranthene	$C_{16}H_{10}$	202	95
	pyrene	$C_{16}H_{10}$	202	93
27.85	pyrene	$C_{16}H_{10}$	202	95
	fluoranthene	$C_{16}H_{10}$	202	94
31.69	chrysene	$C_{18}H_{12}$	228	98
	benz[a]anthracene	$C_{18}H_{12}$	228	97
31.79	chrysene	$C_{18}H_{12}$	228	97
	benz[a]anthracene	$C_{18}H_{12}$	228	91
34.89	perylene	$C_{20}H_{12}$	252	97
	benzo[k]fluoranthene	$C_{20}H_{12}$	252	96
	benzo[j]fluoranthene	$C_{20}H_{12}$	252	95
35.76	benzo[j]fluoranthene	$C_{20}H_{12}$	252	97
	benzo[a]pyrene	$C_{20}H_{12}$	252	97
	benzo[e]pyrene	$C_{20}H_{12}$	252	95
38.87	indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	97
	benzo[ghi]perylene	$C_{22}H_{12}$	276	93
39.01	1,2:3,4-dibenzoanthracene	$C_{22}H_{14}$	278	95
	benzo[b]chrysene	$C_{22}H_{14}$	278	72
39.69	benzo[ghi]perylene	$C_{22}H_{12}$	276	97

[*] injection volume was 2 µL, File Name: ST1617.D

Table 3.10
Compounds identified in semi-volatile sampling that may be biodegradation PAH products.

Compound	Formula	Molecular Weight
Butanoic acid, butyl ester	$C_8H_{16}O_2$	144
Butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172
Propanoic acid, 2-methyl-, 3-hydroxy-	$C_{12}H_{24}O_3$	216
Propanoic acid, 2-methyl-, 2-ehtyl-3-	$C_{12}H_{24}O_3$	216
1,2-benzenedicarboxylic acid, dipropyl	$C_{14}H_{18}O_4$	250
1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278
1,2-benzenedicarboxylic acid, butyl 2-ehtyl	$C_{20}H_{30}O_4$	334

Table 3.11

Qualitative analysis of semi-volatiles in landfarm emissions on 4/14/93[a]

Time (min)	Peak	Mol. Formula	Mol. Weight	% Match
major peaks				
16.79	butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172	64*
	propanoic acid, 2-methyl-, 3-hydroxy-2,4	$C_{12}H_{24}O_3$	216	59*
25.6	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	97
28.62	dotriacontane	$C_{32}H_{66}$	451	83
	tridecane	$C_{13}H_{28}$	184	80
	heneicosane	$C_{21}H_{44}$	296	74
29.77	tetracosane, 2,6,10,15,19,23-hexamethyl-	$C_{30}H_{62}$	422	78
	tetradecane	$C_{14}H_{30}$	198	64*
	nonadecane	$C_{19}H_{40}$	268	64*
30.87	dotriacontane	$C_{32}H_{66}$	451	86
	octacosane	$C_{28}H_{58}$	394	74
	eicosane	$C_{20}H_{42}$	282	72
other peaks				
8.1	3-(methylthio)butanoic acid	$C_6H_{12}O_2S$	148	38*
9.64	cyclohexanol, 4-chloro-, trans-	$C_6H_{11}ClO$	134	32*
16.37	propionic acid, 2-methyl-, 2,2-dimethyl-			35*
20.38	butanoic acid, 1-methyloctyl ester	$C_{13}H_{26}O_2$	214	50*
24.33	1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	278	78

[a]5 micro liters injected Date Sampled: 4/14/93 Date Analyzed: 6/17/93 File Name: SV2414.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.12

Qualitative analysis of semi-volatiles in landfarm emissions on 4/21/93[a]

Time, min	Peak	Mol. Formula	Mol. Weight	% Match
major peaks				
16.36	propionic acid, 2-methyl-, 3-hydroxy-2,4	$C_{12}H_{24}O_3$	216	50*
16.79	propionic acid, 2-methyl-,2-ethyl-3-hydroxyhexyl ester	$C_{12}H_{24}O_3$	216	64*
	butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172	64*
20.38	propionic acid, 2-methyl-, 2-(hydroxymethyl)-1-propylbutyl ester	$C_{12}H_{24}O_3$	216	45*
24.34	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	78
	1,2-benzenedicarboxylic acid, dipropyl ester	$C_{14}H_{18}O_4$	250	72
25.61	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	96
	1,2-benzenedicarboxylic acid, butyl 2-methylpropyl ester	$C_{16}H_{22}O_4$	278	90
28.63	dotriacontane	$C_{32}H_{66}$	451	86
	docosane	$C_{22}H_{46}$	310	80
	nonadecane	$C_{19}H_{40}$	268	76
29.78	tricosane	$C_{23}H_{48}$	324	93
	heptadecane	$C_{17}H_{36}$	240	80
30.88	pentadecane	$C_{15}H_{32}$	212	87
	tridecane, 4,8-dimethyl-	$C_{15}H_{32}$	212	86

[a] Semi-Volatiles (Carbotrap), 4 micro liters injected. Date Sampled: 4/21/93 Date Analyzed: 6/17/93 File Name: SV421.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.13

Qualitative analysis of semi-volatiles in landfarm emissions on 5/5/93[a]

Time, min	Peak	Mol. Formula	Mol. Weight	% Match
major peaks				
16.36	propionic acid, 2-methyl-, 2,2-dimethyl-	$C_{12}H_{24}O_3$	216	50*
	propionic acid, 2-methyl-, 3-hydroxy-2,4	$C_{12}H_{24}O_3$	216	38*
	butanoic acid, butyl ester	$C_8H_{16}O_2$	144	37*
16.79	butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172	64*
	propionic acid, 2-methyl-, 3-hydroxy-2,4	$C_{12}H_{24}O_3$	216	53*
20.37	2-methoxyallyl bromide	C_4H_7BrO	150	50*
	propionic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	$C_{16}H_{30}O_4$	286	38*
24.33	1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	278	72
	1,2-benzenedicarboxylic acid, butyl 2-methylpropyl ester	$C_{16}H_{22}O_4$	278	72
	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	72
25.59	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	96
28.62	tridecane	$C_{13}H_{28}$	184	86
	dotriacontane	$C_{32}H_{66}$	451	86
	hexadecane	$C_{16}H_{34}$	226	72
29.76	hexatriacontane	$C_{36}H_{74}$	507	90
	dotriacontane	$C_{32}H_{66}$	451	90
	heptadecane	$C_{17}H_{36}$	240	80
30.86	hexatriacontane	$C_{36}H_{74}$	507	90
	octacosane	$C_{28}H_{58}$	394	87

[a] Semi-Volatiles (Carbotrap), 3 micro liters injected Date Sampled: 5/5/93 Date Analyzed: 6/18/93 File Name: SV505.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.14

Qualitative analysis of semi-volatiles in landfarm emissions on 5/14/93^a

Time, min	Peak	Mol. Formula	Mol. Weight	% Match
major peaks				
16.37	propionic acid, 2-methyl-, 2-ethyl-3-hydroxyhexyl ester	$C_{12}H_{24}O_3$	216	38*
16.79	butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172	72
20.38	furan, 2-butyltetrahydro-	$C_8H_{16}O$	128	58*
	pentan-1, 3-dioldiisobutyrate, 2,2,4-trimethyl-	$C_{16}H_{30}O_4$	286	50*
24.33	1,2-benzenedicarboxylic acid, dipropyl ester	$C_{14}H_{18}O_4$	250	64*
	1,2-benzenedicarboxylic acid, butyl 2-ethylhexyl ester	$C_{20}H_{30}O_4$	334	64*
	1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	278	64*
25.6	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	97
28.63	docosane	$C_{22}H_{46}$	310	89
	nonadecane	$C_{19}H_{40}$	268	72
29.77	heptadecane	$C_{17}H_{36}$	240	72
	tricosane	$C_{23}H_{48}$	324	68*
30.87	undecane, 3-methyl-	$C_{12}H_{26}$	170	78
	tetracosane	$C_{24}H_{50}$	338	76

^{a}Semi-Volatiles (Carbotrap), 3 micro liters injected. Date Sampled: 5/14/93 Date Analyzed: 6/17/93 File Name: SV1514.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.15

Qualitative analysis of semi-volatiles in landfarm emissions on 5/21/93^a

Time, min	Peak	Mol. Formula	Mol. Weight	% Match
16.36	propionic aicd, 2-methyl-, 2,2 dimethyl-1-	$C_{12}H_{24}O_3$	216	50*
16.78	propionic acid, 2-methyl-, 3-hydroxy-2,4	$C_{12}H_{24}O_3$	216	90
	butanoic acid, hexyl ester	$C_{10}H_{20}O_2$	172	56*
20.37	propionic aicd, 2-methyl-, 1-(1,1-dimethyl	$C_{16}H_{30}O_4$	286	59*
24.34	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	64
25.6	1,2-benzenedicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	278	96
28.63	hexatriacontane	$C_{36}H_{74}$	506	58*
	eicosane	$C_{20}H_{42}$	282	58*
29.76	hexadecane, 3-methyl-	$C_{17}H_{36}$	240	59*
30.87	octacosane	$C_{28}H_{58}$	394	50*
	eicosane	$C_{20}H_{42}$	282	50*

^{a}Semi-Volatiles (Carbotrap), 4 micro liters injected. Date Sampled: 5/21/93 Date Analyzed: 6/18/93 File Name: SV521.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.16

Qualitative analysis of semi-volatiles in landfarm emissions on 6/4/93[a]

Time, min	Peak	Mol. Formula	Mol. Weight	% Match
9.65	1-nonen-3-ol	$C_9H_{18}O$	142	10*
16.38	propanoic aicd, 2-methyl-, 2-methylpropyl ester	$C_8H_{16}O_2$	144	38*
16.80	propionic aicd, 2-methyl-, 3-hydroxy-2,4,4-trimethyl pentyl ester	$C_{12}H_{24}O_3$	216	64*
20.40	butanoic acid, 1-methyloctyl ester	$C_{13}H_{26}O_2$	214	47*
24.34	1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	278	38*
25.62	1,2-benzenedicarboxylic acid, butyl 2-methylpropyl ester	$C_{16}H_{22}O_4$	278	87
28.63	dotriacontane	$C_{32}H_{66}$	450	64*
	nonadecane	$C_{19}H_{40}$	268	64*
29.78	tridecane	$C_{13}H_{28}$	184	76
30.88	dotriacontane	$C_{32}H_{66}$	450	86
	tetracosane	$C_{24}H_{50}$	338	76
31.94	tricosane	$C_{23}H_{48}$	324	76

[a] Semi-Volatiles (Carbotrap), 4 micro liters injected. Date Sampled: 6/4/93 Date Analyzed: 7/1/93 File Name: BSV64.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Soil Extraction

The compounds present in the PAH standard used for the soil extraction analyses are given in Table 3.17 together with the experimentally determined elution times. Compounds identified in the soil extraction analyses are given in Table 3.18 through 3.25. Quantitative analysis was possible for the three target PAHs and the results are presented in Table 3.25 and Figure 3.3.

Summary

The results of this experiment can be summarized as follows:

1. Naphthalene was the only one of the three PAH contaminants that appeared in the volatile samples analysis.
2. Butanoic acid, butyl ester (a possible biodegradation product) was detected in the volatile compounds samples six weeks after the beginning of the experiment.
3. Several acids (table 3.1) were detected in the semi-volatile compound samples. The presence of these acids is consistent with these compounds being products of aerobic biodegradation. The concentrations of these compounds could not be estimated because of the lack of matching standards.
4. The results of the soil extractions confirmed that biodegradation was occurring as the contaminants' concentrations were decreasing with time. Since phenanthrene and chrysene were not detected in the volatile or the semi-volatile compounds samples, it is believed that they disappeared mostly through biodegradation.

Table 3.17

Qualitative analysis of soil extract PAH Standard experiments[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
13.27	Naphthalene	$C_{10}H_8$	128	95
18.34	Biphenylene	$C_{12}H_8$	152	86
	Acenaphthylene	$C_{12}H_8$	152	70
18.88	Acenaphthylene, 1,2-dihydro-	$C_{12}H_{10}$	154	95
20.46	9H-Fluorene	$C_{13}H_{10}$	166	93
23.45	Phenanthrene	$C_{14}H_{10}$	178	95
23.61	Anthracene	$C_{14}H_{10}$	178	96
27.21	Fluoranthene	$C_{16}H_{10}$	202	95
27.88	Fluoranthene	$C_{16}H_{10}$	202	96
	Pyrene	$C_{16}H_{10}$	202	87
31.71	Chrysene	$C_{18}H_{12}$	228	98
	Benz[a]anthracene	$C_{18}H_{12}$	228	98
31.82	Chrysene	$C_{18}H_{12}$	228	98
34.93	Benzo[a]pyrene	$C_{20}H_{12}$	252	97
35.00	Benzo[j]fluoranthene	$C_{20}H_{12}$	252	99
35.79	Benzo[j]fluoranthene	$C_{20}H_{12}$	252	97
	Benzo[e]pyrene	$C_{20}H_{12}$	252	95
	Benzo[a]pyrene	$C_{20}H_{12}$	252	93
38.93	Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	99
	Benzo[ghi]perylene	$C_{22}H_{12}$	276	95
39.10	1,2:3,4-Dibenzoanthracene	$C_{22}H_{14}$	278	87
	Dibenzo[a,h]anthracene	$C_{22}H_{14}$	278	87
39.80	Bnezo[ghi]perylene	$C_{22}H_{12}$	276	93

[a] PAH standard, 2 micro liters injected. Date Sampled: 7/1/93 Date Analyzed: 7/1/93 File Name: BST71.D

Table 3.18

Qualitative analysis of soil extract from landfarm experiments 4/1/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
5.18	Benzene, ethyl-	C_8H_{10}	106	91
	Benzene, 1,2-dimethyl-	C_8H_{10}	106	91
5.42	Benzene, 1,3-dimethyl-	C_8H_{10}	106	95
	Xylene	C_8H_{10}	106	94
13.26	Azulene	$C_{10}H_8$	128	95
	Naphthalene	$C_{10}H_8$	128	91
23.05	Dibenzothiophene	$C_{12}H_8S$	184	97
23.55	Phenanthrene	$C_{14}H_{10}$	178	95
29.78	Eicosane	$C_{20}H_{42}$	282	95
30.91	Benzo[b]naphtho [2,1-d]thiophene	$C_{16}H_{10}S$	234	98
31.87	Chrysene	$C_{18}H_{12}$	228	98

[a] Soil extract (only PAH fraction), 4 micro liters injected. Date Sampled: 4/1/93 Date Analyzed: 7/1/93 File Name: BSO41.D

Table 3.19

Qualitative analysis of soil extract from landfarm experiments 4/7/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
5.19	Benzene, ethyl-	C_8H_{10}	106	91
5.43	Xylene	C_8H_{10}	106	95
	Benzene, 1,3-dimethyl-	C_8H_{10}	106	95
13.24	Azulene	$C_{10}H_8$	128	94
	Naphthalene	$C_{10}H_8$	128	94
23.50	Phenanthrene	$C_{14}H_{10}$	178	96
30.91	Benzo(b)naphtho (2,3-d)thiophene	$C_{16}H_{10}S$	234	97
31.88	Chrysene	$C_{18}H_{12}$	228	97

[a] Soil extract (only PAH fraction), 4 micro liters injected. Date Sampled: 4/7/93 Date Analyzed: 7/1/93 File Name: BSO47.D

Table 3.20

Qualitative analysis of soil extract from landfarm experiments 4/14/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
5.18	Benzene, ethyl-	C_8H_{10}	106	90
5.42	Xylene	C_8H_{10}	106	95
	Benzene, 1,4-dimethyl-	C_8H_{10}	106	95
5.46	Benzene, 1,2-dimethyl-	C_8H_{10}	106	95
5.93	2-Pentene, 4,4-dimethyl-	C_7H_{14}	98	27*
	4-Hexen-2-one, 3,4-dimethyl-	$C_8H_{14}O$	126	16*
7.48	3-Hexanol	$C_6H_{14}O$	102	43*
	Butanoic acid, 3-hydroxy-3-methyl-,	$C_6H_{12}O_3$	132	40*
7.73	Pentanoic acid, propyl ester	$C_8H_{16}O_2$	144	50*
13.21	Azulene	$C_{10}H_8$	128	94
	Naphthalene	$C_{10}H_8$	128	93
23.45	Phenanthrene	$C_{14}H_{10}$	178	95
30.91	Benzo[b]naphtho [2,1-d]thiophene	$C_{16}H_{10}S$	234	95
31.87	Chrysene	$C_{18}H_{12}$	228	98

[a] Soil extract (only PAH fraction), 3 micro liters injected. Date Sampled: 4/14/93 Date Analyzed: 7/1/93 File Name: BSO414.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.21

Qualitative analysis of soil extract from landfarm experiments 4/21/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
23.45	Phenanthrene	$C_{14}H_{10}$	178	95
31.92	Chrysene	$C_{18}H_{12}$	228	96

[a] Soil extract (only PAH fraction), 3 micro liters injected. Date Sampled: 4/21/93 Date Analyzed: 7/1/93 File Name: BSO421.D

Table 3.22

Qualitative analysis of soil extract from landfarm experiments 4/28/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
23.44	Phenanthrene	$C_{14}H_{10}$	178	94
26.97	methanone, bis [4-(diethylamino) phenyl]-	$C_{21}H_{28}N_2O$	324	59*
28.64	octadecane	$C_{18}H_{38}$	254	70
29.79	eicosane, 10-hexyl-10-methyl-	$C_{27}H_{56}$	380	38*
30.90	eicosane, 10-butyl-10-propyl-	$C_{27}H_{56}$	380	47*
31.84	Chrysene	$C_{18}H_{12}$	228	98
33.00	tricosane	$C_{23}H_{48}$	324	60*

[a]Soil extract (only PAH fraction), 4 micro liters injected Date Sampled: 4/28/93 Date Analyzed: 7/1/93 File Name: BSO428.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.23

Qualitative analysis of soil extract from landfarm experiments 5/14/93[a]

Time,min	Peak	Mol. Formula	Mol. Wt	% Match
5.4	Benzene, 1,3-dimethyl-	C_8H_{10}	106	96
23.44	Phenanthrene	$C_{14}H_{10}$	178	97
27.44	Tritetracontane	$C_{43}H_{88}$	605	72
	Heneicosane	$C_{21}H_{44}$	296	70
28.64	Hexatriacontane	$C_{36}H_{74}$	507	76
	Docosane	$C_{22}H_{46}$	310	70
	Eicosane	$C_{20}H_{42}$	282	58*
29.78	Tetracosane	$C_{24}H_{50}$	338	91
30.89	Tetracosane	$C_{24}H_{50}$	338	86
31.85	Chrysene	$C_{18}H_{12}$	228	98
31.94	Dotriacontane	$C_{32}H_{66}$	451	64*
	Eicosane	$C_{20}H_{42}$	282	62*
32.98	Heptadecane	$C_{17}H_{36}$	240	76
33.98	Eicosane	$C_{20}H_{42}$	282	95
34.96	Eicosane	$C_{20}H_{42}$	282	95
35.94	Eicosane	$C_{20}H_{42}$	282	90
36.93	Eicosane	$C_{20}H_{42}$	282	74
38.01	Cyclotrisiloxane, hexamethyl-	$C_6H_{18}O_3Si_3$	222	43*
	Eicosane	$C_{20}H_{42}$	282	35*

[a]Soil extract (only PAH fraction), 3 micro liters injected Date Sampled: 5/14/93 Date Analyzed: 7/1/93 File Name: BSO514.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.24

Qualitative analysis of soil extract from landfarm experiments 5/28/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
23.42	Phenanthrene	$C_{14}H_{10}$	178	49*
31.84	Chrysene	$C_{18}H_{12}$	228	96

[a] Soil extract (only PAH fraction), 4 micro liters injected. Date Sampled: 4/21/93 Date Analyzed: 7/1/93 File Name: BSO528.D

*Compounds having a match quality less than about 70 to 80% are highly suspect.

Table 3.25
Qualitative analysis of soil extract from landfarm experiments 6/21/93[a]

Time, min	Peak	Mol. Formula	Mol. Wt	% Match
5.17	Benzene, ethyl-	C_8H_{10}	106	81
5.42	Benzene, 1,3-dimethyl-	C_8H_{10}	106	95
23.44	Phenanthrene	$C_{14}H_{10}$	178	93
31.83	Chrysene	$C_{18}H_{12}$	228	98

[a] Soil extract (only PAH fraction), 3 micro liters injected. Date Sampled: 6/21/93 Date Analyzed: 7/1/93 File Name: BSO621.D

Table 3.26
Concentration of target PAHs in soil

		Concentration, mg/kg of soil		
date	day	Naphthalene	Phenanthrene	Chrysene
4/1/93	0	85.2	96.9	50.7
4/7/93	7	51.5	59.7	75.3
4/14/93	14	0.9	5.9	39.1
4/21/93	21	bd	0.8	2.0
4/28/93	28	bd	0.3	6.7
5/5/93	35	bd	0.9	4.8
5/14/93	44	bd	0.2	12.7
5/28/93	58	bd	0.3	5.9
6/21/93	82	bd	0.3	7.3

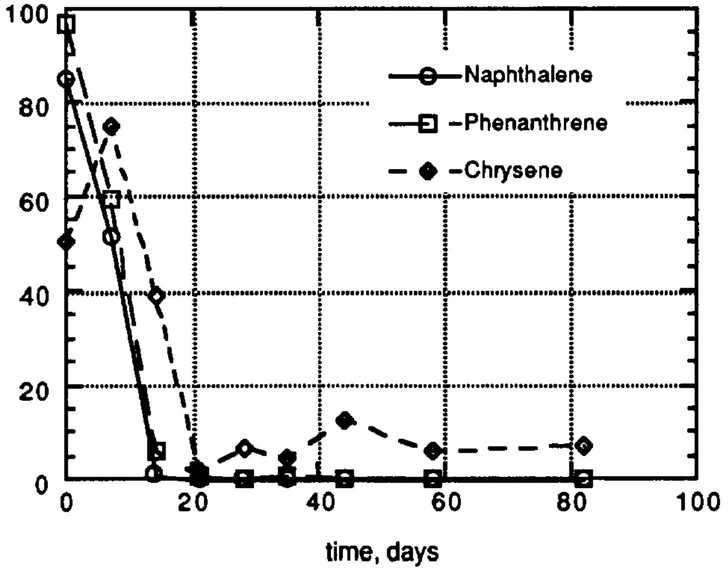


Figure 3.3
Concentrations of target PAH compounds with time in laboratory scale landfarm experiment

REFERENCES

American Public Health Association, *Standard Methods For The Examination of Water and Wastewater*, 16th edition, American Public Health Association, Washington, D.C., 1985

IV. CONCLUSIONS

Aerobic soil bioremediation processes were studied to determine the potential of these systems to act as sources of VOCs other than the primary contaminants. Of particular concern is the possibility that non and semi-volatile compounds would, in the course of biodegradation, be transformed into compounds of greater volatility. The principal example of such conversions is the production of vinyl chloride from trichloroethene and tetrachloroethene under anaerobic conditions. In this study the available literature (see Volume I, Literature Review) was examined and two sets of experimental studies were performed. The conclusions below are based on the information gathered in the literature review and the experimental studies.

