United States
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Agency

Office of Research and
Development
Washington, DC 20460

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May 1996

1 EPA

# Seminars

# Bioremediation of Hazardous Waste Sites: Practical Approaches to Implementation

May 29--30, 1996—Chicago, IL

June 4--5, 1996—Kansas City, MO

June 6--7, 1996—Atlanta, GA

June 18--19, 1996—San Francisco, CA

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# Seminars on
# Bioremediation of Hazardous Waste Sites:
# Practical Approaches to Implementation

Office of Research and Development
U.S. Environmental Protection Agency
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Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# Contents

## Sources of Information

Recent EPA Bioremediation Publications
http://www.epa.gov/docs/ORD

Bioremediation in the Field Bulletin
Latest edition EPA/540/N-96/500

Bioremediation in the Field Search System: Database on national and some international field applications
Version 2.0 EPA/540/R-95/508b
Also on the Internet

Request to be on EPA's bioremediation mailing list or to request specific bioremediation documents
513-569-7562

NRMRL/SPRD Home Page
http://www.epa.gov/ada/kerrlab.html

# Background Information for Bioremediation Applications

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## Introduction

This technology transfer seminar series is sponsored by the U.S. Environmental Protection Agency's (EPA's) Biosystems Program. The Biosystems Program coordinates research, development, and evaluation of full-scale bioremediation activities. The seminar series provides participants with state-of-the-art information on the practical aspects of implementing bioremediation. The series is divided into the following sections:

- Background for Bioremediation Applications
- In Situ Treatment of Soils, Sediments, and Shorelines
- Ex Situ Treatment With and Without a Reactor
- Natural Attenuation
- Treatment of the Subsurface

Each section includes discussion of advantages and limitations, materials handling, types of waste amenable to the treatment process, pre- and posttreatment requirements, and capital and operation and maintenance costs. The overall focus is on field applications in use today, with some information on processes that are nearing readiness for field use.

This section has been organized to address the following topics:

- Biodegradation and metabolism
- Environmental factors affecting biodegradation
- Site characterization
- General concept of treatability studies

## Biodegradation and Metabolism

Biodegradation involves chemical transformations mediated by microorganisms that satisfy nutritional requirements, satisfy energy requirements, detoxify the immediate environment, or occur fortuitously such that the organism receives no nutritional or energy benefit (1). Mineralization is the complete biodegradation of organic materials to inorganic products, and often occurs through the combined activities of microbial consortia rather than through a single microorganism (2). Co-metabolism is the partial biodegradation of organic compounds that occurs fortuitously and that does not provide energy or cell biomass to the microorganism(s). Co-metabolism can result in partial transformation to an intermediate that can serve as a carbon and energy substrate for microorganisms, as with some hydrocarbons, or can result in an intermediate that is toxic to the transforming microbial cell, as with trichloroethylene (TCE) and methanotrophs.

Two classes of biodegradation reactions are aerobic and anaerobic. Aerobic biodegradation involves the use of molecular oxygen ($O_2$), where $O_2$ (the "terminal electron acceptor") receives electrons transferred from an organic contaminant:

$$\text{organic substrate} + O_2 \rightarrow \text{biomass} + CO_2 + H_2O + \text{other inorganics}$$

Thus, the organic substrate is oxidized (addition of oxygen), and the $O_2$ is reduced (addition of electrons and hydrogen) to water ($H_2O$). In this case, the organic substrate serves as the sources of energy (electrons) and the source of cell carbon used to build microbial cells (biomass). Some microorganisms (chemoautotrophic aerobes or lithotrophic aerobes) oxidize reduced inorganic compounds ($NH_3$, $Fe^{+2}$, or $H_2S$) to gain energy and fix $CO_2$ to build cell carbon:

$$NH_3 \text{ (or } Fe^{+2} \text{ or } H_2S) + CO_2 + H_2 + O_2 \rightarrow \text{biomass} + NO_3 \text{ (or } Fe^{+3} \text{ or } SO_4) + H_2O$$

At some contaminated sites, as a result of consumption of $O_2$ by aerobic microorganisms and slow recharge of $O_2$, the environment becomes anaerobic (lacking $O_2$), and mineralization, transformation, and co-metabolism depend upon microbial utilization of electron acceptors other than $O_2$ (anaerobic biodegradation). Nitrate ($NO_3$), iron ($Fe^{+3}$), manganese ($Mn^{+4}$), sulfate ($SO_4$), and carbon dioxide ($CO_2$) can act as electron acceptors if the organisms present have the appropriate enzymes (3). JP-4 jet fuel constituents were observed to be biodegraded in the presence of $NO_3$ as the electron acceptor (4). Iron and manganese are important microbial electron acceptors, with background concentrations in soils ranging from 20 to 3,000 mg/kg for Mn and 3.8 to 5.2 percent for iron. An evaluation of the degradation of polycyclic aromatic hydrocarbons (PAHs) in aerobic and anaerobic environments was conducted based on thermodynamic principles (5). Biodegradation of pentachlorophenol (PCP) has been observed to increase the presence of added Mn (6).

Halogenated compounds can be used as growth substrates or co-metabolized by aerobic and anaerobic microorganisms. Dehalogenation can be spontaneous, as in the loss of halogens during ring cleavage, or enzymatically catalyzed through hydrolytic cleavage or reductive dehalogenation (1). Halogenated compounds can often serve as the electron acceptor and become reduced in environments where there is a source of electrons; for example, under methanogenic conditions (production of methane in reduced environments) reductive dehalogenation of perchloroethylene (PCE) to TCE, trans-1, 2-dichloroethylene (DCE), vinyl chloride, and ethylene occurs (1). In such situations, alternative electron acceptors such as $NO_3$ and $SO_4$ may compete with the halogenated compounds for electrons. TCE can also be biodegraded co-metabolically in an aerobic environment by