1. Aerobic soil bioremediation systems are not conducive to the transformation of compounds of lesser volatility into compounds of greater volatility. Most aerobic oxidation reactions produce acids, alcohols, ketones, or aldehydes that have greater water solubility and lower Henry's law coefficients than the parent compounds.

2. Bioremediation processes are extremely heterogeneous environments and local anaerobic conditions are possible. Thus production of compounds of greater volatility through anaerobic biotransformations is possible. In a well designed and operated on-site bioremediation system anaerobic local conditions should be short lived and of minor importance. In *in situ* process, where there is less control of the reaction environment greater consideration of the possibility of local anaerobic conditions may be necessary.

3. On-site bioremediation processes, such as bioventing, where air is pulled through the soil, or land farming, where soil tilling and mixing is applied, can result in emission of significant fractions of the volatile compounds as a result of soil agitation.

4. Biodegradation of PAHs up to four carbon rings (e.g. chrysene) appears to be very straightforward under aerobic conditions.

5. Quantitative measurement of emissions from bioremediation systems is difficult. The surface isolation flux chamber is a useful device for measurement of emissions from bioremediation processes but factors such as difficulty in maintaining seals at the soil surface and methods for cleaning are problems.

6. In design of on-site bioventing systems, such as discussed in Chapter II of this report, potential problems include channeling of the vent air, soil medium heterogeneity and moisture content control. A bin design, rather than a conical pile, would minimize operational problems and result in decreased VOC emissions to the atmosphere.

APPENDIXES

A
Soxhlet Extraction

Analysis for VOCs sorbed onto soils was accomplished by Soxhlet extraction using dichloromethane as the solvent and GC/MS. The Soxhlet extraction apparatus was arranged as shown below in Figure A.1. A 25 g soil sample was placed in the cellulose thimble and about 250 ml of solvent dichloromethane was placed in the 500 ml flask. The flask was placed on a heater and heated at the boiling temperature of the solvent (about 50 °C) The solvent condensed above the thimble, passed through the soil sample, drained into the cellulose thimble as droplets, then returned to the flask. The total extraction period was 16 hours with 30 min for each soil extraction (about 32 extraction cycles).

The extract and solvent were concentrated by rotary evaporation to 10 mL. Approximately 1 μL of sample was injected into the GC/MS (Hewlett Packard 5980A) for analysis. For 25 g of soil sample a detection limit of approximately 100 ppb was expected. For PAH analysis a 30m DB-5.625 (J &W Scientific), 0.25 mm ID and 0.25 mm film capillary column was used.

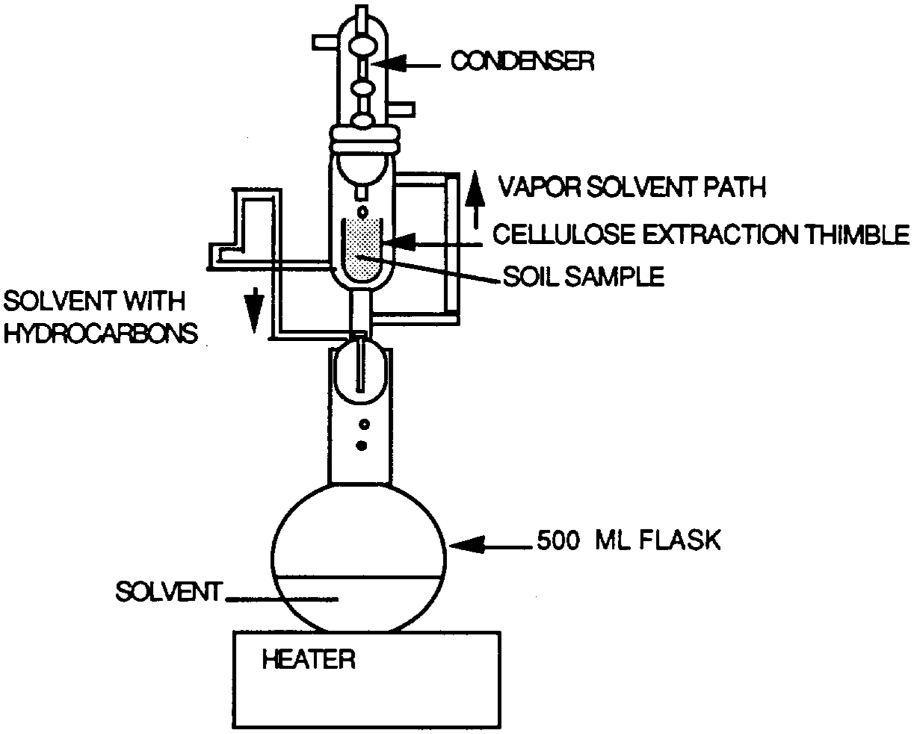


Figure A.1
Soxhlet extraction apparatus

B
GC/MS Temperature Programs

Gas samples were analyzed by GC/MS using a DB-625 column and three temperature programs. Samples taken on days one and two were analyzed using program number 1 (10°C/min ramp). As the peaks in the spectrum were found to be very close to each other or over lapping. For the third day samples, temperature program number 2 was used (5°C/min ramp). Later samples were analyzed using program number 3 as concentrations of the hydrocarbons decreased to decrease the run time.

Table B.1
Temperature Program for gas sample analysis

Program number	Initial time, min	Initial temp, °C	Initial time, min	Temp. rate, °C/min	Final temp, °C	Final time, min	Total Run time, min.
1	0	40	4	10	250	5	30
2	0	40	0	5	250	5	47
3	0	40	0	7	250	5	35

Soil samples were analyzed by GC/MS using a DB-5.625. Both soil sample extracts and standards were injected directly into the GC column. The temperature program used is summarized in Table B.2.

Table B.2
Temperature Program for soil sample analysis

Initial time, min.	Initial temp, °C	Initial time, min	Temp. rate, °C/min	Final temp, °C	Final time, min.	Total Run time, min.
0	40	4	8	300	20	56.50

C PL pile dimensions

Average radius of the base of the pile, r = 8.25 ft = 2.5 m

Height of the pile, h = 5.24 ft = 1.6 m

Volume of the pile before compressing the top flat = 342.1 ft^3 = 9.69 m^3.

The above volume includes pea gravel base and perforated pipe at the base of the pile.

Volume of the gravel pad = 55 ft^3 = 1.56 m^3.

Volume of the pile excluding pea gravel volume = 9.69 - 1.56 = 8.13 m^3.

Curved surface area of the pile, assuming a conical shape, $S = \pi r(\mathrm{sqrt}(r^2+h^2)) = 23.31\ m^2$.

B720 pile dimensions:

Average radius of the base of the pile = 8.25 ft = 2.5 m (approximately)

Height of the pile = 5.24 ft = 1.6 m (approximately)

Volume of the pile before compressing the top flat = 373.5 ft^3 = 10.58 m^3.

The above volume includes pea gravel base and perforated pipe at the base of the pile.

Volume of the gravel pad = 55 ft^3 = 1.56 m^3.

Volume of the pile excluding pea gravel volume = 10.58 - 1.56 = 9.02 m^3.

Curved surface area of the pile, assuming a conical shape, $S = \pi r(\mathrm{sqrt}(r^2+h^2)) = 23.31\ m^2$

D
Estimation of Emission Rates From PL Pile Surface

Emission flux, E_i,, of a species i is given by Equation D.1.

$$E_i\ (\mu mol/m^2\ min) = \frac{C_iQ}{A} \tag{D.1}$$

where C_i = concentration of class of compounds i, µmol/L
Q = purge gas flow rate into the surface isolation chamber, L/min
A = surface area enclosed by the chamber, m^2.

$$\text{Emission rate of class of compounds } (\mu mol/min) = E_iS \tag{D.2}$$

where S = surface area of the pile, m^2.
Here S is the curved surface area of the pile shown in Appendix D.

The concentrations C_i are estimated from the methyl benzene based concentrations in ppbv. Units of concentrations are converted to µmol/L, by assuming that 1 mole of air contains 24.5 L.

$$C_i = \frac{\text{concentration in ppbv or } 10^{-3}\ \frac{\mu mol}{mol}}{24.5\ L/mol} \tag{D.3}$$

E.

Estimation of Emission Rates at Port 1

Methyl benzene based concentrations of the compounds are converted to C_i as shown in Appendix E.

$$\text{Emission rate of a class of compounds, } \mu\text{mol/min} = C_iQ_i \qquad \text{(E.1)}$$

Where Q_i is the flow rate at which the air is drawn through the pile. Here the Q_i was 20 scfm or 560 L/min.

SECTION III

ANNOTATED ABSTRACTS

ABSTRACT

This document contains the annotated abstracts of a total of 124 references. The references cover three main areas: application of bioremediation, microbial transformations related to bioremediation, and analytical and experimental methods. Each entry includes key words and an abstract that was obtained either from the original document, or from the American Chemical Society (ACS), or from the EPA ATTIC data base, or from a summary of the article written by the editors. Some of the entries also include comments written by the editors.

Introduction

This document is divided into three sections: Application of Bioremediation, Microbial Transformations, and Analytical and Experimental Methods. Abstracts are repeated in the three sections, as appropriate. In most cases the abstract given is taken from the source document. Comments made by the editors of this document are listed separatelyely. Within each section the abstracts are listed alphabetically by first author.

Application of Bioremediation

Alm, R. R.; Olson, K. A.; Peterson, R. C.; "Using foam to maintain air quality during remediation of hazardous waste sites, Proceedings, 80th Annual Meeting, Air Pollution Control Association, Vol. 1, 87/18.3, 1987.

Key Words bioremediation sites, air pollution control

Abstract (copyright ACS): Water-based temporary and stabilized foams for maintaining air quality during remediation of hazardous waste site give 80-90% effectiveness in vapor and particulate suppression. Both types of foam can be applied to sites up to several acres in size using com. foam generators. Though limited in lifetime to apprx.30 min, temporary foams are effective in reducing volatile org. compd. and air toxic emissions in situations where waste is disturbed during excavation. Stabilized foams generated by injecting a proprietary agent into the temporary foam stream prior to foaming are useful in longer-term situations, such as overnight waste site cover or consolidation of loose debris.

Barnhart, M. J., Myers, J. M.; "Pilot bioremediation tells all about petroleum contaminated soil," *Pollution Engineering*, Vol. 21, no. 10, pp 110-12, 1989.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Biol. treatment of contaminated soils at an abandoned oil gasification site in Canada resulted in benzene, toluene, and xylene removals of 73% in 4 mo. Av. total polyarom. hydrocarbon removal efficiencies were 86%. The excavation of oil tar-contaminated soil resulted in localized air quality deterioration within the immediate work space.

Brown, R. A., and Hawke, T.; "The Biological Treatment of Soils and Sludges," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-27.01, 1992.

Key Words soil bioremediation

Abstract (from document) The biological treatment of soils and sludges represents a significant remedial tool. A proper understanding of the technology is, however, necessary to its proper use. This understanding entails two aspects - microbiological and engineering. From the microbiological aspect it is important to understand what are the limitations to the technology and what are the key process variables. From the engineering aspect there are three items of concern. These are, the need for and the type of containment system; the need for soil conditioning; and, the type of aeration system. When properly designed and operated, soil/sludge biological treatment is a cost effective process and has been successfully used on a wide range of sites.

Buck, F. A. M.; Smith, C. A.; "Control of air emissions from soil venting systems," Innovative Hazardous Waste Treatment Technol. Series, 2 (Phys./Chem. Processes), pp 205-210,

Key Words VOCs, soil bioremediation

Abstract (copyright ACS): The control of thermal/catalytic oxidn. of volatile org. compds. (VOC) in air extd. from contaminated soil remediation is described.

Coho, J. W., Larkin, R. G.; "Preliminary Results of a Vapor Extraction Remediation in Low Permeability Soils," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-7.08, 1992.

Key Words soil vapor extraction, VOCs

Abstract (from document):A pressurized underground pipeline ruptured and released approximately 80,000 gallons of JP-4 jet fuel in June, 1988 at Kelly AFB, Texas. The JP-4 spill contaminated unsaturated silt and clay-rich soils. A December 1990 Soil Vapor Extraction (SVE) pilot-scale test at the site showed that SVE was feasible in low permeability soils. The pilot test utilized one vapor extraction well and 12 multi-depth piezometers. Application of 72 inches of water vacuum (iwv) at the extraction well caused pressure drawdowns at piezometers within 20 feet of the extraction well. Pressure data indicated an extraction well radius of influence of 20 feet at a flow rate of 13 standard cubic feet per minute (scfm). The maximum hydrocarbon extraction rate was 286 pounds per day. A full-scale SVE system was designed and installed. Preliminary results indicate an initial hydrocarbon extraction rate of 29 pounds per hour which decreased to approximately 12 pounds per hour after 2 months of operation. Concurrently, the system air flow rate increased from 300 scfm to 500 scfm, and wellhead vacuums dropped from 70 iwv to 23 iwv. In-situ biodegradation of jet fuel is being studied at the site. An in-situ respiration test indicated a biodegradation rate of about 1 milligram of JP-4 removed per kilogram of soil per day.

Dasappa, S. M., Loehr, R. C.; "Toxicity Reduction in Contaminated Soil Bioremediation Processes," *Water Research*, vol.25, no. 9, pp:1121-1130, 1991.

Key Words: bioremediation, chlorinated phenols.

Abstract (from document): Bioremediation processes are used to treat contaminated soil, aquifer material, sludges and residues. The success of such treatment processes lies in: (a) degrading the organic contaminants and (b) reducing both the toxicity and the migration potential of the hazardous constituents. Laboratory studies were conducted using phenolic compounds to characterize overall chemical degradation and toxicity reduction in a contaminated soil, solid phase bioremediation process. The results indicated that: (a) first-order kinetics satisfactorily fit the loss of phenolic compounds and the decrease in toxicity that occurred, (b) contaminant loss in the water soluble fraction (WSF) was faster than loss of the same chemicals in the soil, (c) the toxicity of the WSF decreased as the soil chemical and the WSF chemical concentrations decreased and (d) no enhanced mobilization of the applied chemicals resulted as the degradation and detoxification occurred. Results indicated that detoxification as well as chemical loss occur in soil bioremediation processes and suggest that by-products of the degradation and chemical loss mechanisms do not increase the toxicity of the water soluble fraction from such processes.

Dong, T., Childress, A. S.; "Air emissions issues related to contaminated soil cleanup in populated areas," *Proceedings*, 84th Annual Meeting, Air & Waste Management Association, Vol 10B, 91/13.8,1991.

Key Words control of VOCs, soil remediation

Abstract (copyright ACS): Air quality issues and regulations for selection, implementation, and monitoring of soil remediation alternatives for southern California are discussed. Control of volatile org. compd. emissions during cleanup, case histories, and testing and risk factor assessment methods for carcinogens and hazardous substances are described.

Dumdei, B. E., Henderson, R.; "Air toxics monitoring program during bioremediation of a superfund site," *Proceedings*, 84th Annual Meeting, Air Pollution control Association, Vol 1, 88/5.3,1988.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): During bioremediation of an industrial sludge disposal site outside of Houston, Texas, controlled by sparging of air into the sludge and overlying water, pollutant emission was monitored by real-time measurements of total ionizables using a photoionization detector, real-time syringe sampling for volatiles with on-site gas chromatog. (GC) anal., real-time sampling of naphthalene on charcoal adsorbent and on-site GC anal., and time-integrated sampling for volatiles on Tenax followed by GC/mass spectrometry lab. anal. The results of the anal. were used for adjusting the aeration rate.

Comment: The site, a 7.3 acre lagoon, used to be an industrial waste disposal facility. The contaminants included chlorinated organics. Bioremediation was achieved by aerating the lagoon to supply oxygen to the indigenous bacteria. The paper focuses on the air monitoring program which was partly set to control emission levels. 7 compounds were targeted; any time the concentration levels of these compounds exceeded pre-assigned levels, the aeration was shut down or reduced. The targeted compounds were: benzene, toluene, ethylbenzene, trichloroethene, tetrachloroethene, chloroform, and naphthalene. During the project, the concentration levels of these compounds were never high enough to cause shut down of aeration.

Lagoon aeration is not a soil bioremediation process. The paper does not discuss treatment efficiency (initial and final concentration levels of contaminants are not included).

Durham, J. F.; "Energy, Waste and Cost Considerations Associated with Controlling Air Streams Containing Low Concentrations of Organic Compounds," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, Vol 10B, 92-11.04, 1992.

Key Words polycyclic aromatic hydrocarbons, adsorption

Abstract (from document): Air stripping systems and soil-vapor extraction systems are commonly used to remove volatile organic compounds (VOC) from contaminated water and soil. When high volumes of air are used relative to the quantities of VOC, the VOC ends up in the air at low concentrations. This paper estimated the penalties associated with using thermal oxidation, catalytic oxidation and carbon adsorption to oxidize or remove VOC from air at low concentrations. The penalties include (1) the fuel consumed to operate the systems, (2) the emissions and solid wastes produced from the fuel combustion, (3) the formation of contaminated water, and (4) the investment and operating costs. When air contains high concentrations of VOC, these penalties are generally small relative to the amount of VOC in the air. However, at low concentrations, they are significant and should be considered in selecting and designing the method of remediation. Estimates are prepared for four situations: benzene at concentrations of 10 and 100 ppmv and methylene chloride at 10 and 100 ppmv. The energy usage and waste production are expressed in pounds per pound of VOC in the air. Costs are expressed in dollars per ton of VOC.

Dzombak, D. A., Luthy, R.G.; "Estimating Adsorption of Polycyclic Aromatic Hydrocarbons on Soils," *Soil Science*, vol. 137, no. 5, pp. 292-308, 1984.

Abstract (from document): This paper presents a synthesis of information available on the adsorption of polycyclic aromatic hydrocarbons (PAH) in water/soil systems. Included is an analysis of how limited adsorption data for PAH on soils may be used in conjunction with PAH molecular characteristics to predict adsorption properties for a wide range of PAH and soils. Also presented is an evaluation of procedures that enable prediction of adsorption characteristics of PAH on soils based on soil organic carbon content and physical-chemical or structural characteristics of the particular compound.

Ehrenfeld, J. R., Ong, J. H.; "Control of emissions from hazardous waste treatment facilities," *Proceedings*,. 78th Annual Meeting, Air Pollution Control Association, vol 6, 85-70.1, 1985

Key Words control, volatile organic emissions, land treatment

Abstract (copyright ACS): The efficiencies of volatile compd. emission control from waste disposal facilities such as surface impoundments, tanks, landfills, and land treatment range from 10-15% for wind screens at surface impoundments to >95% for floating internal roof at tank facilities. Pretreatment and posttreatment are >90% efficient. These ests. were generated from 1st principles or derived from experience at related types of facilities.

Eklund, B,, Ranum, D., Orr, D., Summerhays, J.; "Estimation of VOC emissions from soils handling operations at Superfund sites," *Proceedings*, 83rd Annual Meeting, Air & Waste Management Association, vol. 8, 90/161.6, 1990.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Soil handling operations did not cause significant increases in ambient volatile org. compd. (VOC) concns. over baseline levels at the 2 field sites. Excavation of contaminated soil, however, stripped most (>50%) of the VOCs that were present from the soil. This implies that excavation of contaminated soil could adversely impact air quality at other sites where the levels of contamination were higher or the vol. of soil being moved per h was greater. The predictive models showed excellent agreement (within a factor of 2-3) with the field data for soil excavation and grading operations.

Comment The study involved two sites. The primary contaminants in site A were xylenes and ethylbenzene; in site B they were relatively heavy olefins and paraffins. The transect technique was used to measure VOC emissions resulting from excavation and grading. The flux chamber was used to measure VOC emission rates from waste storage piles. Soil samples were also analyzed before and after handling. Soil handling, excavation and grading, increased the total non methane hydrocarbon (TNMHC) concentrations by 0.5 ppm. VOC concentrations measured downwind at site A ranged from 5 to 50 ppb, and at site B ranged from 1 to 10 ppb. VOC emission rates from the storage piles decreased dramatically over a 24 hr period. No bioremediation was involved.

Eklund, B., Durham, J. F.; "Estimation of VOC Emissions, Ambient Air Concentrations, and Health Effects from the Excavation of Contaminated Soil," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-11.11, 1992.

Key Words air emissions, soil excavation

Abstract (from document): The U.S. Environmental Protection Agency's Office of Air Quality Planning and Standards and the Regional Air Offices have been given the responsibility to evaluate air impacts for Superfund sites. An important part of this program is the analysis of air impacts from various alternatives to cleaning up Superfund sites. Since these analyses are frequently required for planning purposes prior to actual cleanup, they depend on estimated emissions and ambient concentrations rather than on field measurements. This paper provides procedures for roughly estimating the ambient air concentrations associated with the excavation of contaminated soil. Excavation and off-site removal is a common remediation approach and excavation is also a necessary initial step of remediation approaches such as thermal desorption, incineration, ex-situ stabilization, and ex-situ bioremediation. Procedures are given to evaluate the effect of concentration and physical properties of volatile contaminants in the soil on the emission rates. Information is also given about the typical operating rates for excavation and the types of emission controls that may be employed. The effect of the excavation rate is related to the ambient air concentrations at selected distances from the excavation pit. Health-based ambient air action levels are also provided for comparison to the estimated ambient concentrations.

Eklund, B. M., Thompson, P. A., Durham, J. F.; "Emission factors for Superfund remediation technologies," *Proceedings*, 84th Annual Meeting, Air & Waste Management Association, 91/180.57, 1991.

Key Words emission factor, remediation technologies

Abstract (copyright ACS): It is possible to develop general emission ests. for remediation technologies using certain simplifying assumptions. An initial attempt at deriving such emission factors was made and the results are presented here for a no. of commonly considered remedial alternatives. The work is based on very limited data sets in some cases; more air emission characterization data is needed to improve the accuracy of the emission factors.

English, C.W., Loehr, R. C.; "Degradation of Organic Vapors in Unsaturated Soils," *Journal of Hazardous Materials*, Vol. 28, pp 55-63, 1991 .

Key Words degradation of VOCs, benzene, TCE

Abstract (from document); To predict the fate of volatile organic compounds (VOCs) in unsaturated soil, it is necessary to understand the physical and chemical processes that occur in the soil system. Two important removal mechanisms of organic vapors in soil are sorption and biodegradation. Modeling efforts to describe the removal of organic vapors in soil require constitutive relationships that are developed for laboratory data. This paper reports measurements of removal coefficients for three VOCs in fine sandy loam soil. Sorption coefficients and degradation removal rates were determined from batch reactors for three compounds: benzene, trichloroethylene (TCE) and o-xylene. Results indicate organic vapors are sorbed and then removed by biodegradation in the unsaturated soil system. This information has potential for use in the bioremediation of soils contaminated with VOCs and for impacting decisions on air emissions, regulatory limits and on-site controls.

Comments The paper describes the laboratory procedure used in comparing between the sorption and degradation of the three organic compounds mentioned above. Each set of experiments, sorption and degradation was conducted separately. In the degradation study, removal rates were reported but no degradation products were identified.

Epstein, E., Alpert, J. E.; "Composting of industrial wastes," *Toxic Hazardous Waste Disposal*, Vol. 4, chapter 15, pp 243-52, 1980.

Key Words Composting, industrial waste

Abstract (from document) The article includes a review of the composting of organic industrial waste and provides some design considerations. Examples from the composting of pesticides, TNT and PAH contaminated sludge are provided as evidence of the efficiency of composting in degrading industrial waste. The article includes 11 references.

Fiorenza, S., Duston, K.L., Ward, C. H.; "Decision Making- Is Bioremediation a Viable Option?," *Journal of Hazardous Materials*, Vol. 28, pp 171-183, 1991.

Key Words bioremediation, soil remediation

Abstract (from document): Bioremediation, as it pertains to hazardous wastes, is a process technology that uses microorganisms to degrade organic chemicals of interest. Often, the biodegradation can occur without transferring the contamination from one part of the environment to another, as is often the case with other remediation methods. Air stripping of contaminated ground water, incineration of contaminated material, and even carbon adsorption all contribute to cross-media pollution by producing hazardous residues, often more concentrated than the original form, that must be disposed. The diversity of bioremediation technologies ensures that one or more of them may be suitable for at least part of a remediation scheme. With our increased understanding of subsurface processes, we are shifting from the treatment of effects, i.e., treatment of contaminated ground water, to the treatment of contaminated sources.

Comments The authors identify some of the bioremediation technologies that are in use and give examples from past experiences. The authors also discuss the biological and chemical factors that are involved in improving biodegradation efficiency. Comparisons are made between the different processes in terms of cost considerations and applicability to specific sites or specific contaminants. Emissions from bioremediation processes are not generally discussed, however, the paper presents the reader with a very good over view of bioremediation technologies.

Folsom, B.R., Kurisko, P. R., Ensley, B. D.; "Performance Characteristics of a two State Treatment System for the Destruction of Hydrocarbons & Trichloroethylene in Groundwater," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-27.02, Kansas City, MO, 1992.

Key Words groundwater treatment, TCE removal

Abstract (from document): Many aqueous waste streams are composed of a complex mixture of chemicals belonging to several classes of compounds. Biological treatment of these complex mixtures often requires a knowledge of toxic interactions and degradative pathway incompatibilities. These issues may necessitate the use of specialized microorganisms and/or treatment systems designed to overcome these limitations. One strategy for the treatment of complex waste which can not be source separated, such as contaminated groundwater, is to develop a modular reactor system to degrade groups of biologically compatible chemicals. This approach was taken in the treatment of benzene and TCE which simulates a mixture of hydrocarbons and chlorinated solvents. Two aqueous reactor designs, fixed film and activated sludge, were constructed and operated to treat benzene and TCE contaminated groundwater. This first stage operation resulted in greater than 90% destruction of the benzene component. As expected, TCE passed through this first stage essentially unaffected. The remaining benzene and TCE were then passed to a second stage reactor designed for the cometabolic degradation of TCE. This second stage has demonstrated greater than 90% destruction of TCE with the added capability of degrading the residual benzene component. This two stage treatment system is currently being scaled to a field pilot demonstration unit.

Gerstle, R. W.; "Controlling Volatile Air Emissions During Hazardous Waste Excavation," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-11.02, Kansas City, MO, 1992.

Key Words air emission, soil remediation

Abstract (from document): A trial excavation of highly acidic petroleum refinery waste was performed at a Superfund site to better determine the nature of this waste, any treatment needed to improve its handling characteristics, and the extent of air emissions that might occur during excavation. This type of information was desirable to plan full-scale remediation at this site. When disturbed, this waste emitted high concentrations of SO_2 and volatile hydrocarbons. The trial excavation was conducted within a temporary enclosure with air exhausted from the enclosure through a sodium hydroxide-based wet scrubber and activated-carbon bed adsorber to reduce air emissions of sulfur dioxide and organic compounds. Foam was used in an attempt to suppress atmospheric releases from the raw waste during excavation, storage, and processing. The air exhaust was monitored for total hydrocarbons and sulfur dioxide before and after the air emission control system. In addition, total hydrocarbons and sulfur dioxide were monitored along the site perimeter to determine impact of air emissions on the nearby community. This paper describes the techniques used to minimize air emissions, and associated problems resulting from working in an enclosure. The equipment used to measure and control emissions and the emissions before and after the air control system during excavation are also presented as well as an assessment of the foam vapor suppressants.

Hansen, C. L., Stevens, D. K., Zhang, S., Warner, D.N.; "Biologically Enhanced Removal of Mercury from Contaminated Soil," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-25.03, Kansas City, MO, 1992..

Key Words mercury removal, soil remediation

Abstract (from document): Mercury is a hazardous heavy metal from many industrial sources; it is found in waste water, sludge, and soil. A common treatment method for mercury-contaminated soils has been to attempt to permanently immobilize the metal by either chemical or physical methods. Mercury-resistant strains of bacteria have been shown to be effective in the detoxification of mercury from waste water. This research was a preliminary investigation to determine if soil contaminated with high levels of mercury can be detoxified biologically. Specific objectives were to investigate the effect of reactor type, moisture content, soil sterilization, and amendment of the soil with nutrients on the extent of mercury volatilization. The results demonstrated that a mixed reactor (slurry-phase system) was able to remove more Hg from soil than an unstirred reactor with all other factors equal. Mass transfer resistances are clearly important in the extent of mercury removal over a fixed-time period. Nutrient addition tended to reduce the extent of mercury removal from soil.

Hinchee, R.E., Downey, D.C., Dupont, R.R., Aggarwal, P.K., Miller, R.N.; "Enhancing Biodegradation of Petroleum Hydrocarbons through Soil Venting," *Journal of Hazardous Materials*, Vol. 27 , pp 315-325, 1991.

Key Words soil venting, *in situ* bioremediation

Abstract (from document): Aerobic bioremediation of jet fuel in contaminated soil in an unsaturated vadose zone at Hill Air Force Base, Utah, was stimulated by soil venting. *In situ* respiration studies conducted at the contaminated site revealed that microbial respiration was occurring as a result of oxygen introduced by the venting process. Stable isotopic ratios ($^{13}C/^{12}C$) in soil gas were measured to confirm a biogenic source of carbon during venting of the contaminated soil. Although volatilization was the primary mechanism of removal, from 15 to 25% of the jet fuel was biodegraded *in situ*, making soil venting a promising approach for enhancing the aerobic remediation of contaminated vadose zones.

Comments Contamination at the site was caused by a 27,000 gallon spill of JP-4 jet fuel. Hydrocarbon concentrations in the soil were up to 15,000 mg/kg. The gases removed by venting were treated by catalytic incineration. Initially the off-gases had to be diluted to bring the concentration levels to below explosive limits. Monitoring wells were used to measure soil gas and vacuum composition. A reduction in the oxygen levels, and an increase in the carbon dioxide levels in the off-gases from the contaminated soil provided evidence of biological activity. Bioremediation was stimulated by the introduction of oxygen through soil venting. The moisture content of the soil was not adjusted, and nutrients were not added.

Hinchee, R. E., Miller, R. N.; Dupont, R. R.; "Enhanced biodegradation of petroleum hydrocarbons: an air-based in situ process," Innovative Hazardous Waste Treatment Technology, Ser., 3 (Biol. Processes), pp 177-83, Battelle Memorial Institute, Columbus, OH 43201, 1991.

Key Words bioremediation sites, soil venting, air emissions

Abstract (copyright ACS) Soil venting was initiated at apprx 45 m3/min and was increased gradually to apprx.2500 m3/min at a site contaminated by JP-4 jet fuel at Hill Air Force Base in Utah. Cumulative hydrocarbon removal between Dec. 1988 and Feb. 1990 was .apprx.47,000 kg volatilized and .apprx.15,000 kg biodegraded. When JP-4-contaminated soils at Tyndall Air Force Base, Florida, were aerated at .apprx.1 air-filled void vol. exchanged/day, biodegrdn. and volatilization rates were much higher than those obsd. in Utah. The data are preceded by a review on conventional and air-based enhanced biodegrdn.

Comments The article includes a good introduction to enhanced *in situ* biodegradation both in saturated and unsaturated soils. Soil venting is discussed in more detail. References are made to soil venting projects where significant biodegradation was shown to have occurred. Also, brief summaries are provided of the conditions and results of the soil venting projects at the two air force bases mentioned above. The paper does not include information on biodegradation products other than carbon dioxide.

Huddleston, R.E., Pixie A.B. Newman, Boersma, P. M.; "Ex Situ BTEX Treatment: A Viable Alternative to Dig-and-Dump," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-7.09, Kansas City, MO, B1992.

Key Words bioremediation sites, BTEX

Abstract (from document): Soil contaminated with benzene, toluene, ethylbenzene, and xylenes (BTEX) was discovered at a food processing plant during the removal of a 10,000-gallon gasoline underground storage tank. Following a site investigation, the area of affected soils (as defined by State of Illinois cleanup objectives) was estimated. An onsite land treatment system, consisting of a lined treatment cell with leachate collection and treatment, was designed for soil bioremediation. To minimize disruption of the plant's primary production period, the system design, regulatory agency review, permitting, construction, and soil excavation were completed within 6 weeks of authorization to proceed. Because the plant was active during cell construction and soil excavation, special measures were implemented to improve the traffic flow of raw material deliveries and final product shipping. Soil treatment was accomplished with manure and moisture additions to enhance BTEX biodegradation; and with twice-weekly tilling to improve soil aeration and mixing. The remediation of an estimated 3,750 cubic yards of soil was completed at a slightly higher cost than the cost estimated for soil excavation and disposal. When adequate space exists onsite for the treatment system, this technology can be implemented quickly and cost-effectively within the constraints posed by active facilities.

Huggins, C. B.,. Money, R. D.; "The Risk Assessment: A Site Specific Approach to Establishing Acceptable Soil Clean-up Levels, From CERCLA to RCRA UST Sites," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-7.06, Kansas City, MO, 1992.

Key Words soil remediation, bioremediation sites

Abstract (from document): Though the environmental Risk Assessment evolved with the passing of CERCLA in 1980, it is now a commonly used tool in other areas of environmental compliance include RCRA. The Risk Assessment has two primary purposes: (1) to evaluate potential risks to human health and the environment posed by the release of materials into the environment and (2) to establish safe clean-up levels based on the number and type of potentially effected receptors and the toxicity and mobility of the subject contaminants. The length and complexity of a Risk Assessment is dependent upon the governing regulations, the policies of the reviewing agencies and the nature of the release. As an overview, three case studies are presented. The first involves establishing clean-up levels for a chlorinated solvent release at a SUPERFUND site. The second and third case studies present Risk Assessments associated with the closure of solvent and petroleum underground storage tanks. A site specific approach is emphasized in all cases.

Kampbell, D. H., Wilson, J. T.; "Bioventing to Treat Fuel Spills from Underground Storage Tanks," *Journal of Hazardous Materials* , vol. 28, pp: 75-80, 1991.

Key Words bioventing, air emissions

Abstract (from document): Bioventilation is a procedure to cleanse soil gas of volatile fuel hydrocarbons originating from storage tank leaks. The rate of vapor degradation is a controlling parameter in the design of a bioventing system. A laboratory microcosm procedure using sandy soil from an aviation gasoline spill site was used to measure relative kinetics of some fuel vapors.

Kampbell, D. H., Wilson, J. T., Read, H. W., Stocksdale, T. T.; "Removal of Volatile Aliphatic Hydrocarbons in a Soil Bioreactor," *Journal Air Pollution Control Association,* vol.37, no. 10, pp. 1236-1240, 1987.

Key Words Volatile organic emissions, laboratory study

Abstract (from document): Soil removal of propane, isobutane and n-butane from a waste air stream was evaluated in the laboratory. Laboratory investigation indicated first-order kinetics and the potential to degrade light aliphatic hydrocarbons and trichloroethylene, a compound ordinarily resistant to aerobic biological treatment. The predicted behavior of the bioreactor, based on the laboratory studies, agreed closely with the actual behavior of the field system. The prototype bioreactor reduced the hydrocarbon concentrations in the air by at least 90 percent with a residence time of 15 minutes and a pressure drop of 85 cm of water. The bioreactor functioned well through a range of temperatures, 12°C to 24°C.

Comments In the prototype study, air containing about 200 ppm(v/v) total hydrocarbons was injected through perforated PVC pipes embedded in 90 cm deep soil. In the laboratory studies, soil contained in sealed glass bottles was syringe injected with propellant gases at different concentrations. The experiments involved air biofiltration and not soil bioremediation.

Lewis, R. F.; "Site Demonstration of Slurry-Phase Biodegradation of PAHs in Contaminated Soil," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92/26.02, Kansas City, MO, 1992.

Key Words slurry phase bioremediation, PAHs

Abstract (from document): A pilot-scale test of the slurry bioremediation technology was performed by Ecova Corporation at the U.S. EPA Test and Evaluation facility in Cincinnati from May 8, through July 10, 1991 as a joint SITE demonstration-BDAT Study. The five parallel slurry-phase bioreactors were tested on the treatment of a creosote-contaminated soil from the Burlington Northern aromatic hydrocarbon (PAH) degraders was added to the 30 percent slurry (soil:water, w/v). During the study levels of soil-bound and liquid-phase PAHs, total petroleum hydrocarbons, nutrients, pH, dissolved oxygen, temperature, and microbial activity were measured. Total percent reduction of the PAHs over the 12 weeks ranged from 72 to 94 percent. Emissions of total hydrocarbons measured as methane were determined for 2 of the reactors. The rate was as high as 0.14 lb/h for the first day and a half but then rapidly dropped down to the background level. Moderately high levels (3 to 860 micrograms per liter of air of naphthalene, 2-methyl naphthalene, acenaphthene, phenanthrene, fluorene, and dibenzofuran were also emitted during the first 4 days of operation and then dropped to the background level.

Comments: The slurry-phase bioremediation was enhanced through mixing, aeration, controlling the temperature, moisture content, and the nutrients (Carbon, nitrogen and phosphorus). Degradation of PAHs was also enhanced through bioaugmentation. PAH degraders, isolated from a pervious study, were used. The microorganisms included two *Pseudomonas* species and one *Alcaligenes* specie. Both the degradation rates and the air emission levels were monitored over the 12 weeks. Total PAH concentration was dropped from an average level of 10,973 ppm to about 653 ppm. Emissions of 2 and 3 ring PAHs were observed for the first four days and relatively low concentrations of VOCs, mainly BTEX were also observed over the first few days.

Long, G.; "Bioventing and Vapor Extraction: Innovative Technologies for Contaminated Site Remediation," *Journal of the Air & Waste Management Association*, vol. 42, no.3, pp 345-348, 1992

Key Words bioventing, soil vapor extraction

Abstract (from document:): Bioventing and vapor extraction are two technologies which are finding increasing use in performing cleanup at hazardous and nonhazardous waste sites. Both processes are characterized by the controlled use of air as a carrier to either remove contaminants from soil or to supply oxygen for aerobic bioremediation of the compounds in the unsaturated zone into less toxic materials. These topics will be the focus of a unique Bioventing Satellite Seminar to be broadcast on April 15, 1992. The seminar, a joint venture between the Air & Waste Management Association (A&WMA) and the Hazardous Waste Action Coalition (HWAC), is the second in a series of satellite seminars that will deal with innovative hazardous waste remediation technologies.

Marsh, J. W., Bider, W. L., Svec, E. J.,] Wheatley, J. D.; "In-Situ Soil Vapor Extraction Removal of Volatile Organic Compounds from an Industrial Landfill: A Case Study," *Proceedings*,85th Annual Meeting, Air & Waste Management Association, 92-10.03, Kansas City, MO, 1992.

Key Words soil vapor extraction, *in situ* bioremediation

Abstract (from document): In-situ soil vapor extraction (SVE) has been identified as a viable innovative technology for the remediation of soils contaminated with volatile organic compounds (VOCs). Successful application of this technology, however, depends on numerous site-specific conditions such as chemical and physical characteristics of the waste, vertical and horizontal distributions of the waste, soil vapor permeability, and depth to groundwater. This paper discusses the results from an SVE Pilot Study conducted at a RCRA industrial waste landfill in Kansas City Area. The landfill was primarily composed of construction debris and fill, with localized areas of VOCs resulting from fuels, paints, chlorinated solvents, etc. Unique and challenging aspects of this Pilot Study included the diverse composition of VOCs in the extracted soil gas (more than 80 different compounds detected), extreme heterogeneity of the subsurface materials and fill, and the presence of perched water. This paper addresses the rationale for the Pilot Study, the data collected as a result of the project, and the impact of the results on the full-scale remediation.

McCarty, P. L.; "Engineering Concepts for *in situ* Bioremediation," *Journal of Hazardous Materials*, Vol. 28, pp 1-11, 1991.

key words: bioremediation, *in situ*

Abstract (from document): Most organic material that contaminate soil and the subsurface environment are readily degraded by natural biological processes. Thus, bioremediation can be thought of as a highly successful purification process. However, some organic molecules are naturally refractory to biodegradation, the proper microbial population is not present, or the environmental conditions are not suitable to biodegradation so that the compounds become recalcitrant to biodegradation and persist in the environment for years. Where natural processes are slow, the best strategy may still be to wait for the natural degradation to occur because of the current high costs and lack of reliability of engineered solutions. In other cases, the natural recalcitrance may be changed by the introduction of degrading populations of microorganisms or by changing the environmental conditions by introduction of chemicals or through mixing and dilution. The potential success of engineering procedures to enhance degradation rates also depends to a large degree upon the complexity of the hydrogeology at a given site. With complex hydrogeology, most remediation approaches are rendered difficult if not impossible. This must be recognized by regulatory authorities and the public. In such cases alternative strategies to site remediation itself should be sought. More attention to such alternatives is needed in order to reduce unproductive expenditure of scarce resources.

Comments This article provides a detailed discussion of the different factors that cause certain compounds, under certain conditions, to be resistant to degradation. Those factors include properties of the compound itself, and environmental factors related to the ability of the microorganisms to break down organics. Explanations and examples are given as to how some of these factors may be corrected in a bioremediation process. There is no discussion of degradation products and air emissions from bioremediation processes.

McGinnis, G. D., Borazjani, H., Hendrix, F., McFarland, L., Pope, D., Strobel, D., Wagner, J.; "Bioremediation Studies at a Northern California Superfund Site," *Journal of Hazardous Materials*, vol. 28, pp 145-158, 1991.

Key Words bioremediation sites, contaminated soil

Abstract (from document): Laboratory analysis of land treatment of wood preservative contaminated soils was performed as part of an investigation of remediation alternatives for an EPA Superfund site. Experimental procedure involved 6 different site soils with different supplementary nutrients placed in lined steel boxes, 6'X12"X5' deep, and analyzed for, among other things, creosote pentachlorophenol, acclimated and total bacteria populations, polynuclear aromatic hydrocarbons (PAHs), and pentachlorophenol (PCP) with both single and multiple loadings. The best overall percentage reduction occurred where there were moderate initial constituent concentrations and the highest level of manure.

Molchan, G. A., Kang, S. J.; "On-Site Portable Bioremediation Unit," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-7.04, Kansas City, MO, 1992.

Key Words on-site bioremediation, underground storage tanks

Abstract (from document): A large industrial underground storage tank farm containing 22 tanks exists in a patient plant in southeast Michigan. Due to the age of the tanks and the tank contents, and the nature of the geology, a number of products were found in the soil and groundwater surrounding the tank farm. During the site characterization it was determined that a recovery system should be installed to contain the plume within the tank farm boundaries. The recovery system was installed and a portable bioremediation unit was designed to treat a variety of chemicals and meet the local town discharge standards for industrial pretreatment. The bioremediation unit consisted of an anaerobic and aerobic modified treatment chamber and clarifier. The system was constructed on skids to assure portability to other remediation sites. Reduction efficiencies of 98-99% were realized during the testing periods from 1989-1990. BTEX effluent was reduced from 165 ppm to 0.8 ppm with a maximum flow of 10 gpm as a result of the project.

Morrison, B. A.; "On-Site Bioreclamation of Creosote-Contaminated Soil," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-27.04, Kansas City, MO, 1992.

Key Words bioremediation, creosote

Abstract (from document): An abandoned wood preserving facility in Alton, Missouri, underwent a clean-up action performed by Region VII, U.S. EPA under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act

(CERCLA). Following a surface debris cleanup of buildings, retort tanks, and drip pads, EPA decided to remediate contaminated soil on site using a biological treatment process. A contract was awarded to Remediation Technologies, Inc. (RETEC), to perform the bioremediation using a land treatment process commonly referred to as landfarming. Retec constructed a 6.8-acre land treatment unit (LTU) at the site which eventually treated 15,941 tons of creosote-contaminated soil. Construction of the LTU and soil treatment required a 27-month time period. Site action levels were established at 500 ppm for total polyaromatic hydrocarbons (PAHs) and 14 ppm benzo-a-pyrene (BAP). Final treated soil concentrations were 160 ppm total PAHs and 12 ppm BAP.

Park, K.S., Sims, R.C., Dupont, R. R.; "Transformation of PAHs in Soil Systems," *Journal of Environmental Engineering*, ASCE, vol. 116, no. 3, pp 632-640, 1990.

Key Words Soil pollution, Laboratory study, PAHs

Abstract (from document): Transformation kinetics, corrected for abiotic loss and for volatilization, of 14 polycyclic aromatic hydrocarbons (PAH) compounds were studied in two nonacclimated soils. Mean volatilization losses for naphthalene and 1-methylnaphthalene were measured as 31% and 22% respectively, of the total masses applied. Volatilization of the other twelve PAH compounds studied was less than 0.1%. The abiotic loss (1.8-17.4%) of two- and three-ring PAH compounds in soil samples bio-inhibited by 2% $HgCl_2$ was statistically significant ($p < 0.05$). No significant loss from bio-inhibited soil was found for PAH compounds with more than three rings. Transformation half-lives corrected for volatilization and for abiotic loss were approximately 2 days for two-ring PAHs including naphthalene and 1-methylnaphthalene. Half-lives values for nonvolatile PAHs increased from 59 days for three-ring PAHs (anthracene and phenanthrene) to more than 300 days for PAH compounds containing more than three rings. The PAH transformation rate was inversely propotional to molecular weight and compound ring number.

Comments .The article describes the laboratory procedure and results. Soil samples, in 500 mL flasks, contaminated with known amounts of PAHs and incubated at 25°C, were monitored for volatilization, abiotic loss and loss due to biotransformation. Air was purged through the capped flasks and the collected gases were analyzed using a gas chromatograph. The article does not mention whether the constituents of the off gases were identified.

Partridge G. P., Vuong, D; "Volatile Organic Carbon (VOC) Emissions from biological Treatment Processes of Gasoline Tank Bottoms," *Proceedings* , 84th Annual Meeting, Air & Waste Management Association, 91/92.8, Vancouver, B C, 1991.

Key Words VOC emissions, water treatment, gasoline

Abstract (copyright ACS): Air pollution by volatile org. compds. (VOC) from gasoline tank bottom wastewater is controlled by biol. treatment. Studies of efficiencies of a sequencing batch reactor (SBR) and a rotating biol. contactor (RBC) show that the RBC has less total VOC emissions than the SBR.

Preslo, L., Miller, M., McLearn, M., Suyama, W., Kostecki, P.; "Leaking Underground Storage Tank Site Remediation Alternatives," *Proceedings*, 80th Annual Meeting, Air Pollution Control Association, 87/16.2, New York, 1987.

Key Words underground storage tanks, soil remediation

Abstract (copyright ACS): The review with 7 refs. covers remediation alternatives for leaking underground storage tank sites, including the environmental fate of hydrocarbon constituents, relative costs of applicable technologies, and remedial action practices.

Schlauch, M., Clark, D.; "Biodegradation Studies of Diesel-Contaminated Soils and Sediments," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-27.05, Kansas City, MO, 1992.

Key Words bioremediation, contaminated soil

Abstract (from document): Radian corporation is currently remediating the Atchison, Topeka and Sante Fe Railway Superfund site in Clovis, New Mexico. Biodegradation of the petroleum hydrocarbon-contaminated soils and sediments was chosen as the remedial alternative. In order to evaluate the optimum conditions for full-scale bioremediation at this site, Radian designed and implemented various laboratory and field studies. The initial laboratory treatability study was conducted to determine if hydrocarbons in both soils and sediments could be biodegraded using indigenous microorganisms, and determine that the soil were biodegradable, while the sediments were not due to inhibitory factors. To further evaluate the biodegradability of the sediments, a laboratory study was initiated which introduced chloride-resistant microbes. The study showed that the sediment bioremediation was possible by utilizing these microbes; however, the cost was not favorable. Finally a field plot study was initiated to determine how soil biodegradation would proceed in field conditions, to optimize influencing factors such as moisture and nutrient levels and bioseed addition, and to investigate alternate methods of bioremediating the sediments. Results showed that hydrocarbons in the soils biodegraded much faster in the field than in the lab, and that hydrocarbons in sediments applied to biotreated soils containing acclimated microorganisms were successfully biodegraded.

Sharp-Hansen, S.; "Available Models for Estimating Emissions Resulting from Bioremediation Processes : a Review," EPA/600/3-90/031, Athens, Georgia, 1990.

Key Words bioremediation, air emissions, soil, models for estimating emissions

Abstract (from document): The use of bioremediation processes to treat hazardous waste has increased in the last 10 years. Biological treatment offers the advantage of contaminant destruction rather than transfer to other media. There is concern, however, that significant amounts of organic pollutants are emitted to the air from biological treatment activities before they can be degraded. To estimate the magnitude of emissions from these facilities, overall fate models that incorporate the effects of several competing removal mechanisms are needed. this report focuses on the state-of-the-art in modeling air emissions from bioremediation processes. The biological treatment systems are described, as are the important pathways that affect the fate of organic pollutants in those systems. Currently available models are identified, described, and evaluated for each bioremediation process. Finally, some limitations of the models and the need for additional research are discussed.

Shonnard, D. R.; Bell, R. L.; "A method for determining VOC and toxic emissions from gasoline contaminated soils," *Proceedings*, 80th Annual Meeting, Air Pollution Control Association, vol 1, 87/11.4, New York, 1987.

Key Words volatile organic emissions, gasoline, laboratory study

Abstract (copyright ACS): A lab. method for the assessment of volatile org. compd. emissions from gasoline-contaminated soil is described and exptl. measured gasoline emission fluxes from soil under controlled lab. conditions are presented. The transport processes are described by correlating the emission data with a simple model. Emission results from 3 replicate expts. were within .apprx.5% agreement with each other. Approx. 30% of the initial gasoline was volatilized after 12 h for the conditions studied. The agreement with the diffusion model suggests that the mass flow of gasoline (in the aq. phase) caused by water evapn. is not an important transport mechanism for gasoline. The soil phase mass transfer resistance is the limiting factor in volatilization from soil into atm.

Comments Emissions from soil contaminated with 1000 ppm unleaded gasoline were monitored for two sets of soil moisture content. One set was for a soil moisture content of 35% of soil void volume, and the other was for no moisture content. Both sets of experiments were conducted at room temperature. Gasoline emission components were not analyzed. Measurements were recorded on a total hydrocarbon basis. Biodegradation was not part of the study. Soil microbial activity was suppressed by using $HgCl_2$.

Simpkin, T. J., Walter, D., Doesburg, J.; "Treatment of Fuel Product Contaminated Soil in a Cold Climate Using Composting Technology". *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-27.06, Kansas City, MO, 1992.

Key Words composting, bioremediation

Abstract (from document):As part of the environmental restoration program at Eielson Air Force Base in Alaska, a field test of composting was conducted from September to November 1991. The field test was designed to evaluate the effectiveness of composting in a cold climate, and to evaluate methods of enhancing its performance. The field test involved constructing three composting test cells, one of which was amended with anaerobically digested sewage sludge. Temperature data suggest that significant quantities of heat can be generated by the decomposition of the fuel products. The temperatures increased up to greater than 90°F in the test cell that was only amended with inorganic nutrients. Even greater temperatures (greater than 100°F) were achieved in the test cell amended with the sewage sludge. Total petroleum hydrocarbons data suggest that the process will significantly reduce the levels of petroleum hydrocarbons (from about 1,700 milligrams per kilogram [mg/kg] to less than 200 mg/kg in 70 days).

Speitel, G. E. Jr., Alley, E. R., Jr.; "Bioremediation of Unsaturated Soils Contaminated with Chlorinated Solvents," *Journal of Hazardous Materials*, vol.28, pp 81-90, 1991.

Key Words bioremediation, chlorinated solvents

Abstract (from document:) One- and two-carbon chlorinated aliphatic solvents are common environmental contaminants, as a result of the large quantities produced, their widespread use and their mobility in the environment. Chlorinated solvents are regularly identified in unsaturated soils, saturated soils, ground water and landfill leachates. This research focused on *in situ* bioremediation as one possible treatment process for unsaturated soil contaminated with chlorinated solvents. Biodegradation of chlorinated solvents in unsaturated soils is feasible through the stimulation of indigenous methanotrophic organisms by the addition of methane and oxygen. At the concentrations studied on our experiments bioremediation would require weeks to several months to accomplish. The experiments also provided a clear indication of toxicity effects as the concentration of chlorinated hydrocarbons becomes too large. Likewise, extended absence of methane from the soil environment greatly reduced microbial activity.

Suder, D. R., Schmidt, C.E. ; "Control Efficiencies and Costs of Various Technologies for Reduction of Volatile Organic Compound Emissions from Exposed Hazardous and Nonhazardous Waste," *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-11.15, Kansas City, MO, 1992.

Key Words air emissions, soil remediation

Abstract (from document): Control of hydrocarbon emissions from all sources has become an increasing concern over the last decade, particularly in ozone nonattainment areas. With most of the "easy" control measures and emissions reductions already in place, emissions reduction efforts have focused more recently on the more difficult sources, including fugitive emissions from area sources. Hazardous waste sites, remediation projects and hazardous waste landfills are such sources. Because some of the hydrocarbon species (e.g., benzene) potentially emitted from these sources are potentially toxic, or are either precursors to ozone or are ozone-depleting substances, efficient control of emissions is especially important. This paper examines recently-collected data regarding the control effectiveness of soil cover applied by various techniques, and of several commercially-available synthetic membranes and vapor-suppressant foams. Overall costs of the methods are compared, and qualitative observations of the practicality of each are discussed in the context of both remediation projects and operating hazardous waste landfills.

Thompson, G. M.; "Solvent Vapor Behavior in the Vadose Zone above Contaminated Groundwater" *Proceedings*, 85th Annual Meeting, Air & Waste Management Association, 92-3.09, Kansas City, MO, 1992.

Key Words vadose zone, VOCs

Abstract (from document):Analysis of a soil gas demonstrates solvent vapor concentrations and distributions are primarily controlled by a chemical's aqueous solubility, resistance to degradation of the molecule in unsaturated soil, the geologic parameters affecting vadose zone water, and its mode of release into the environment. A controlled release of CCl_3H, C_2Cl_3H, and C_2Cl_4 was made in a shallow aquifer. Comparison of the resulting vapor phase plumes in the vadose zone reveal that chemicals with high aqueous solubility concentrate in liquid phase water and have very low vapor phase concentrations in the presence of water. Degradation products are less stable in the vadose zone than the primary solvents. Field data indicates that their distributions in the vadose zone are seldom similar. Geologic factors affecting distribution of vadose zone water are critically important to interpretation of soil vapor data. Vadose zone water impedes the diffusive transport of vapor. Topographic features which concentrate rain water reduce vapor concentrations in those areas. Mode of release impacts vadose plume development. Shallow or areal releases will create extensive vadose zone contamination that may migrate equal distances up-gradient from groundwater flow and down-gradient from source. Deep releases may produce little or no vapor phase contamination, resulting in narrower vapor plumes.

Thompson, P., Inglis, A., Eklund, B.; "Emission factors for Superfund remediation technologies," U. S. Environmental Protection Agency, Office of Air Quality Planning Standards, [Tech. Rep.] EPA, EPA-450/1-91-001, 1991.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Techniques are presented for the estn. of air emissions from Superfund site cleanup by thermal treatment, air stripping, soil vapor extn., solidification and stabilization, physicochem. treatment, biol. treatment, and land treatment.

U. S. Environmental Protection Agency, Final Report: Soil Treatment Pilot Study--Brio/DOP Site (Technical Report No. 8610), EPA Region 6 (212) 655-6444,ECOVA Corporation, June, 1987.

Key Words bioremediation sites, air emissions

Abstract (from EPA ATTIC database): Abstract: Bench- and pilot-scale studies were conducted to demonstrate the feasibility of using solid-phase biodegradation for destroying organic constituents in soil at the Brio/DOP site. A diverse microbial population resided in the soil. The pilot-scale solid-phase treatment facility consisted of a lined soil treatment area with a collection system, water/nutrient distribution system, emission controls, microbiological management system, greenhouse enclosure, and support facilities. The facility operated 94 days. 200 cu yds of soil were removed and inoculated with microorganisms to ensure aeration. Volatile organic compounds (VOCs) were trapped by activated carbon absorbers at the pilot facility. The pilot-scale treatment facility demonstrated under field conditions that a solid-phase treatment process could be used to successfully treat the organic constituents present in the site soil. The process removed the VOCs by air stripping, and destroyed semi-volatile organic compounds by biodegradation. More than 99% of the VOCs were removed within the first 21 days of operation. Biodegradation for semi-volatiles was much slower, taking 131 days to reduce phenanthrene concentrations below detection limits.

U.S. Environmental Protection Agency, Record of Decision--Brio Refining, TX, EPA/Superfund Office, Region 6 (214) 655-6444,

Key Words bioremediation sites, air emissions

Abstract (from EPA ATTIC database): The Brio Refining site is broken into two parcels, Brio north and Brio south. Between 1957 and 1982 the site refined crude oil and styrene tars to produce toluene, ethylbenzene, aromatic solvents, naphthalene, diesel fuel and kerosene. Various owners of the site stored styrene tars in 24 open pits. Other waste products and sludges were stored in above-ground tanks. Site investigation indicates that between 500,000-700,000 cubic yards of onsite soil have measurable contamination, and that high levels of VOCs exist in groundwater underlying the site. The selected remedial action for this site includes excavation and incineration or biological treatment of all onsite soils, sludges, and liquids found to be above action levels defined in the endangerment assessment, with backfilling of all treated material passing the TCLP. If the Brio Site Task Force PRPs can successfully demonstrate the effectiveness of aqueous phase biological treatment will be considered, otherwise incineration will be selected; excavation of all visual onsite seeps; further investigation of Pit G to locate sludge or contaminated soil underlying the existing onsite wastewater treatment impoundment; consolidation and disposal of all inert debris; disposition of mud gully the flood control ditch; inplace stabilization of wastes existing in the wastewater treatment impoundments, and installation of a package wastewater treatment system or route wastewater to a POTW; removal and disposal of tank contents, and decontamination, dismantling and selling or offsite disposal of tanks and process equipment; monitoring program; control of air emission from the treatment process; venting waste enclosures; treatment of groundwater in the numerous sand channel zone to a level to be determined in design; natural attenuation of the 50-foot sand aquifer; regrading and vegetating areas outside excavation areas; construction of a stormwater transmission system draining to mud gully; and imposition of deed restrictions.

U. S. Environmental Protection Agency, Guide for Identifying Cleanup Alternatives at Hazardous-Waste Sites and Spills: Biological Treatment. EPA/600/3-83/063, Corvallis Environmental Research Laboratory, OR, 1985

Key Words biodegradation, soil, water, land treatment, bioreactors

Abstract (from document):This document provides guidance to help decide whether or not biological treatment is an appropriate component of the remedial action process at a hazardous-waste site or spill. The guide describes biological treatment methods, conditions and factors that limit the use of biotreatment, and types of data needed to evaluate and select biotreatment methods. Flow charts are included to help users determine the usefulness of each biotreatment method at specific hazardous-waste sites and spills.

U. S. Environmental Protection Agency, Technology Screening Guide for Treatment of CERCLA Soils and Sludges, EPA/540/2-88/004, 1988

Key Words bioremediation, soil, composting, slurry-phase, in situ, soil washing

Abstract (from document): The Technology Screening Guide for Treatment of CERCLA Soils and Sludges is a guide for screening feasible alternative treatment technologies for soils and sludges at Superfund sites. The guide provides a screening methodology to identify treatment technologies that may be suitable for the management of soils and sludges containing CERCLA wastes. A simplified screening methodology flowchart presents the decision steps necessary to identify suitable treatment technologies, while the waste/technology matrix tables included in this guide can be used to ascertain whether the treatment technologies have demonstrated effectiveness, potential effectiveness, or no effectiveness in the treatment of organic, inorganic, and reactive wastes or whether the technologies could adversely impact the environment. For each of the treatment technologies, information is presented on (a) the generic system, (b) individual, unique systems, (c) developmental status, (d) process schematics, (e) characteristics affecting treatment performance, and (f) contacts. Some limited information is also presented about pretreatment, materials handling, and residuals management requirements.

U. S. Environmental Protection Agency, Air Emissions from the Treatment of Soils Contaminated with Petroleum Fuels and Other Substances, EPA-600/R-92-124, Control Technology Center, 1992

Key Words air emissions, control, biodegradation, soil vapor extraction, in situ, slurry-phase, soil washing

Abstract (from document): This document summarizes available information on air emissions from the treatment of soils contaminated with fuels. Soils contaminated by leaks or spills of fuel products, such as gasoline and jet fuel, are a nationwide concern. Air emissions during remediation are a potential problem due to the volatile nature of many of the fuel components and the remediation processes themselves, which may promote or result in contaminant transfer to the vapor-phase. Limited information is also included on air emissions from the treatment of soils contaminated with hazardous wastes. The document will allow staff from State and local regulatory agencies, as well as staff from EPA regional offices, to assess the different options for cleaning up soil contaminated with fuels. Seven general remediation approaches are addressed in this report. For each approach, information is presented about the remediation process, the typical air emission species of concern and their release points, and the available air emissions data. Control technologies for each remediation approach are identified and their reported efficiencies are summarized. Cost data are given for each remediation approach and for its associated control technologies. Emission factors and other emission estimation procedures for each remediation approach are presented along with a brief case study.

Yare, B. S.; Hathorn, J. W.; "Site-wide, real-time air monitoring during remediation, *Journal of Hazardous Material Control*, vol. 4, no. 4, pp 33-37, 1991.

Key Words bioremediation sites, air monitoring

Abstract (copyright ACS): To insure that work-zone air pollutants did not leave a Superfund site during remediation, a real-time air monitoring system was installed to measure fence-line air quality. The site is a 58-acre abandoned oil refinery and petroleum plant located .apprx.15 mi south of Houston, Texas. Automatic monitoring stations (AMS) were installed consisting of hydrocarbon analyzers (CtC with F10), operating at the 0-100 ppm scale. High-vol. particulate samplers were also installed on the same transportable platform as the hydrocarbon analyzer. A computer controlled the system and acquired data from a meteorol. tower as well as from the AMS and displayed real-time data at the site office. Instantaneous, 1 min, 15 min, hourly avs. of CH4 and nonmethane hydrocarbons, wind speed and direction were displayed on the monitor. Different audible and visual alarms were used to distinguish between alert and alarm conditions. Activities were modified to reduce emissions.

Microbial Transformations

Alexander, M.; "Biodegradation of Chemicals of Environmental Concern," *Science*, Vol 211, pp 132-138, January 9, 1981

Key Words Microbiology, Biodegradation

Abstract (from document) Microorganisms in soils and waters convert many synthetic organic chemicals to inorganic products. Other compounds are transformed only by cometabolism. These microbial processes may lead to environmental detoxification, the formation of new toxicants, or the biosynthesis of persistent products. Type reactions are proposed for major categories of enzymatic transformation of synthetic chemicals in soils, natural waters, and sewage. Some organic molecules are resistant to microbial attack, and explanations for the persistence of such compounds are suggested.

Comments This paper with 91 references gives a review of the extensive literature which exists with regard to microbial degradation of synthetic chemicals. A general discussion of cometabolism, whereby organisms are capable of using one substrate as an energy source and metabolizing another compound at the same time, is given. Cometabolism plays an important role in the biodegradation of many chlorinated and nonchlorinated molecules. This may point to the need to add a primary substrate in order to remove some of the organic compounds present in soils. Although the mineralization of toxic chemicals is characteristically detoxification, accumulation of toxic intermediates has been observed in natural environments, in model ecosystems, and microbial cultures in artificial media. An example of this phenomena is the conversion of phenoxy herbicides in soil to yield phytotoxic intermediates. Care must be taken in transferring the results of laboratory studies of microbial degradation of synthetic chemicals to actual field behavior of biofilter units. In laboratory studies, the test compound is usually present in high concentration, the microorganisms are acting individually, and none of the complex materials which characterize the biofilter media are present. Of particular concern is the presence of surfaces which may adsorb certain classes of compounds and thereby sequester them from the microorganisms. Also, if the chemicals are present in very low concentrations, the organism may not get enough energy to maintain itself and so chemicals in low concentrations may persist in the environment.

Alexander, M.; "Biodegradation of Organic Chemicals," *Environmental Science and Technology*, Vol 19, p. 106, , 1985.

Key Words Microbiology, Biodegradation

Abstract (written by S. Ergas) This paper discusses the effects of concentration on the degradation rates of synthetic organic chemicals. Degradation rates observed in the laboratory for these compounds may not hold for compounds in the natural environment. Chemicals may be present in concentrations lower than the threshold concentration which will support growth or maintenance of the microbial population. Examples of this phenomena 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 in minute amounts. 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 than laboratory microorganisms. Compounds that are degraded via cometabolism generally do not inhibit biodegradation because these compounds are not incorporated into the cell. Microbial kinetics for different ranges of substrate concentration and microbial population are discussed.

Alexander, M,; *Introduction to Soil Microbiology*, Krieger Publishing Company, Malabar, Florida, USA, 1991

Key Words Microbiology, Biodegradation

Abstract (written by S. Ergas) soil microbiology text, recently updated: This text book contains chapters on microbial ecology especially with regard to the soil environment, carbon, nitrogen, and mineral transformation cycles, and interactions between organisms.

Comments: 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. Soil contains a vast array of bacteria, actinomycetes, fungi, algae, and protazoa and is the site 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. 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 about half the volume. Mineral matter makes up most of the rest with organic matter comprising about 3 to 6 percent of the total. Small animals and microorganisms make up less than 1 percent of the total volume. Properties of the soil have a profound influence on nutrient availability, aeration, and water retention. Among these are porosity, moisture content, aeration status, chemical composition, clay fraction, cation exchange capacity, and organic fraction.

Alm, R. R.; Olson, K. A.; Peterson, R. C.; "Using foam to maintain air quality during remediation of hazardous waste sites," Proceedings of 80th Annual Meeting, Air Pollution Control Association, Vol 1. 87/18.3, St. Paul, MN, 1987.

Key Words bioremediation sites, air pollution control

Abstract (copyright ACS): Water-based temporary and stabilized foams for maintaining air quality during remediation of hazardous waste site give 80-90% effectiveness in vapor and particulate suppression. Both types of foam can be applied to sites up to several acres in size using com. foam generators. Though limited in lifetime to .apprx.30 min, temporary foams are effective in reducing volatile org. compd. and air toxic emissions in situations where waste is disturbed during excavation. Stabilized foams generated by injecting a proprietary agent into the temporary foam stream prior to foaming are useful in longer-term situations, such as overnight waste site cover or consolidation of loose debris.

Alvarez-Cohen, L.; McCarty, P. L.; "Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture," Applied Environmental Microbiology, vol 57, no. 1, pp 228-235, 1991.

Key Words methanotrophic bacteria, trichloroethylene transformation

Abstract (copyright ACS): The trichloroethylene (TCE) transformation rate and capacity of a mixed methanotrophic culture at room temp. were measured to det. the effects of time without methane (resting), use of an alternative energy source (formate), aeration, and toxicity of TCE and its transformation products. The initial specific TCE transformation rate of resting cells was 0.6 mg of TCE/mg of cells/day, and they had a finite TCE transformation capacity of 0.036 mg of TCE/mg of cells. Formate addn. resulted in increased initial specific TCE transformation rates (2.1 mg/mg of cells/day) and elevated transformation capacity (0.073 mg of TCE/mg of cells). Significant declines in methane conversion rates following exposure to TCE were obsd. for both resting and formate-fed cells, suggesting toxic effects caused by TCE or its transformation products. TCE transformation and methane consumption rates of resting cells decreased with time much more rapidly when cells were shaken and aerated than when they remained dormant, suggesting that the transformation ability of methanotrophs is best preserved by storage under anoxic conditions.

Atlas, R. M., "Microbial hydrocarbon degradation - bioremediation of oil spills," Journal Chemical Technology and Biotechnology, vol. 52, no. 2, pp 149-156, 1991.

Key Words biotransformation, petroleum hydrocarbons

Abstract (copyright ACS): The review with 34 refs. covers microbial bioremediation of petroleum spills.

Barnhart, M. J.; Myers, J. M.; "Pilot bioremediation tells all about petroleum contaminated soil," *Pollution Engineering*, vol. 21, no.10, pp 110-112, 1989.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Biol. treatment of contaminated soils at an abandoned oil gasification site in Canada resulted in benzene, toluene, and xylene removals of 73% in 4 mo. Av. total polyarom. hydrocarbon removal efficiencies were 86%. The excavation of oil tar-contaminated soil resulted in localized air quality deterioration within the immediate work space.

Bartha, R.; "Biotechnology of petroleum pollutant biodegradation," Microbial Ecology, Vol. 12, no.1, pp 155-172, 1986.

Key Words biotransformation, petroleum hydrocarbons

Abstract (copyright ACS): A review with 68 refs. on the physiol. ecol. of petroleum hydrocarbon biodegrdn. and the biotechnol. approaches that can be applied to maximize the process for pollution abatement. Microbial cleanup of accidental oil spills at sea and on land, the treatment of refinery effluents and ballast water from tankers, and the land treatment of oil sludge are discussed.

Boush, G. M.; Matsumura, F.; "Pesticide degradation by marine algae," U. S. NTIS, Avail. NTIS From: Gov. Rep. Announce. Index (U. S.) 1975, 75(12), 47, AD-A Rep., No. 008275, 1975

Key Words microbial metabolism, algae, pesticides

Abstract (copyright ACS): Various algae species were tested for their susceptibilities towards chlorinated hydrocarbon insecticides. Dieldrin (I) [60-57-1], which is the most frequently found pesticidal contaminant in the U.S., and its analogs were found to inhibit the growth of certain algae species. Anacystis nidulans in particular showed marked susceptibility to endrin [72-20-8], I, ketoendrin [21038-31-3] and photodieldrin [13366-73-9]. This species was also susceptible towards I metabolites such as metabolite F and G. Among DDT metabolites DDD (TDE) [72-54-8] was found to be the most toxic material, followed by DDE [72-55-9], DDT [50-29-3] and FW-152 [3567-18-8]. It has not been known that DDT should be more toxic to algae. In terms of acute toxicity phenylmercuric acetate [62-38-4] was by far the most algicidal agent among all pesticidal chems. tested. This pesticide is toxic to both A. nidulans and A. quadruplicatum at the concn. of 1 ppb.

Bumpus, J. A.; Tien, M.; Wright, D.; Aust, S.D.; "Oxidation of persistent environmental pollutants by a white rot fungus," *Science*, Vol. 228, no. 4706, pp 1434-1436, 1985.

Key Words microbial metabolism, white rot fungus

Abstract (copyright ACS): The white rot fungus Phanerochaete chrysosporium degraded DDT [50-29-3], 3,4,3',4'-tetrachlorobiphenyl [32598-13-3], 2,4,5,2',4',5'-hexachlorobiphenyl [35065-27-1], TCDD [1746-01-6], lindane [58-89-9], and benzo[a]pyrene [50-32-8] to CO2. Model studies, based on the use of DDT, suggest that the ability of P. chrysosporium to metabolize these compds. is dependent on the extracellular lignin-degrading enzyme system of this fungus.

Cerniglia, C.E.; "Microbial metabolism of polycyclic aromatic hydrocarbons," *Advances in Applied Microbiology,* Vol. 30, pp 31-71, 1984.

Key Words biotransformation, polycyclic aromatic hydrocarbons, PAH

Abstract (copyright ACS): A review with many refs.

Claxton, L. D.; Houk, V. S.; Williams, R.; Kremer, F.; "Effect of bioremediation on the mutagenicity of oil spilled in Prince William Sound, Alaska," *Chemosphere*, Vol. 23 no. 5, pp 643-650, 1991.

Key Words microbial metabolism, activation, mutagenicity

Abstract (copyright ACS): On 24 Mar. 1989, .apprx.11 Mgal of Prudhoe Bay crude oil spilled into the waters of Prince William Sound, Alaska, contaminating .apprx.1000 mi of shoreline. Approx. 300 mi of beach were considered amenable to cleanup by bioremediation. To det. whether or not bioremediation would be effective in this geophys. setting and under such climatic conditions and to identify potential deleterious effects, the US EPA conducted in situ bioremediation field demonstration research projects. One of the methods used to assess potential health effects assocd. with this and similar efforts was the examn. of mutagenicity assocd. with the oil spill and the products of bioremediation. Salmonella mutagenicity was assessed using a semi-automated plating device (spiral plater) that requires less sample than the std. assay. Both the Prudhoe Bay crude oil and its weathered counterpart collected from oil-impacted water were weakly mutagenic. The mutagenicity of samples collected from the contaminated beaches (undergoing both enhanced and natural bioremediation) declined over time.

Dumdei, B. E.; Henderson, R.; "Air toxics monitoring program during bioremediation of a superfund site," *Proceedings* 81st Annual Meeting, Air Pollution Control Association, Vol. 1, 88/5.3, Lombard, IL, 1988.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): During bioremediation of an industrial sludge disposal site outside of Houston, Texas, controlled by sparging of air into the sludge and overlying water, pollutant emission was monitored by real-time measurements of total ionizables using a photoionization detector, real-time syringe sampling for volatiles with on-site gas chromatog. (GC) anal., real-time sampling of naphthalene on charcoal adsorbent and on-site GC anal., and time-integrated sampling for volatiles on Tenax followed by GC/mass spectrometry lab. anal. The results of the anal. were used for adjusting the aeration rate.

Eklund, B., Ranum, D., Orr, D. Summerhays, J.; "Estimation of VOC emissions from soils handling operations at Superfund sites," *Proceedings*, 83rd Annual Meeting, Air and Waste Management Association, vol. 8, 90/161.6, 1990.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Soil handling operations did not cause significant increases in ambient volatile org. compd. (VOC) concns. over baseline levels at the 2 field sites. Excavation of contaminated soil, however, stripped most (>50%) of the VOCs that were present from the soil. This implies that excavation of contaminated soil could adversely impact air quality at other sites where the levels of contamination were higher or the vol. of soil being moved per h was greater. The predictive models showed excellent agreement (within a factor of 2-3) with the field data for soil excavation and grading operations.

English, C. W., Loehr, R. C.; "Degradation of organic vapors in unsaturated soils," *Journal of Hazardous Material*, vol. 28, no. 1-2, pp 55-64, 1991.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Removal coeffs. for 3 volatile org. compds. (VOCs) in a fine sandy loam soil are detd. Sorption coeffs. and degrdn. rates were detd. from batch reactors for C6H6, ClCH:CCl2, and o-xylene. Org. vapors are sorbed and then removed by biodegrdn. of soils contaminated with VOCs and for impacting decisions on air emissions, regulatory limits and on-site controls. This information has the potential for use in the bioremediation of soils contaminated with VOCs and for affecting decisions on air pollution, regulatory limits and on-site controls.

Freedman, D. L., Gossett, J. M.; "Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions," *Applied Environmental Microbiology*, vol. 55, no. 9, pp.2144-2151, 1989.

Key Words biotransformation, halogenated aliphatics, chlorinated ethenes

Abstract (copyright ACS): A biol. process for remediation of groundwater contaminated with tetrachloroethylene (PCE) and trichloroethylene (TCE) can only be applied if the transformation products are environmentally acceptable. Studies with enrichment cultures of PCE- and TCE-degrading microorganisms provide evidence that, under methanogenic conditions, mixed cultures are able to completely dechlorinate PCE and TCE to ethylene, a product which is environmentally acceptable. Radiotracer studies with [14C]PCE indicated that [14C]ethylene was the terminal product; significant conversion to 14CO2 or 14CH4 was not obsd. The rate-limiting step in the pathway appeared to be conversion of vinyl chloride to ethylene. To sustain reductive dechlorination of PCE and TCE, it was necessary to supply an electron donor; methanol was the most effective, although hydrogen, formate, acetate, and glucose also served. Studies with the inhibitor 2-bromoethanesulfonate suggested that methanogens played a key role in the obsd. biotransformations of PCE and TCE.

Gibson, D. T.; "Microbial Metabolism of Aromatic Hydrocarbons and the Carbon Cycle," in *Microbial Metabolism and the Carbon Cycle*, Hagedorn, S.R., R.S. Handson, and D.A. Kunz (eds), Harwood Academic Publishers, 1988.

Key Words microbial metabolism

Abstract: Gives a general discussion of microbial metabolism and specific pathways for degradation of C1 compounds, aliphatics, aromatics, alicyclics and others.

Glaser, J. A., Lamar, R., Dietrich, D., Kirk, T. K.; "Treatment of wood-preserving soil contaminants by white-rot fungi, Innovative Hazardous Waste Treatment Technology, Ser., 3 (Biol. Processes), pp 73-78, Risk Reduction Engineering Laboratory, US Environmental Protection Agency, Cincinnati, OH 45268, 1991.

Key Words biodegradation, wood preservatives, fungi

Abstract (copyright ACS): Detoxification of soil polluted by wood-treating waste through use of specialized microorganisms is discussed. Degrdn. by fungi and bacteria is covered, and efforts to assist the growth of a wood-degrading fungus, Phanerochaete chrysosporium in soil (not the natural habitat of the species) are described. Degrdn. of pentachlorophenol-U-14C was studied for 8 wk with 3 soils. Both mineralization and volatilization were greater in soils inoculated with P. chrysosporium than in uninoculated soils.

Hinchee, R. E.; Miller, R. N.; Dupont, R. R.; "Enhanced biodegradation of petroleum hydrocarbons: an air-based in situ process," Innovative Hazardous Waste Treatment Technology, Ser., 3 (Biol. Processes), pp 177-183, Risk Reduction Engineering Laboratory, US Environmental Protection Agency, Cincinnati, OH 45268, 1991.

Key Words , soil venting, air emissions

Abstract (copyright ACS) Soil venting was initiated at .apprx.45 m3/min and was increased gradually to .apprx.2500 m3/min at a site contaminated by JP-4 jet fuel at Hill Air Force Base in Utah. Cumulative hydrocarbon removal between Dec. 1988 and Feb. 1990 was .apprx.47,000 kg volatilized and .apprx.15,000 kg biodegraded. When JP-4-contaminated soils at Tyndall Air Force Base, Florida, were aerated at .apprx.1 air-filled void vol. exchanged/day, biodegrdn. and volatilization rates were much higher than those obsd. in Utah. The data are preceded by a review on conventional and air-based enhanced biodegrdn.

Kaska, D.D., Polne-Fuller, M., Gibor, A.; "Biotransformation of alkanes and haloalkanes by a marine amoeba," *Applied Microbiol Biotechnology*, vol. 34, no.6, pp 814-817, 1991.

Key Words biotransformation, amoeba, chlorinated alkanes

Abstract (copyright ACS): A marine amoeba, Trichosphaerium I-7, originally found feeding on macroalgae in a region of natural oil seepage, was maintained in the lab. for prolonged periods on hexadecane, octadecane, 1-chlorooctadecane, or 1-bromooctadecane as a C source. The cells attached readily and eroded holes in thin layers of these compds. Cryst. and clear spherical inclusions appeared in the cytoplasm of cells fed these xenobiotics followed by a marked cell darkening. Thin layer chromatog. analyses of acetone exts. from amoeba grown for 12 days on [1-14C]octadecane demonstrated the formation of labeled substances of higher polarity than the original alkane. SDS-PAGE followed by autoradiog. revealed that 14C derived from [1-14C]octadecane was incorporated into acetone-insol. macromols.

Kilbane, J. J.; "Genetic aspects of toxic chemical degradation," *Microbial Ecolgoy*, vol. 12, no. 1, pp 135-145, 1986.

Key Words microbial metabolism, genetics

Abstract (copyright ACS) A discussion with 40 refs.

Matsumura, F.; Esaac, E. G.; "Degradation of pesticides by algae and aquatic microorganisms," ACS Symposium Series, Vol. 99 (Pest. Xenobiotic Metab. Aquat. Org.), pp 371-87, 1979.

Key Words microbial metabolism, algae

Abstract (copyright ACS): Photodegrdn. of DDT (I) [50-29-3] by the protease-liberated flavoprotein from TX-20 strain of Anacysis nidnlans resulted in the formation of TDE [72-54-8] as the major product. Dieldrin [60-57-1] formed photodieldrin [13366-73-9] as the major product. Among the organochlorine insecticides studied, lindane [58-89-9] was surprisingly the least affected compd. esp. because it is susceptible to dechlorination and also dehydrochlorination just like I. Degrdn. of I, dieldrin, and lindane by the flavoprotein prepns. was almost more efficient in the absence than in the presence of FMN [146-17-8]. Photodegrdn. of mexacarbate [315-18-4] was, however, greatly enhanced by FMN and other flavin cofactors. Thus, photodegrdn. of mexacarbate and the other 3 insecticides appears to be different. As was the case with dieldrin, photodecompn. of parathion [56-38-2] and toxaphene [8001-35-2] was relatively extensive, and the addn. of FMN had almost no effect on enhancing or decreasing its decompn. A similar flavoprotein system was isolated from Pseudomonas putida. Flavoprotein systems isolated from algae and bacteria have good potential for pesticide degrdn. in aquatic environment.

McCarty, P.; "Bioengineering Issues Related to In Situ Remediation of Contaminated Soils and Groundwater," in *Environmental Biotechnology*, G. S. Omenn (ed), pp 143-162, Plenum Publishing Company, 1988.

Key Words Microbiology, Biodegradation

Abstract: A general review on microbial degradation in soils. Many contaminants of concern are present in surface soils, in the vadose zone, or in the saturated zones. In situ biological treatment has been used as an approach to cleaning up these environments. This paper addresses some of the issues of importance to in situ biotransformation of hazardous chemicals. These issues include a discussion of relevant biotransformation processes, reaction kinetics, and reaction stoicheometry.

Comments This paper gives a review with 40 references of much of the literature on in-situ bioremediation of contaminated soils and groundwater. Some points to note: while many compounds are easily degraded as primary substrates under both aerobic and anaerobic conditions other compounds can only be transformed by cometabolism, other compounds are present in such low concentrations that they can only be utilized as secondary substrates. In these cases, primary substrates must be supplied to provide the energy requirements for bacterial growth. Little is known about substrate interactions and how to optimize these processes. In addition, further research is needed about methods of getting the correct amount of chemicals to the locations needed in the form needed.

Park, K. S.; Sims, R. C.; Dupont, R. R.; "Transformation of PAHs in soil systems," *Journal of Environmental Engineering*, ASCE, Vol. 116, no. 3, pp 632-640, 1990.

Key Words biotransformation, polyaromatic hydrocarbons, PAH

Abstract (copyright ACS): Transformation kinetics, cor. for abiotic loss and for volatilization, of 14 polycyclic arom. hydrocarbon (PAH) compds. were studied in two nonacclimated soils. Mean volatilization losses for naphthalene and 1-methylnaphthalene were measured as 31% and 22%, resp., of the total masses applied. Volatilization of the other twelve PAH compds. studied was <0.1%. The abiotic loss (1.8-17.4%) of 2- and 3-ring PAH compds. in soil samples bio-inhibited by 2% $HgCl_2$ was statistically significant. No significant loss from bio-inhibited soil was found for PAH compds. with >3 rings. Transformation half-lives cor. for volatilization and for abiotic loss were .apprx.2 days for 2-ring PAHs including naphthalene and 1-methylnaphthalene. Half-lives values for nonvolatile PAHs increased from 59 days for 3-ring PAHs (anthracene and phenanthrene) to >300 days for PAH compds. contg. >3 rings. The PAH transformation rate was inversely proportional to mol. wt. and compd. ring no.

Pitter, P., Chudoba, J.; *Biodegradability of Organic Substances in the Aquatic Environment*, CRC Press, Boca Raton, FL, 1990.

Key Words microbial metabolism, general

Abstract: A general discussion of microbial metabolism and biodegradability of organic compounds. Gives pathways for hydrocarbons, halogenated compounds and others.

Semprini, L., Hopkins, G. D., Roberts, P. V., Grbic-Galic, D., McCarty, P. L.; "A field evaluation of in situ biodegradation of chlorinated ethenes: part 3, studies of competitive inhibition," *Ground Water*, Vol. 29, no. 2, pp 239-250, 1991.

Key Words biotransformation, chlorinated ethenes, halogenated aliphatics

Abstract (copyright ACS): Results are presented that demonstrate the in situ biotransformation of vinyl chloride (I), trans-1,2-dichloroethylene (II), cis-1,2-dichloroethylene (III), and $ClCH:CCl_2$ by an enhanced population of CH_4-utilizing (methanotrophic) bacteria. Biostimulation was accomplished by introducing dissolved CH_4 and O into a shallow, confined aquifer, to encourage the growth of the native methanotrophic bacteria. Biotransformation of the target compds. ensued immediately after the commencement of CH_4 utilization, and reached steady-state values within 3 wk. The approx. extents of transformation achieved in the 2-m biostimulated zone were as follows: I, 95%; II, 90%; III, 50%; and ClCH:CCl2, 20%. The biotransformation of I and II was obsd. to be competitively inhibited by CH4. Cyclic variations in CH4 concn. caused by the alternate pulse injection of dissolved CH4 into the test zone caused oscillations of the aq. concns. of I and II. When formate and MeOH were substituted for CH4 as alternative electron donors, inhibition ceased (no oscillations), and concns. were reduced to levels achieved during periods when no CH4 was present, confirming the inhibition by CH4. Higher transformation rates were achieved temporarily, i.e., for several days, through the addn. of formate or MeOH. When electron donor addn. was terminated, the concn. of target compds. rapidly increased, indicating that the transformation promptly ceased. Although these expts. indicated that CH4 competitively inhibits transformation rates, this competition is a 2nd-order effect: CH4 as substrate for growth was also required for transformation of I, II, III, and ClCH:CCl2 by methanotrophs.

Spain, J. C.; "Microbial adaptation in aquatic ecosystems," ACS Symposium Series, Vol. 426 (Enhanced Biodegrad. Pestic. Environ.), pp 181-90,1990.

Key Words microbial metabolism, acclimation

Abstract (copyright ACS): A review with 22 refs. Aquatic microbial communities can adapt to degrade a novel substrate if the chem. can serve as a source of nutrients. Biodegrdn. of p-nitrophenol (PNP) has been studied in lab. test systems and in the field. Adaptation in freshwater microbial communities required from 3 to 10 days, and biodegrdn. rates increased as much as 1000-fold at PNP concns. as low as 10 mg/L. Populations of PNP degraders increased dramatically during adaptation, and no evidence of genetic change assocd. with adaptation was detected. Bacteria able to grow at the expense of PNP were detected in microbial communities prior to treatment with PNP. They did not begin to grow and degrade PNP until several days after initial exposure. The results indicate that accurate prediction of biodegrdn. rates requires a better understanding of the factors that control adaptation in the environment. These include enzyme induction, genetic changes, increases in microbial populations, predation, and nutrient limitation.

Strand, S. E.; Shippert, L.; "Oxidation of chloroform in an aerobic soil exposed to natural gas," *Applied Environmental Microbiology*, Vol. 52, no.1, pp 203-205, 1986.

Key Words biotransformation, chlorinated aliphatic compounds, chloroform, TCE

Abstract: Exposure of a sandy soil to an air-natural gas mixt. stimulated the biol. oxidn. of CHCl3 [67-66-3] to CO2. C2H2 [74-86-2] and CH4 [74-82-8] inhibited CHCl3 oxidn, which continued .ltoreq.31 days in the absence of CH4. CHCl3 oxidn. rates increased at CHCl3 concns. .ltoreq.5 .mu.g/g soil.

Thompson, P., Inglis, A., Eklund, B.; "Emission factors for Superfund remediation technologies," U.S. Environ. Prot. Agency, Off. Air Qual. Plann. Stand., [Tech. Rep.] EPA, EPA-450/1-91-001, 89 pp., 1991.

Key Words bioremediation sites, air emissions

Abstract (copyright ACS): Techniques are presented for the estn. of air emissions from Superfund site cleanup by thermal treatment, air stripping, soil vapor extn., solidification and stabilization, physicochem. treatment, biol. treatment, and land treatment.

U. S. Environmental Protection Agency, EPA guide for Identifying Clean Up Alternatives at Hazardous Waste Sites and Spills: Biological Treatment, EPA 600/3-83/063, 1983.

Key Words bioremediation sites, regulations

Abstract (copyright ACS): This EPA publication gives guidance for the consultant or regulatory agency in determining whether bioremediation is a viable alternative for a particular site. An extensive description of bioremediation processes is given. Microbial metabolism is discussed. A table containing biotransformation products for hundreds of compounds is included.

U.S. Environmental Protection Agency, Technology Screening Guide for Treatment of CERCLA Soils and Sludges, EPA 540/2-88/004, 1988.

Key Words bioremediation sites, regulations

Abstract: A guide for the decision maker at a potential bioremediation site. Especially useful are names, addresses, and phone numbers of EPA, industry, and vendor contact people.

U.S. Environmental Protection Agency, Final Report: Soil Treatment Pilot Study--Brio/DOP Site (Technical Report No. 8610), EPA Region 6 (212) 655-6444, 1987.

Key Words bioremediation sites, air emissions

Abstract (abstract from ATTIC database): Bench- and pilot-scale studies were conducted to demonstrate the feasibility of using solid-phase biodegradation for destroying organic constituents in soil at the Brio/DOP site. A diverse microbial population resided in the soil. The pilot-scale solid-phase treatment facility consisted of a lined soil treatment area with a collection system, water/nutrient distribution system, emission controls, microbiological management system, greenhouse enclosure, and support facilities. The facility operated 94 days. 200 cu yds of soil were removed and inoculated with microorganisms to ensure aeration. Volatile organic compounds (VOCs) were trapped by activated carbon adsorbers at the pilot facility. The pilot-scale treatment facility demonstrated under field conditions that a solid-phase treatment process could be used to successfully treat the organic constituents present in the site soil. The process removed the VOCs by air stripping, and destroyed semi-volatile organic compounds by biodegradation. More than 99% of the VOCs were removed within the first 21 days of operation. Biodegradation for semi-volatiles was much slower, taking 131 days to reduce phenanthrene concentrations below detection limits.

U.S. Environmental Protection Agency, Record of Decision--Brio Refining, TX, EPA/Superfund Office, Region 6 (214) 655-6444,

Key Words bioremediation sites, air emissions

Abstract (copyright EPA ATTIC database): The Brio Refining site is broken into two parcels, Brio north and Brio south. Between 1957 and 1982 the site refined crude oil and styrene tars to produce toluene, ethylbenzene, aromatic solvents, naphthalene, diesel fuel and kerosene. Various owners of the site stored styrene tars in 24 open pits. Other waste products and sludges were stored in aboveground tanks. Site investigation indicates that between 500,000-700,000 cubic yards of onsite soil have measurable contamination, and that high levels of VOCs exist in groundwater underlying the site. The selected remedial action for this site includes excavation and incineration or biological treatment of all onsite soils, sludges, and liquids found to be above action levels defined in the endangerment assessment, with backfilling of all treated material passing the TCLP. If the Brio Site Task Force PRPs can successfully demonstrate the effectiveness of aqueous phase biological treatment it will be considered, otherwise incineration will be selected; excavation of all visual onsite seeps; further investigation of Pit G to locate sludge or contaminated soil underlying the existing onsite wastewater treatment impoundment; consolidation and disposal of all inert debris; disposition of mud gully the flood control ditch; inplace stabilization of wastes existing in the wastewater treatment impoundments, and installation of a package wastewater treatment system or route wastewater to a POTW; removal and disposal of tank contents, and decontamination, dismantling and selling or offsite disposal of tanks and process equipment; monitoring program; control of air emission from the treatment process; venting waste enclosures; treatment of groundwater in the numerous sand channel zone to a level to be determined in design; natural attenuation of the 50-foot sand aquifer; regrading and vegetating areas outside excavation areas; construction of a stormwater transmission system draining to mud gully; and im- position of deed restrictions.

Vogel, T. M., Criddle, C. S., McCarty, P. L.; "Transformations of halogenated aliphatic compounds," Environmental Science & Technology, Vol. 21, no. 8, pp 722-736, 1987.

Key Words biotransformations, halogenated aliphatic compounds

Abstract (copyright ACS): A review, with 114 refs., on transformation of halogenated aliph. compds., including substitution, dehydrohalogenation, oxidn. and redn., microbially mediated reactions, and environmental applications.

Vogel, T. M.; McCarty, P. L.; Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions," Applied Environmental Microbiology, Vol. 49, no. 5, pp 1080-1083, 1985.

Key Words biotransformation, chlorinated ethenes, halogenated aliphatics

Abstract (copyright ACS): Biotransformation of C_2Cl_4 (I) [127-18-4] and $CHCl_3$ (II) [513-35-9], common industrial solvents and among the most frequent contaminants found in groundwater supplies, was studied to evaluate their environmental fate. The results of this study confirm that I can be transformed by reductive dehalogenation to II, $C_2H_2Cl_2$ [25323-30-2], and C_2H_3Cl (III) [75-01-4] under anaerobic conditions. In addn., [14C]-I was at least partially mineralized to CO_2. Mineralization of 24% of the I occurred in a continuous-flow fixed-film methanogenic column with a liq. detention time of 4 days. II was the major intermediate formed, but traces of dichloroethylene isomers and III were also found. In other column studies under a different set of methanogenic conditions, nearly quant. conversion of I to III was found. These studies clearly demonstrate that II and III are major intermediates in biotransformation under anaerobic conditions and suggest that potential exists for the complete mineralization of I to CO_2 in soil and aquifer systems and in biol. treatment processes.

Yare, B. S.,Hathorn, J.W.; "Site-wide, real-time air monitoring during remediation," *Hazardous Material Control*, Vol. 4, no. 4, pp 33-37, 1991.

Key Words bioremediation sites, air monitoring

Abstract (copyright ACS): To insure that work-zone air pollutants did not leave a Superfund site during remediation, a real-time air monitoring system was installed to measure fence-line air quality. The site is a 58-acre abandoned oil refinery and petroleum plant located .apprx.15 mi south of Houston, Texas. Automatic monitoring stations (AMS) were installed consisting of hydrocarbon analyzers (CtC with F10), operating at the 0-100 ppm scale. High-vol. particulate samplers were also installed on the same transportable platform as the hydrocarbon analyzer. A computer controlled the system and acquired data from a meteorol. tower as well as from the AMS and displayed real-time data at the site office. Instantaneous, 1 min, 15 min, hourly avs. of CH4 and nonmethane hydrocarbons, wind speed and direction were displayed on the monitor. Different audible and visual alarms were used to distinguish between alert and alarm conditions. Activities were modified to reduce emissions.

Analytical & Experimental Methods

Aggarwal, P. K., "Monitoring In Situ Biodegradation of Hydrocarbons by Using Stable Carbon Isotopes", *Environmental Science & Technology*. Vol. 25, No. 6, pp. 1178-1180, 1991

Key Words in situ bioremediation, petroleum hydrocarbons, soil bioremediation

Abstract: Spilled or leaked nonhalogenated petroleum hydrocarbons in the soil can be generally metabolized by indigenous, aerobic bacteria. In situ biological degradation of hydrocarbons may be accelerated by supplying inorganic nutrients and/or oxygen. Approaches to monitoring and verifying enhanced in situ biodegradation have included measurements of changes overtime in the (a) concentration of hydrocarbons, (b) temperature, (c) number of hydrocarbon-degrading microorganisms, (d) ratio of fast degrading hydrocarbons (e.g., n-C17 or n-C18) to slowly degrading hydrocarbons (e.g., pristanes or phytanes), and (e) metabolic intermediates. Measurements of oxygen consumption over time and elevated carbon dioxide concentrations in soil gas also have been used as indicators of hydrocarbon degradation (1). All of these methods have some merit; however, because of the high variability at many sites and difficulty in obtaining an accurate mass balance, it is difficult to demonstrate that the disappearance of hydrocarbons is due to biodegradation rather than volatilization, dissolution, or simply dilution. Methods based on changes in soil gas composition also are less accurate because these changes may occur by processes other than hydrocarbon degradation.

An alternative approach that may help substantiate biodegradation is to measure stable carbon isotope ratios in soil gas CO_2. Stable carbon isotope ratio analysis is inexpensive and commercially available at many laboratories. carbon dioxide produced by hydrocarbon degradation may be distinguished from that produced by other processes based on the carbon isotopic composition characteristic of the source material and/or fractionation accompanying microbial metabolism. Here we demonstrate the applicability of the stable isotope technique for monitoring enhanced, aerobic biodegradation of hydrocarbons using data from three locations in the United States. A laboratory study is currently underway to extend this technique to estimate the amount of hydrocarbons degraded over a certain period of time.

Babb, T.; "Ambient air monitoring during the cleanup of hazardous waste sites contaminated by polychlorinated dioxins," ACS Symposium Series, 338 (Solving Hazardous Waste Problems), pp 267 277, 1987.

Key Words chlorodibenzodioxin sampling air analysis

Abstract (copyright ACS): The use of a high-vol. air sampler with a module contg. a polyurethane foam cartridge (R. G. Lewis and M. D. Jackson, 1982) for detn. of particulate matter and polychlorinated dibenzodioxins in air is described. Data on the continuous monitoring of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8--

tetrachlorodibenzofuran in air near contaminated sites during their clean-up are provided. Quality control, assurance, data management and reporting are described.

Balfour, W. D., Schmidt, C. E., "Sampling Approaches for Measuring Emission Rates From Hazardous Waste Disposal Facilities.", *Proceedings* 77th Annual Meeting Air Pollution Control Association, Vol. 1, pp 84-3.3, 1984

Key Words Air emissions, assessment, volatile org emission sampling approach; waste disposal org emission sampling, SIC, C-P, vent, mass balance

Abstract Fugitive air emission data have been collected for treatment , storage and disposal operations to support a Regulatory Impact Analysis (RIA) for Hazardous Waste Disposal Facilities. Five sampling approaches have been used for measuring air emission rates from these operations. They are: 1) emission isolation flux chamber 2) vent sampling 3) concentration profile technique and 4) mass balance. Each of these techniques are compared as to their precision, potential applications, and specific limitations of the approaches. Data are presented from sites at which the approaches were applied. Results were compared and contrasted where different techniques were used to measure emission rates of the same operation. Finally, recommendations are made for selection of an appropriate sampling approach based on the field experience gained. 13 refs.

Comments Surface isolation chamber (SIC) was used to sample active and inactive landfills, surface impoundments and a land treatment facility. Transect technique was used to estimate emissions from active landfill, and surface impoundments. Vent sampling was used on inactive landfill, drum storage buildings and storage tanks. Concentration profile (C-P) technique was used on surface impoundments and a land treatment facility. From these applications the authors concluded the following: Where ever applicable the surface isolation chamber should be used to measure the VOC emissions as SIC is very sensitive and the scope for variability is low. However, SIC is not recommended for very large waste bodies of variable composition or highly agitated liquid surfaces. Among C-P technique and transect technique C-P technique is preferable over transect method when SIC is not applicable and based on other factors like type of source and environmental conditions.

Balfour, W. D.; Eklund, B. M. and Williamson, S. J.; "Measurement of Volatile Organic Emissions from Subsurface Contaminants," *Air Monitoring*, pp.77-80

Key Words Air emissions, assessment, surface isolation chamber

Comments: This paper presents the results of field measurements at a spill site, at a Marine Corps helicopter facility in Tustin, California. Balfour et. al. used surface isolation chamber to measure the VOC emission rates. The soil was contaminated with JP-4 aviation fuel. The compounds contributing to emissions were identified as the aviation fuel components. Apart from assessment of emissions from the site, effect of specific operating variables on measured emission rates and suitability of the statistical sampling procedure for area sources were evaluated and sources of variability were analyzed. The factors contributing to variability in measurements investigated were chamber geometry, sunlight, relative humidity of air inside the chamber, sweep flow rates of air into the chamber, chamber air temperature, diurnal variations, sampling location, and accuracy and precision of sampling and analytical techniques.

The authors found that the chamber geometry and relative humidity did not affect the measurements. Shielding the chamber from sunlight decreased the measured emission rates. This decrease was accounted to soil and air temperatures. Decrease in sweep flow rate resulted in decrease in measured emission rates. The author suggests the adjustment of air temperature to an average temperature so that the emission measurements could be less variable. These conclusions show the need for further investigation into these factors. Effort has been made to optimize the surface isolation chamber design and operation on different types of facilities by various authors like Dupont [1987], Gholson et. al [1991] and Reinhart et. al. [1992].

Batterman, S. ; McQuown, B., McFarland, A.; "A passive soil gas flux sampler: laboratory and field evaluation," *Proceedings* of the 84th Annual Meeting, Air Pollution Control Association, Vol. 10B 91/13.7, 1991.

Key Words soil gas emission, passive sampler.

Abstract (copyright ACS): A flux sampler for soil gas anal. consists of a passive sampling element and the related detector consists of a passive sampling charcoal element. The evaluation results indicated a passive to active flux ratio of 0.91 .+-. 0.11. A precision of .apprx. 90% was obtained for passive sampling.

Card, T. R; Cagwin, D; Witherspoon, J; Chang, D; & Ergas, S; "Air Toxics and Related Compounds: Control of Emissions,"

Key Words Air emissions, control techniques, air toxics, volatile organic compounds

Abstract: This paper represents the results of a literature review into the current air emission control technologies available for wastewater treatment facilities. Technologies discussed include covering systems, process modifications, adsorption systems, thermal destruction systems, traditional odor control devices, and biofiltration. In addition, the implications of enclosing wastewater treatment systems are discussed including ventilation, safety, corrosion, and operator access.

Comments: Different types of covering systems described in this paper are fixed roof covers, rigid floating covers, flexible floating covers, air-supported structures, and floating spheres. Applications of fixed roof covers indicate that 95 percent air emission control is possible provided the fixed roof cover is completely sealed and well-maintained. Depending on the material of construction (aluminum, steel, concrete, etc.) of fixed roof covers corrosion may be a problem. Other problems faced are degradation of the cover, seams or seals and fire hazard. About 85 to 90 percent efficiency has been achieved by using rigid floating covers to control the emissions from a wastewater treatment surface. Typically these rigid floating covers are made of metals or polymeric compounds reinforced with carbon, fiberglass or other materials. Flexible floating covers made of polymers like polyvinyl chloride and polyethylene float on the water surface. Some problems associated with flexible floating covers are degradation of cover material, and diffusion of VOCs through the cover. 85% efficiency has been estimated from benchscale studies. Covers could be used at emissions hazardous waste treatment and disposal sites, refinery operations, POTWs and many other type of sources to control VOC emissions as well as odor.

Coover, J. R., and Walker, S. L.; "Estimating Emissions from Land Treatment Facilities: A Case Study," Presented at the 83th Annual Meeting Air & Waste Management Association, Pittsburgh, Pennsylvania, June 24-29, 1990

Key Words air emissions, bioremediation, land treatment

Comments: Main objective was to estimate emissions from land treatment units by soil flux measurements and perimeter monitoring techniques and then compare the field results with a field validated emission model called CHEMDAT6 and a dispersion model (ISC). The wastes applied to land treatment unit were refinery API Separator sludge wastes. A high flow flux chamber (HFCC) was used to measure the fluxes of benzene, toluene, ethylbenzene and xylene. Two upwind, four downwind and one background ambient air samples were collected each day.

The following conclusions were made from comparison of field results with model prediction results. The results obtained by CHEMDAT6 model did not match very well with the field results. CHEMDAT6 model did not predict the decrease in emission rates with time. But the predicted emissions were reasonable when expressed as mass fractions lost to air except for benzene. Emission estimates obtained from ISC model compared well with measured downwind ambient air concentrations.

Comparing the experimental results with theoretical models is one of the ways of establishing the accuracy of results obtained experimentally. Another way is to get repetitive experimental results under variable operating conditions.

Cowherd, C., Jr.; "Measurement of particulate emissions from hazardous waste disposal sites." *Proceedings* of the 78th Annual Meeting, Air Pollution Control Association, Vol. 6 85/73.3, 1985.

Key Words dust emission hazardous waste measurement, wind tunnel

Abstract: The quantification techniques developed for fugitive dust emission factors are applicable to the measurements of dust emissions and particle size distributions for hazardous waste disposal facilities. The portable wind tunnel method is advantageous for conventional upwind-downwind sampling for the measurement of wind-generated particle emissions. Exposure profiling is not feasible for large sources which emit plumes >10 m high.

Draves, J. A.; Eklund, B.; and Padgett, J.; "Applicability of Open Path Monitors for Use at Superfund Sites," Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, Missouri, June 21-26, 1992.

Key Words Air monitoring, Spectrometry

Abstract: This paper provides an overview of a document entitled "Applicability of Open Path Monitors to Superfund Sites". The document provides guidance as to when Open Path Monitors (OPMs) may be applicable to monitoring at Superfund sites. Information is provided as to general capabilities of OPM systems. More specific information is presented for the three widely used OPM methods for ambient air monitoring (AAM) applications: fourier transform infrared (FTIR) spectrometry, ultraviolet-differential absorbance spectrometry (UV-DOAS), and gas filter correlation (GFC) spectrometry. The detection limits of each type of instrument are discussed and compared to the detection limits achievable using conventional AAM techniques such as EPA Method TO-14 as well as to short term and long-term health based action levels. The data turnaround time and the ability to resolve temporal variations in emissions are also discussed. OPM systems are not considered generally applicable for use during the Site Investigation, Remedial Investigation, or O&M, but may be preferred method for the Feasibility Study and the Remedial Action.

Dumdei, B. E.; Henderson, R.; "Comparison of air toxics measurements methods used at a hazardous waste site," *Proceedings* of the 81st Annual Meeting, Air Pollution Control Association, Vol. 1 88/5.2, 1988.

Key Words waste site air pollution monitoring

Abstract: Time-integrated measurements vs. real-time grab sampling were compared as methods for monitoring volatile org. air pollution at a hazardous waste site. Both methods gave complimentary data which reflected differences in the site operational conditions, heterogeneity of wastes, meteorological. conditions, and imprecision of the measurements themselves.

Dupont R. R. and Reineman, J. A., "Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites", USEPA EPA/600/S2-86/071, Nov. 1986

Key Words Air emissions, Surface Isolation Chamber

Abstract The volatilization of hazardous organics from hazardous waste land treatment systems was evaluated in laboratory and field studies using complex petroleum refining hazardous wastes. Laboratory experiments were conducted using two soils and an inert construction sand to investigate the emission flux rates of seven volatile constituents, i.e., benzene, toluene, ethylbenzene, p-, m-, o-xylene, and naphthalene, from API Separatory Sludge and Slop Oil Emulsion Solids wastes in column and flask laboratory units. Emission flux rates were monitored as a function of waste application rate , application method (surface versus subsurface), soil type and soil physical characteristics. Field experiments were conducted at an active petroleum refinery hazardous waste land treatment site to which a combined API Separator Sludge/DAF bottom sludge was surface applied.

Pure constituent collection and quantification in both laboratory and field studies were carried out using an emission flux chamber and split stream Tenax^{TM} sorbent tube concentration system. Suggested operating procedures in terms of purge flow rates, split stream sampling rates, sample collection volumes for minimal contaminant sorbent tube breakthrough, etc., are presented.

Measured laboratory and field data were compared to the Thibodeaux-Hwang Air Emission Release Rate (AERR) model in an effort to validate this state-of-the-art land treatment emission model. Once specific data are collected which describe the physical environment of the land treatment system, prediction of pure constituent air emissions from surface application and tilling can be provided by the model, within a factor of two to ten, even for complex hazardous wastes applied to complex soil systems.

This project summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title. 5 refs.

Comments Laboratory surface application experiments followed the linear relationship of flux versus 1/time$^{1/2}$ similar to the results predicted by Thibodeaux-Hwang model. But the subsurface application experiments result did not match well with this theoretical model. The authors thinks that this must be due to the variable upper boundary condition with time, and unsteady state diffusion during the development of an upper uncontaminated soil zone compound concentration gradient following waste application.

The authors reported that the measured flux values from the field were within a factor of two to ten of Thibodeaux-Hwang model predictions for most of data during specific constituent emission sampling following waste addition. There was an increased divergence from predicted values with time. The authors think that this could be due to biodegradation and/or adsorption within the soil column that is not accounted for in the Thibodeaux-Hwang AERR model.

The authors emphasized the need for strict quality control and quality assurance procedures to ensure adequately prepared, stored and analyzed sorbent tubes. Dupont and Reineman made the following conclusions regarding the chamber/Tenax sorbent collection system. 1) Mean recoveries from the collection system for the seven aromatic compounds ranged from 61 to 94 percent. 2) Tenax breakthrough volumes were found to be a strong function of collected mass and temperature. 3) In order to minimize chamber internal pressures and potential soil emission suppression the purge flow rates of the sampling system must be less than 1 liter/min or in conjunction with a downstream purge pump.

Dupont, Ryan R.; "Evaluation of Air Emission Release Rate Model Predictions of Hazardous Organics From Land Treatment Facilities", *Environmental Progress*, Vol. 5, NO. 3, pp. 197-206, 1986

Key Words Air emissions, model assessment, petroleum refining

Abstract The Thibodeaux-Hwang Air Emission Release Rate (AERR) model for volatile emissions from land treatment systems was evaluated on a constituent specific basis utilizing API Separator Sludge and a Slop Oil Emulsion Solids waste stream applied to laboratory sand and soil microcosms. Literature correlation equations were used for estimating air:oil partition coefficients necessary for model input. Measured data suggested that vapor partitioning and retardation by soil organic matter are of minor importance in the overall vapor soil transport process, and that volatile organic vapor soil diffusion can be adequately described simply by the physical environment through which the vapor is traveling.

Subsurface waste application produced a two- to ten-fold decrease in emission rates as predicted from the Thibodeaux-Hwang AERR model compared with surface application conditions. Measured data followed the predicted linear relationship of flux rate versus concentration indicating the diffusional nature of soil vapor movement. The Thibodeaux-Hwang AERR model and the parameter estimation approach consistently overestimated flux rates for the pure constituents by only a factor of approximately 2 to 10, and consequently appear quite effective for the estimation of volatile organic emissions from complex waste/soil systems. 12 refs.

Comments This paper is based on the EPA [1986] report written by Dupont and Reineman.

Eklund, B; "Practical Guidance for Flux Chamber Measurements of Fugitive Volatile Organic Emission Rates," Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, MO, June 21-26,1992.

Key Words Air emissions, assessment, SIC

Abstract: Emission flux measurements provide an estimate of the amount of single species being emitted from a given surface area per unit time. These data can then be used in predictive modeling for population exposure assessments and for remedial action design. This paper describes the use of a direct emission measurement approach using an emission isolation flux chamber - to measure emission rates of various compounds (VOCs) from contaminated soil and water.

Flux chamber measurements are now commonly used at Superfund sites as part of the site investigation process. A variety of measurement equipment and operating procedures are employed, and problems have been noted with samplers following a "cookbook" approach to perform these measurements. This paper discusses the theory of the sampling approach and discusses the controlling variables that affect the accuracy and precision of the method. Guidance is given related to the optimal size of chamber to use, when opaque versus transparent construction materials are preferred, techniques to ensure a well-mixed atmosphere within the chamber, special considerations related to various sampling media or instrumentation, and so on for both solid and liquid surfaces. A generic quality control program is also presented that gives the minimum number of duplicate, blank, background, and repeat samples and discusses why and how these tests should be performed. Finally, the use of the data for modeling purposes is given (e.g., how to calculate the effective wind speed across the sampling surface).

Eklund, B; Thompson, P; Adrienne, I & Dulaney, W; " Air Emissions from the Treatment of Soils Contaminated with Petroleum Fuels and Other Substances," EPA-600/R-92-124, July, 1992

Key Words Air emissions, assessment, control techniques

Abstract: This report summarizes available information on air emissions from treatment of soils contaminated with fuels. Soils contaminated by leaks or spills of fuel products, such as gasoline and jet fuel are a nationwide concern. Air emissions during remediation are a potential problem due to the volatile nature of many fuel components and the remediation processes themselves, which may promote or result in contaminant transfer to the vapor-phase. Limited information is also included on air emissions contaminated with hazardous wastes.

The document will allow staff from State and regulatory agencies as well as staff from EPA regional offices, to assess the different options for cleaning up soil contaminated with fuels. Seven general remediation approaches are addressed in this report. For each approach, information is presented about the remediation process, the typical air emission species of concern and their release points, and the available air emission data. Control technologies for each remediation approach are identified and their reported efficiencies are summarized. Cost data are given for each remediation approach and for its associated control technologies. Emission factors and other emission estimation procedures for each remediation approach are presented along with a brief case study.

Comments: This report gives a brief description of various remediation techniques including in-situ and ex-situ bioremediation techniques for treatment of soils contaminated with gasoline, diesel fuel or oil. Applicable techniques (depending on the type of remediation process and expected emissions) to control the VOC emissions are also addressed in this report. To reduce the VOC emissions from in situ treatment, subsurface injection of waste is recommended. But subsurface injection is applicable only to liquid wastes. Efficiency of subsurface injection is limited by soil tilling (in process like land treatment).

The authors identified slurry-phase biotreatment as an exsitu type of treatment. Suggested air emission control techniques to control emissions from a process vent (point source), are carbon adsorption, thermal and catalytic oxidation. Carbon adsorption is applicable to contaminants of molecular weights between 50 and 150 and low VOC concentrations (< 500-1000 ppmv). Catalytic oxidation is most efficient air flow rate is constant and when VOC concentration is below 3000 ppmv. When the air emissions are from an area source the control options suggested are vapor collection hood (enclosure) to capture the VOC emissions and then pass these emissions through a control device, and oil film or foam that could be spread on top of the slurry to suppress evaporative losses. Applications indicate that vapor suppression foam is not very efficient. Another control option of importance is biofiltration. Biofiltration works on the principle of bioremediation. One typical use is passing the VOC emissions from soil vapor extraction through the biofilter. Other options suggested for controlling VOC emissions from soil vapor extraction are condensers, packed bed thermal processors.

Eklund, B., et. al.; "Estimation of VOC Emissions From Soils Handling Operations at Superfund Sites," Presented at t 83 Annual Meeting of the Air & Waste Management Association, no. 90-161.6, Pittsburgh, PA, June 24-29, 1990

Key Words Air emissions, assessments, SIC, transect technique

Comments: This paper presents the assessment of air emissions from two NPL cleanup sites. The field results obtained were compared to predictive models. The main objectives of field work were to determine the VOC emission levels from soil handling operations and to find the relative increase in emissions over baseline values due to material handling operations and also the duration of these increases. One site was a midwestern disposal pit with xylenes and ethylbenzene as primary contaminants. The cleanup treatment plan was to excavate the contaminated soil, move it to a place where liquid and solid sludges were separated and then transport to a site where the soil could be incinerated or disposed in a RCRA landfill. The other site was located at a military base in the western U.S. The soil was contaminated with oil-separator waste, diesel fuel, JP-4/JP-5 aviation fuels, cleaning solvents, and hydraulic and other aviation fuels. Primary contaminants were identified as olefins and paraffins. This information is useful for bioremediation processes such as landfarming as very often the soil has to be excavated and/or shifted to another place.

The methods used to measure the emission rates were transect technique (indirect technique) which makes use of Gaussian plume dispersion model and surface isolation chamber (direct technique). The air samples were collected in stainless steel canisters and analyzed by a gas chromatograph with multiple-detectors (GC-MD). The hydrocarbons were quantified using flame-ionization detector (FID), photoionization detector (PID) and a Hall electrolytic-conductivity detector (HECD). Soil samples were also taken and analyzed.

The results indicated low and variable levels of VOC concentrations in the soil at both the sites. There was no significant increase in ambient VOC concentrations over baseline levels at both the sites. However excavation of soil resulted in stripping of above 50% VOCs from the soil. The results obtained from predictive models matched very well with the experimental results. 7 refs.

Ergas, S. J., Schroeder, E. D., and Chang, D. P.Y., " Control of Volatile Organic Compound Emissions from a POTW Using a Compost Biofilter," Presented at the 85th Annual Meeting Air & Waste Management Association, Kansas City, Missouri, 1992.

Key Words Air emissions, control technique, Biofiltration

Abstract: Biofiltration is an air pollution control technology which may hold promise for controlling volatile organic compound (VOC) emissions from publicly owned treatment works (POTWs). Several concerns arise however, due to the possible effects of low concentrations and high fluctuations of multiple contaminants on a biological system. A pilot scale (approx. 200cfm) biofilter was evaluated for its feasibility in controlling air emissions from a large municipal wastewater treatment plant. Initial testing with a synthetic gas stream containing benzene, toluene, methylene chloride, trichloroethylene, chloroform, and perchloroethylene achieved 50-80% removal efficiencies. Further testing with gaseous emissions from primary wastewater treatment showed high removal efficiencies for VOCs as well as H_2S and odors.

Esplin, G. J.; "Boundary Layer Emission Monitoring," *Journal of the Air Pollution Control Association*, Vol. 38, no. 9, pp. 1158, 1988.

Key Words Air emissions, air monitoring, boundary-layer monitoring

Abstract: A new methodology is described for determining the atmospheric emission rate of pollutants from large heterogeneous area sources, such as hazardous waste sites. The procedure hinges upon measuring average pollutant concentrations, at three or more different elevations, while traversing the plume downwind of the area source. A helium-filled tethersonde balloon is used to elevate the sampling lines to their appropriate height. During plume traversing the sampling rate is adjusted to be proportional to the sine of the angle between the wind vector and the direction of the traverse path. The average concentrations are corrected for any upwind, background concentration and then used to derive an average vertical concentration profile. This profile is numerically integrated, with the wind velocity profile, over the pollutant boundary layer to yield the area source emission rate. The methodology was tested on several large industrial effluent lagoons and proved to be easy to use, robust, and precise.

Comments: The author thinks that the proposed new methodology, based on boundary layer monitoring, was a better alternative to estimate emissions from heterogeneous area sources. This method was tested only on industrial effluent lagoons. More applications are necessary on large heterogeneous area sources to establish this method as a better alternative as compared to other indirect and direct techniques.

Fellin, P,; "Monitoring of Volatile Organic Hydrocarbon and Reduced Sulfur Compound Fugitive Emissions from An Oil Sands Recovery Facility in Northern Alberta," Presented at the 85th Annual Meeting of the Air and Waste Management Association, June 21-26,1992, Kansas City, Missouri.

Key Words Air emissions, assessment, modeling, Upwind/downwind

Abstract: Syncrude Canada is the largest oil sands recovery and upgrading facility in the world. Activities such as mining, extraction, upgrading and waste discharge into large holding ponds provides the potential for substantial fugitive emissions of volatile organic hydrocarbons and reduced sulfur compounds. A detailed study was performed during worst case conditions to evaluate the incremental downwind concentrations potentially arising from site activities. Flux monitoring was coupled with mass transfer modeling and upwind/downwind profiling to evaluate the emission rates from specific sources. Site export due to fugitive sources was measured to be ca. 600g/s for VOC and 1.9g/s for H_2S. Significant emissions of other reduced sulfur compounds were also found. The main tailings pond (22 sq. km) was found to be the major emitter for both classes of compounds. Dispersion modeling using on site meteorological information measured during the study period was coupled with an area source dispersion model to evaluate concentrations at a point 5 km outside the plant boundary, representing the nearest residential community. Concentrations predicted (and measured) for VOCs and reduced sulfur compounds were at low mg/m^3 and ng/m^3 levels respectively.

Gerstle, R. W,; "Controlling Air Emissions During Hazardous Waste Excavation," Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, Missouri, June 21-26, 1992.

Key Words Air emissions, control techniques, covers, foam

Abstract: A trial excavation of highly acidic petroleum refinery waste was performed at a Superfund site to better determine the nature of this waste, any treatment needed to improve its handling characteristics, and the extent of air emissions that might occur during excavation. This type of information was desirable to plan full-scale remediation at this site. When disturbed, this waste emitted high concentrations of SO2 and volatile hydrocarbons. The trial excavation was conducted within a temporary enclosure with air exhausted from the enclosure through a sodium hydroxide-based wet scrubber and activated carbon bed adsorber to reduce air emissions of sulfur dioxide and organic compounds. Foam was used in an attempt to suppress atmospheric releases from the raw waste during excavation, storage, and processing. The air exhaust was monitored for total hydrocarbons and sulfur dioxide before and after the air emission control system. In addition, total hydrocarbons and sulfur dioxide were monitored along the site perimeter to determine impact of air emissions on the nearby community.

Comments: This paper describes the techniques used to minimize air emissions, and associated problems resulting from working in an enclosure. The equipment used to measure and control emissions and the emissions before and after the air control system during excavation are also presented as well as an assessment of the foam vapor suppressants. The foam used to suppress the emissions was reported to be reacting with the highly acidic wastes. Sometimes the foam was reported to change colors, from greenish yellow to deep red. On an overall basis the temporary foam reduction efficiency was 40% for THC (storage bins) and SO_2 (during excavation). For stabilized foam applied to all waste storage areas, the reduction efficiency for SO_2 was 80% and for THC was 60%. Thus the vapor suppressing foam was deduced to be unreliable to control emissions during waste disturbances.

On the other hand the wet scrubber gave some optimistic results. SO_2 removal efficiency was found to be > 95%. THC removal efficiency using activated carbon was found to vary between 40 to 90.5%.

Gholson, A. R, *et. al.*, "Evaluation of an Enclosure Method for Measuring Emissions of Volatile Organic Compounds From Quiescent Liquid Surfaces", *Environmental Science & Technology,* Vol. 25, N0. 3.. pp. 519-524, 1991.

Key Words: org emission liq surface measurement; volatile org emission liq surface; wastewater org emission detn enclosure; air pollution org emission impoundment

Abstract: An enclosure method for direct measurement of volatile organic emissions from quiescent liquid surfaces was investigated under simulated conditions in the laboratory and in the field at two hazardous waste treatment facilities. In the laboratory study, accuracy and precision of the method was estimated under a variety of environmental and operational conditions including level of emission rates, emission composition, solar intensity and enclosure sweep flow rate. Precision of the method was determined in the field studies at two sites under a range of environmental conditions including winter versus summer, full sun versus shade, low emission rate versus high emission rate, and polar and non-polar compounds. The results of the laboratory study show that precision for a single-component emission rate was 3.0% or less measured as pooled relative standard deviation with sweep flow rate of 5L/min or above. A consistent negative bias of approximately 50% was found, which was independent of emission rate, solar intensity, or sweep flow rate at or above 5 L/min. The bias was found to vary with compound and multi-compound emissions. Precision in the field was found to be approximately 20% expressed as relative standard deviation. 15 refs.

Comments This article is based on the laboratory and field studies conducted and reported in the EPA report published in 1989.

Gholson, A. R.; Jayanty, R. K. M.; Storm, J. F.; "Evaluation of aluminum canisters for the collection and storage of air toxics," *Analytical Chemistry*, vol. 62, no. 17, pp 1899-1902, 1990.

Key Words aluminum canister org compd stability; air org detn storage stability

Abstract (copyright ACS): The use of Al canisters for whole air collection and for storage of samples for volatile org. compd. detn. was investigated, and the results of stability studies for 23 org. compds. in passivated and unpassivated Al canisters are described. The hydrocarbons and halogenated orgs. measured were stable for >1 wk if the levels of water vapor were >500 ppm (vol.) (1.6 relative humidity at 25 degree.). However, Al canisters are more reactive than passivated stainless steel canisters and should not be used for collecting polar org. compds. Recoveries for both passivated and unpassivated Al canisters were <50 for Me_2CO and <10 for 1,4-dioxane. Recoveries of

Me$_2$CO and 1,4-dioxane in a passivated stainless steel canister were 76 and 23, resp., after 14 days.

Gholson, A., R.; et. al., "Evaluation of the flux chamber method for measuring volatile organic emissions from surface impoundments", USEPA EPA/600/S3-89/008, Sept. 1989

Key Words Emission Assessment, Surface isolation chamber

Abstract: The overall objective of this research program was to estimate the precision and accuracy of the flux chamber method for measuring volatile organic emissions from open liquid bodies of waste during the treatment, storage, and disposal of hazardous waste. A simulated surface impoundment was constructed so that the accuracy and variability of the method could be measured under controlled environmental conditions. Flux chamber operational parameters of sweep flow position, and flux chamber depth were studied to determine their effect on precision and accuracy. Environmental factors of wind velocity, solar intensity, emission rate, and chemical composition were investigated. Precision of the method in the field was evaluated at two hazardous waste treatment, storage and disposal facilities. One was a waste treatment facility at a chemical plant, and the other was a waste stabilization facility.

Comments The samples from the flux chamber or SIS were collected as grab samples using a glass syringe or as a 10-min integrated sample using evacuated stainless steel canisters. For concentrations above 1 ppmv a gas sampling valve and for concentrations below 1 ppmv a cryogenic or solid adsorbent concentrations were used for analysis. All samples were analyzed using GC/FID or electron capture detector. Experiments were conducted in the laboratory for both single compound and multi-compound emissions with a simulated surface impoundments. The single compound analyzed was 1,1,1-Trichloroethane. For the three-component precision and study, compounds used were Methyl ethyl ketone, 1,1,1-trichloroethane and Toluene. The authors found that under the laboratory conditions the precision was excellent, but regarding the accuracy a negative bias between 40 and 80 percent was found for all conditions. For three-component emissions also a negative bias was found with the highest being for Methyl ethyl ketone and lowest for 1,1,1-trichloroethane. The negative bias observed was accounted to the changes in the liquid turbulence caused by the flux chamber. Field evaluations were performed on a range of liquid waste mixtures on two very different (varied environmental conditions, etc.) sites. Precisions for the field conditions were higher when compared to the laboratory evaluations. Variability was found to be much higher for the more reactive compounds. Thus the authors think that new measurement techniques for flux chamber method are required for the reactive compounds like nitrobenzene and aniline. The author suggests the need for similar kind of evaluations for the applicability of flux chamber method to estimate VOC emission rates from other hazardous waste TSDFs namely, land farms, landfills and aerated surface lagoons. Laboratory studies were conducted only for three compounds and also (some) compounds different from those found in the field. Repetitive laboratory studies for similar compounds found in the field may give better estimates of precision and accuracy.

Grant, William B.; Kagann, Robert H.; and McClenny, William A.; "Optical Remote Measurement of Toxic Gases", *Journal of Air & Waste Management Association*, Vol. 42, No 1, pp. 18-30, Jan. 1992.

Key Words Air monitoring, optical remote sensing techniques, spectroscopy

Abstract Enactment of the Clean Air Amendments (CAAA) of 1990 has resulted in increased ambient air monitoring needs for industry, some of which may be met efficiently using open-path remote sensing techniques. These techniques include Fourier transform spectroscopy, differential optical absorption spectroscopy, laser long-path absorption, differential absorption lidar, and gas cell correlation spectroscopy. With this regulatory impetus, it is an opportune time to consider applying these technologies to the remote and/or path averaged measurement and monitoring of toxic gases covered by the CAAA. This article reviews the optical remote sensing technology and literature for that application. 146 refs.

Comments This article describes briefly the optical remote sensing methodology and operation and applicability of various techniques in measuring the concentrations of toxic gases. The optical remote sensing techniques are capable of measuring the toxic gas concentration levels of about 10's of ppbv over 100-m path lengths at ground level. Some techniques can be used to detect gas concentrations at very high altitudes (much above ground level). Presently these relatively new techniques are being studied so as to establish standard procedures to measure toxic gas concentrations. Measurements are performed in different spectral regions to know in which spectral regions these methods can be applied for different gases and to evaluate the accuracy of measurements.

Haigh, David M.; "Air monitoring at the Kettleman Hills facility", *Proceedings* of the 81st Annual Meeting, Air Pollution Control Association, Vol. 5 88/95B.3, 1988.

Key Words hazardous waste treatment air pollution; org volatile pollution, hazardous waste

Abstract (copyright ACS): Transport of emissions from the hazardous waste treatment, storage, and disposal facility at Kettleman Hills, California, occurs in such a manner that no significant concns. of volatile org. compds. (VOCs) were detected at the facility boundary. There is no discernible impact of the emissions on the air quality in the surrounding communities (Avenal and Kettleman City). Air is transported from the facility to the local population centers <10% of the time, and exposure of the population to VOCs is extremely low. Sampling of air at the facility and in its vicinity and anal. of the samples are described.

Hanisch, R. C.; McDevitt, M. A.; "Protocols for sampling and analysis of surface impoundments and land treatment/disposal sites for VOCS", *Proceedings* of the 78th Annual Meeting, Air Pollution Control Association, Vol. 6 85/73.1, 1985.

Key Words sampling analysis volatile org; hazardous waste disposal volatile org; monitoring air pollution hazardous waste

Abstract (copyright ACS): Sampling protocols and anal. methods for monitoring volatile org. compds. at hazardous waste disposal sites are described.

Hanst, P. L.; "Infrared Measurement of Fluorocarbons, Carbon Tetrachloride, Carbonyl Sulfide, and Other Atmospheric Trace Gases," *Journal of Air Pollution Control Association*, Vol. 25, no. 12, pp. 1220-1226, 1975.

Key Words Air monitoring, optical remote sensing, spectroscopy

Abstract: A cryogenic procedure for concentrating trace gases in the atmosphere has been developed and applied to the ambient air at Research Triangle Park, NC, Atlantic Beach, NC, and New York City. The concentrated gases have been analyzed by long path infrared absorption spectroscopy, with a detectability down to partial pressures of 10^{-11} atmospheres. Carbonyl sulfide has been detected at partial pressures in the range of 1×10^{-10} atm. to $3X10^{-10}$ atm. Carbon tetrachloride was always detected with a rather narrow partial pressure range of $0.7X10^{-10}$ to $1.1X10^{-10}$ atm. Fluorocarbon-11 values ranged from about $1.3\ X10^{-10}$ atm. at Research Triangle Park to $8X10^{-10}$ atm. at New York City. Fluorocarbon-12 covered the range of $1.8X10^{-10}$ to $1.0X10^{-9}$ atm. Hydrocarbon pollutants varied widely in concentration, but were always detected, even in the clean rural air. 18 refs.

Hwang, S. T., "Measuring Rates of Volatile Emissions From Non-point Source Hazardous Waste Facilities," Presented at the 75th Annual Meeting of the Air Pollution Control Association, paper no. 82-56.7, June 20-25, 1982

Key Words C-P technique, plume-mapping

Abstract: The RCRA requirements include consideration on preventing adverse affects on ambient air quality during the permit evaluation process. In order to assess the potential impact of volatile toxic emissions from large hazardous waste facilities on public health and the environment, knowledge on emission rates is needed. This paper is concerned with reviewing currently available techniques of measuring volatile emissions from a non-point source hazardous waste facilities. In addition, a novel method devised for measuring emission rates from large surface impoundments will be presented. This method, which may be extended to other non-point sources, is derived from fundamental theory on turbulent transport in the atmosphere. This method requires concentration measurements considerably less in number than the current methods. Experimental comparison will be discussed based on the limited amount of data. 13 refs.

Comments: Hwang reviewed the "Concentration Profile Technique" and "Plume Mapping Method" to measure the toxic emissions from area sources. The Plume Mapping Method involves the back-calculation of the emission rate based on the Gaussian Dispersion Models. The application of this Plume Mapping Method is limited to determine the total hydrocarbon emissions, but not component emissions.

The new theory requires background and downwind concentrations measurements. Accurate information on the height of the sampling point relative to the surface impoundment, velocity and temperature profiles are also required. Advantage of this method is, the data needed on downwind concentrations is lesser compared to other methods (available at that time). The author thinks that lack of sufficient data limits the comparison of this method with other methods. This new method is also applicable to landfills, and land treatment facilities.

Jarke, F. H., "Ambient Air Monitoring At Hazardous Waste Facilities", Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21, 1985

Key Words Air monitoring

Comments Some of the methods used in making ambient air measurements at hazardous waste facilities are described in this paper. The methods are Organic Vapor Analyzers, Adsorption Trapping Techniques, Mobile Mass Spectrometers.

Leson, G., Tabatabai, F.; "Control of Hazardous and Toxic Air Emissions by Biofiltration" Presented at the 85th Annual Meeting Air & Waste Management Association, Kansas City, Missouri, 1992.

Key Words Air emissions, control techniques, Biofiltration

Abstract: Control of air toxics is the subject of a variety of regulatory programs on the federal, state and local levels. Many of the targeted air toxics are non-chlorinated, volatile organic compounds, often emitted in concentrations of several hundred ppm, as carbon. Biofiltration, an innovative APC technology has been demonstrated successfully for the treatment of such emissions in many full-scale and pilot scale applications, including several in the U.S. The evaluation of the technical feasibility and competitiveness of biofiltration must usually be conducted on a case-by-case basis. The use of screening criteria can help provide an initial assessment. Our research and project results suggest that examples of beneficial air toxics control applications will be found in the chemical, pharmaceutical and polymer processing industries. This paper discusses the approach to the control of air toxics under several regulatory programs, summarizes screening criteria for the initial assessment of the suitability of biofiltration, and presents recent examples for control of air toxics using biofiltration.

Leson, G and Winer, A. M; " Biofiltration: An Innovative Air Pollution Control Technology for VOC Emissions," *Journal of The Air & Waste Management Association*, Vol. 41, No. 8, pp. 1045-1054, 1991

Key Words Biofiltration, biodegradable VOCs,

Abstract: Biofiltration is a relatively recent air pollution control (APC) technology in which off-gases containing biodegradable volatile organic compounds (VOC) or inorganic air toxics are vented through a biologically active material. This technology has been successfully applied in Germany and The Netherlands in many full-scale applications to control odors, VOC and air toxic emissions from a wide range of industrial and public sector sources. Control efficiencies of more than 90 percent have been achieved for many common air pollutants. Due to lower operating costs, biofiltration can provide significant economic advantages over other APC technologies if applied to off-gases that contain readily biodegradable pollutants in low concentrations. Environmental benefits include low energy requirements and the avoidance of cross media transfer of pollutants.

Comments: This article is a good general reference for biofiltration technology on the whole. The origin, basic design, some references to applications, theory, operation and parameter specification, and types of material typically used for construction of a biofilter are some of the topics addressed in this paper. Biofiltration is particularly useful to treat low concentration off-gases due to its low operating costs and low specific energy demand. Applications indicate that most often biofiltration has been used to treat off-gases, of concentrations < 1000 ppm as methane, from industrial facilities, waste disposal and food processing activities. Typically alcohols, ethers, aldehydes, ketones, and several monocyclic aromatics were reported to have been biodegraded easily.

McClenny, W. A, et. al., "Canister-Based Method of Monitoring Toxic VOCs in Ambient Air", *J. Air Waste Management Association,* Vol 41, No. 10, pp. 1308-1318, 1991

Key Words monitoring VOCs, canisters, stability

Abstract The availability of reliable, accurate and precise monitoring methods for toxic volatile organic compounds (VOCs) is a primary need for state and local agencies addressing daily monitoring requirements related to odor complaints, fugitive emissions, and trend monitoring. The canister-based method for VOCs is a viable and widely used. This activity has involved the testing of sample stability of VOCs in canisters and the design of time integrative samplers. The development of procedures for analysis of canisters, including the procedure for VOC preconcentration from whole air, the treatment of water vapor in the sample, and the selection of an appropriate analytical finish has been accomplished. The canister-based method was initially summarized in the EPA *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* as Method TO-14. Modifications and refinements are being added to Method TO-14 in order to obtain a Statement of Work for the Superfund Contract Laboratory Program for Air. This paper discusses the developments leading to the current status of canister-based method and provides a critique of the method using results obtained in EPA monitoring networks. 57 refs.

Comments McClenny, et. al. compared canisters to solid sorbents in this paper. Based on previous research the solid sorbent, Tenax, was reported to have shown unpredictable inconsistencies in results. Sometimes data return of less than 50% is obtained. This makes the finding of consistent data very expensive. Canisters also have problems regarding leaving traces of degreasers during cleaning procedures and lubricants during fabrication. Inspite of these problems with canisters, the authors think it is a better alternative as this problem can be rectified simply by cleaning or replacing the sampling train. As for the solid sorbents more research is necessary to determine the extent of artifact formation while collecting the sample and during the storage before analysis. Automated gas chromatographs, portable instrumentation, and fenceline dosimeters are three other methods for ambient air monitoring. The applications of these three methods have been briefly discussed in this paper. The Method Quantitation Limits (MQL) for TO-14 compounds are reported to be in the range of concentrations, 0.6 to 6.0 ppbv for 500 cm^3 or less of total air volume, with scanning mass spectroscopy. For selected ion monitoring MQLs are increased by a factor of 2 to 10. The precisions for the urban air toxics monitoring program and toxic air monitoring system are reported for EPA monitoring network operations. Owing to the advantages such as easy cleanup procedures, possibility of multiple analysis, good storage stability, no breakthrough of target compounds, no necessity of electric power for filling the canister and thermal desorption make canisters a suitable means of collection and storage of some polar VOCs and nonpolar VOCs. One main disadvantage associated with canister sampling is as it is the last element in the sample train, there is a possibility of contamination from sampler elements upstream of the canister. Another disadvantage is its limited space volume. The authors pointed out the need for a complete model to explain and predict the storage stability of various compounds, requirement of standard procedures to use canister based methods for particular applications and the need to determine the MQLs for lower concentrations.

Reinhart, D. R, et al.; "Flux Chamber Design and Operation for the Measurement of Municipal Solid Waste Landfill Gas Emission Rates," *Journal of Air & Waste Management Association*, Vol. 42, no. 8, pp. 1067-1070, 1992

Key Words Air emissions, SIC

Abstract: This paper describes a hybrid Flux Chamber-Soil Gas Probe methodology for measuring municipal solid waste (MSW) gas emission rates. Following the design of the flux chamber, the chamber was laboratory tested to define its mixing characteristics and optimum operating parameter values. Flux chamber operating parameters included: chamber pressure, sweep air flow rate, landfill insertion depth, and sweep air velocity. Optimum operating parameter values were determined by operating the flux chamber on a simulated subsurface emission source and varying the operating parameters. The laboratory tests indicated that the flux chamber could be operated to provide zero biasing of gas emission rates, resulting in accurate measurement of gas emission rates. 7 refs.

Comments: The paper is well written by addressing various factors affecting the air emission measurements and determining the optimum operating parameter values using a surface isolation chamber. However the results were not verified on an actual municipal solid waste landfill site to establish the accuracy of the results.

Reisinger, H. J., II; Burris, D. R.; Hendrick, J. F.; "Soil vapor contaminant assessment - SVCA", 19th Toxic and Hazardous Wastes Conference, pp 137-152, 1987

Key Words org vapor contaminant detn soil water

Abstract (copyright ACS): Soil vapor contaminant assessment (SVCA) is a method for sampling and analyzing the vapor state of org. compds. found in shallow depth in the subsurface for evaluation of environmental contamination, esp. of soils and groundwaters.

The method involves driving a soil probe into the shallow subsurface and withdrawing a representative aliquot of interstitial soil vapor. The vapor is analyzed using gas-chromatog. Theor. basis and limitation of the method are discussed, and practical aspects of its use are described. Considerations for proper interpretations of obtained data are outlined. Examples on the efficacy of the method for evaluation of volatile contaminants in the areas of a gasoline service station, residential sites, and an industrial facility are presented.

Schmidt, C. E.; Stephens, R.; Turl, G. A.; "Case study: control and monitoring of air contaminants during site mitigation," *Proceedings* of the 80th Annual Meeting, Air Pollution Control Association, Vol. 1 87/18.2, 1987.

Key Words: waste site cleanup pollution control; volatile org air pollution control; foam stabilization waste pollution control

Abstract: A cost effective air monitoring strategy using real time analyzers, portable monitoring stations, and meteorological. monitoring was successfully used in the excavation of wastes with a potential for volatile org. compd. emission. The emissions from the excavation were controlled to a large extent using a temporary foam to provide short-term vapor control. The temporary foam, applied to all exposed surfaces of the waste materials, was an effective control technol. and was responsible for the successful execution of the excavation. Stabilization of the waste for longer times was accomplished using clean fill materials, plastic tarps, and a permanent foam.

Schmidt, C. E.; Gordy, D. L.; "Designing of air monitoring programs for remediation at hazardous waste sites," *Proceedings* of the 78th Annual Meeting, Air Pollution Control Association, Vol. 6 85/72.2, 1985.

Key Words: hazardous waste air monitor

Abstract: Methodol. is given for development of site-specific air-monitoring programs for hazardous-waste-site remediation. The air-monitoring function provides fugitive air-contaminant levels both on-site and off-site. When there is a high fugitive air-contaminant-emissions potential, the assessment and monitoring of air contaminants may facilitate remediation of the site.

Schmidt, C. E.; Meyer-Schmidt, J. K.; "Assessment, monitoring, and modeling from a Superfund site remedial action." *Proceedings* of the 78th Annual Meeting, Air Pollution Control Association, Vol. 1 85/66.2, 1985.

Key Words: waste disposal site malodorous emission; petroleum refining waste malodorous emission

Abstract (copyright ACS): A study was carried out of gas emissions from an abandoned waste disposal site where acidic sludge from oil refining was dumped in the 1940's. The above-ground SO2 and total hydrocarbons emissions were only apprx. 2 times the background emissions (0.012 and 2.9 ppm, resp.). However, the presence of malodorous S compds. (e.g. tetrahydrothiophenes) was readily detectable by humans 40 m downwind from the site. Procedures used to sample volatile emissions and detg. their ecol. impact are described.

Shah, M. J.; "Comparative Testing of Tedlar Bag and Canister as Sample Collection Media for Toxic Air Contaminants and an Annual Review of the Accuracy and Precision of Selected Toxic Compounds Monitored by the California Air Resources Board," Presented at the 85th Annual Meeting Air & Waste Management Association, Kansas City, Missouri, 1992.

Key Words Air monitoring, sample collection, Canisters, tedlar bags

Abstract: The California Air Resources Board designed the ambient toxics monitoring network to provide data required to measure the average ambient concentrations of toxic air contaminants. Although Tedlar bags had been used for sample collection, there were a few limitations in their use. The Board opted to replace the bags with the SUMMA passivated stainless steel canisters. This paper compares bags with canisters as sample collection media and examines the accuracy and precision associated with the monitoring of eight gaseous organic compounds. ARB conducted a study to determine sample stability in canisters. Most of the compounds evaluated were relatively stable in canisters held up to 28 days.

The precision and accuracy of the data were determined from collocated sampling, through-the probe audits, and laboratory audits, using NIST-certified standards. The results indicated that system precision as determined from collocated sampling was moderately variable both for samples taken by bags and canisters. System accuracy improved with change from bags to canisters by approximately 40 percent, however the accuracy was often very good regardless of the sample collection medium. Contamination and residual materials remaining from previously-filled collection medium was less in canisters than bags. Canisters also provided greater flexibility in scheduling sampling and analysis procedures than bags. Overall, the canisters had certain benefits over the bags in operating a statewide ambient toxics monitoring network.

Shen, Thomas T.; Nelson, Thomas P.; and Schmidt, Charles E., "Assessment and control of VOC Emissions from Waste Disposal Facilities", *Critical Reviews in Environmental Control*, Vol. 20, Issue 1, pp. 43-75, 1990

Key Words VOC emissions, assessment, Organics, waste facilities, measurement, modeling, direct techniques, indirect techniques

Abstract Concerns with emissions of volatile organic compounds (VOC) from waste disposal facilities are increasing because of emission quantity and toxicity and/or carcinogenicity, especially at the superfund sites. Many state regulatory provisions require air quality assessment to be performed by applicants prior to the issuing of an air emission permit for a new or modified waste disposal facility. This article reviews the current published papers and significant government documents related to VOC emissions and their control at waste disposal sites. The review topics include dimensions of the VOC problem, characterization of VOC emission sources, effects of atmospheric processes, air pathway analyses, and technical feasibility of various VOC control options. Discussions include a waste minimization strategy to reduce VOC quantity and concentration in wastewater at sources. 58 refs.

Comments Shen et al., summarized various direct and indirect techniques used to assess VOC emissions from different type of sources. The direct emission measurements such as surface isolation chamber, head space samplers, wind tunnels, subsurface direct emission measurement techniques and indirect emission measurement techniques such as concentration-profile technique, transect method, upwind/downwind etc. are summarized. Surface isolation chamber and head space samplers are applicable to landfills, surface impoundments and land treatment facilities provided the soil is of uniform composition. Concentration-profile and transect technique are applicable to surface impoundments and land treatment facilities when the meteorological conditions are suitable. Subsurface direct emission measurement techniques are suitable when it is important to estimate soil concentration or emission rates at subsurface locations (at landfills, in situ bioremediation sites etc.). Various VOC emission control options such as thermal incineration, catalytic incineration, activated carbon adsorption, condensation, absorption and chemical scrubbing are also summarized in this article.

Siegrist, R. L.; , "Volatile organic compounds in contaminated soils: The nature and validity of the measurement process", *Journal of Hazardous Materials*, Vol. 29, pp. 3-15, 1992

Key Words Assessment, VOCs

Abstract A wide variety of volatile organic compounds (VOCS) such as toluene and trichloroethane routinely appear as principal pollutants in contaminated sites. As part of the site assessment and environmental restoration process, quantitative determination of soil VOCs is required. While accurate and precise measurements are desired, the validity of the current process in which a discrete sample is collected and a 1 to 5 g subsample is analyzed for a suite of organic compounds of widely different processes is questionable. Research has demonstrated that the soil VOC measurement process is complex and current, commonly employed practices can lead to substantial measurement errors. For example, -100 to +25% bias can occur in measurements of some soil VOCs. Knowledge of VOC behavior in soils and the measurement process continues to expand and advances are being made in sampling and analysis techniques. Further research is needed to enable development of a valid soil VOC measurement process. 19 refs.

Comments Siegrist [1992], described VOC distribution in multiple phases (soil) based on literature. The author stated different types of diversions causing errors in soil VOC measurements. Measurement error variance should normally be less than 10% of the total variance between measurements of different populations while measurement bias should be negligible. Negative bias in VOC measurements (measured value< true value) can be caused due to various reasons including volatilization losses during soil surface exposure, soil collection process, sample storage, and sub sampling for analysis, and chemical and biochemical transformations during pre-analytical holding. Rigorous sample collection procedures can reduce this negative bias. Some of the methods suggested are collecting soil sore samples in sleeve-lined, split-barrel samplers, onsite sub sampling with a micro-coring device to reduce soil disturbance, and immersing a soil sample in an organic solvent like methanol in a Teflon-sealed glass vial or jar so that the sample size is increased giving a representative sample. Analyzing the sample soon after the sample collection (small holding or storage time) and minimizing the variability of conditions may help in reducing the measurement error. The author thinks that it is necessary to categorize the VOCs based on sampling considerations. He suggests a development of a valid correlation curve for the application of interest with VOC screening data. For quantitative analysis the author recommends review of sample collection, handling and analysis procedures to ensure and improve the VOC measurements. Finally the author encourages improved and expanded use of onsite instruments and techniques provided their accuracy and precision is established.

Siegrist, R. L. and Jenssen P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Environmental. Science. & Technology, Vol. 24, No. 9, pp. 1387-1392, 1990

Key Words sampling, volatile, emissions, soils

Abstract: An experiment was conducted to evaluate the effects of sample disturbance, container headspace volume and integrity, and sample preservation on volatile organic compound measurements in contaminated soil. A sandy soil was contaminated under controlled conditions at 10 degrees centigrade by an aqueous solution containing six target VOCs: methylene chloride (157.5 mg/L), 1,2-dichloroethane (130 mg/L), 1,1,1-trichloroethane (16 mg/L), toluene (4.5 mg/L), and chlorobenzene (2.85 mg/L). Replicate soil samples were then collected by different methods at an air temperature of 20^{o}C. For all VOCs, the highest concentrations were measured in undisturbed soil samples immediately immersed in methanol in Teflon-sealed glass bottles. With these measurements as a reference, the relative negative bias was highest for container integrity (up to 100%) and lack of methanol immersion (up to 81%) and considerably lower for container headspace volume (up to 17%) and soil disturbance (up to 15%). The potential for negative bias appeared to be correlated with the VOC soil sorption affinity (i.e., low K_h and high K_{ow}) . For accurate measurements of the more volatile compounds, rigorous sampling procedures are necessary. 15 refs.

Comments Siegrist et. al., emphasize the need for improvement and further research in soil sampling, handling and analysis in both the papers [1990, 1992]. From their experiment the authors found that measurement error of up to 100% resulted in the initial runs due to soil disturbance, container headspace volume, container integrity and sample storage.

Small, G. W., et. al.; "Detection of Atmospheric Pollutants by Direct Analysis of Passive Fourier Transform Infrared Interferograms," *Analytical Chemistry*, Vol. 60, no. 3, Feb. 1, 1988

Key Words Air monitoring, Spectroscopy

Abstract: Methodology is developed that allows interferograms from passive Fourier transform infrared (FTIR) spectrometer to be analyzed directly. With a digital filtering approach, a set of generalized procedures is developed for real-time monitoring of atmospheric pollutants. These procedures allow the spectrometer to be mobile, overcoming problems associated with changing spectral backgrounds and with severe data processing requirements. The methodology allows customized digital filters to be developed that remove information from the interferogram except that associated with frequencies characteristic of a target chemical species of interest. To test the methodology, a filter is derived that is specific for SF6, Thereby simulating the action of a mobile pollution monitoring system. Interferograms collected during this experiment are used to evaluate the computed filter.

Thibodeaux, L. J., et. al., " Chemical Emissions from Surface Impoundments", *Environmental Progress*, Vol. 3, No. 2, pp. 73-78, 1984

Key Words volatile organic compounds, emissions, mass transfer, surface impoundments

Comments Most often wastewater and other liquids placed in surface impoundments are source of VOC emissions. In an effort to determine the magnitude of the flux rate of organic compound emissions from surface impoundment facilities a field sampling technique called concentration profile method (CPM) and a laboratory analysis methodology to trap and measure low-molecular weight, volatile organics in air were developed. The CPM uses the principles of micro meteorology and atmospheric transport. The CPM is based on "aerodynamic method" which was used to measure the flux of pesticides. Field studies were conducted at four aerated basins adjacent to four pulp and paper mills in central and southern Arkansas. The concentration profile method is based on obtaining samples of air, wind velocity, and temperature in a two-meter boundary layer region above the water surface. This method can be applied to landfarming sites also.

Solinski, P. J., Scotto, R. L., Minnich, T. R., Kricks, R. J., and Johnson, A. N., "Air Pathway Analyses Using Open-Path FTIR Spectroscopy During Waste Dredging Activities at a Large Industrial Lagoon," Presented at the 85th Annual Meeting Air & Waste Management Association, Kansas City, Missouri, 1992.

Key Words Air monitoring, Spectrometry

Abstract: This paper presents results and methodologies of an air pathway analyses (APA) investigation conducted in October 1991 using open-path Fourier -transform infrared (FTIR) spectroscopy during waste dredging activities at a 17-acre inactive industrial lagoon in New Jersey. The air monitoring investigation was the first of several that are planned to be performed during an 18-month waste removal and solidification project. Contaminants of concern are those established or probable human carcinogens that have been previously detected in the waste. The objective of the air monitoring program is to demonstrate, via actual measurement data, that health risks associated with lagoon dredging are insignificant.

Open-path FTIR concentrations of all contaminants of concern were below instrument minimum detection limits (MDLs) for each monitoring event. Maximum emission rates were calculated using the conservative scenario in which "actual" downwind concentrations were based on the instrument MDLs. These MDL-default-derived emission rates were then used to estimate annual impacts to the maximally exposed individual (MEI). Insignificant health risks associated with lagoon dredging were demonstrated.

Suder, D. R., and Schmidt, C. E.; "Control Efficiencies and Costs of Various Technologies for Reduction of Volatile Organic Compound Emissions from Exposed Hazardous and Nonhazardous Waste," Presented at the 85th Annual Meeting of The Air & Waste Management Association, Kansas City, MO, 1992

Key Words Air emissions, control techniques

Comments: This paper presents recently collected quantitative control efficiency data for various control technologies including covers, foam, clean soil, compaction of waste, stabilization and fixation with sorbents or other materials, and wetting of waste. Factors affecting overall cost estimates and other factors which may affect the usefulness of a specific control technique in a given application are discussed.

Tests to determine the control efficiency of different types of covers were conducted on test pads with soils contaminated with petroleum products. To make the air emission measurements, a sampling and analytical system consisting of surface isolation chamber (EPA-recommended), canisters for sample collection (EPA method, TO-14) and GC/MS for analysis were used.

The reasons that may affect the choice of control technology other than the cost considerations are as follows: 1) volume of waste generated and emissions expected 2) type of site 3)durability of the cover material 4) daily requirement of equipment and labor.

Suder, D. R.; Wooster, A. H.; Schmidt, C. E.; "Comparison of measured to modeled emission rates at an active hazardous waste landfill", Paper no. 90/82.6, Presented at the 83rd Annual Meeting of The Air & Waste Management Association, Pittsburgh, PA, 1990.

Key Words: hydrocarbon air pollution hazardous waste landfill; modeling air pollution hazardous waste landfill

Abstract (copyright ACS): Measurement of nonmethane hydrocarbon air pollution from a hazardous waste landfill in Kern County, California, vs. results from a land treatment model showed that model estns. were several times higher than actual pollution if historical waste characteristics were used. Agreement was better if the actual measured waste characteristics (porosity, moisture content, bulk d., and hydrocarbon content) were used, esp., estn. of emissions for over 10 h. The landfill accepts hazardous and non hazardous solid waste, generated primarily by oil prodn., refining, and distribution including soil contg. gasoline, diesel, and crude oil and refinery sump sediment.

Thibodeaux. L. J.; "Landfarming of Petroleum Wastes - Modeling The Air Emission Problem," *Environmental Progress*, Vol. 1, no. 1, pp. 42-46, 1982

Key Words Air emissions, modeling

Abstract: Potential air emissions from land treatment facilities has been identified as a topic requiring further study. A mathematical model that can be used to estimate emission of selected volatile chemicals from petroleum landfarming operations is presented in this paper. The author showed that subsurface injection can dramatically reduce emissions from landfarming. 10 refs.

Comments: The author discussed gradient models and gradientless model which is soil pore-space evaporation and diffusion model. Validity of the model is limited by the fact that there wasn't enough laboratory data existing at that time to verify the model. This model is capable of estimating emission rates of multiple volatile components from the oil.

Turpin, R. D.; Campagna, P.; "Screening on-site air monitoring samples by use of field flame ionization detection/photo ionization detection gas chromatograph," *Proceedings* 2nd Technical Seminar on Chemical Spills, Proc. Tech. Semin. Chem. Spills, pp 360-366, Evironmental Protection Service, Ottawa, Ontario, Canada, 1985.

Key Words field air analysis hazardous material; gas chromatog field air analysis

Abstract (copyright ACS): The US EPA Environmental Response Team (ERT) uses field screening of air samples to decrease the no. of off-site samples requiring anal. The methods and techniques used by ERT are described. These include air sampling bags, thermal desorption tubes, and a gas chromatog. with field flame ionization detector/photoionization detector.

Vogel, G. A; "Air Emission Control at Hazardous Waste Management Facilities," *Journal of the Air Pollution Control Association,* Vol. 35, no. 5, pp. 558-566, 1985

Abstract: The control of toxic air emissions from hazardous waste management facilities is being investigated by regulatory agencies and the owners and operators of such facilities. Several methods that potentially could be used to control emissions are identified in this article, which addresses emission control methods for storage tanks, surface impoundments, land treatment facilities, landfills and waste storage piles. Based on information obtained from the literature and emission control equipment manufacturers, estimates of the costs and emission control efficiencies of the methods are provided. 36 refs.

Comments: For land treatment process the suggested control techniques are subsurface injection, soil covers and synthetic covers. The subsurface injection of waste is reported to reduce the emissions by 70%.

Williams, C. H.; " Measurement Strategies for Estimation of Air Toxic Emissions from Fixed Site Fugitive Sources at Industrial and Hazardous Waste Sites", Presented at the 85th Annual Meeting of the Air and Waste Management Association, June 21-26,1992, Kansas City, Missouri.

Abstract: Radian has developed and applied a number of innovative strategies for the measurement, both direct and indirect, of emission rates for toxic chemicals from hard-to-characterize fugitive sources. These fugitive sources are found in the petroleum, petrochemical and chemical industries, as well as at hazardous waste sites. Radian has estimated vapor emissions from a diverse array of fugitive sources including: soils and sludges at hazardous waste site, wastewater in ponds, lagoons and separators, process vents and stacks (low temperature, low flow), process buildings and even an entire process unit.

The strategies are designed to meet each project's objective but include the application of: isolation flux chambers for solid and liquid surfaces, temporary enclosures for point and small area sources (such as sewer vents), dynamic dilution for high concentration process streams, sampler arrays in two and three dimensions for measuring emissions from area or volume (process unit) sources, the controlled release of tracer gases and reverse dispersion modeling from measured air concentrations to calculate emission rates. An overview of the different strategies for fugitive emissions will be presented.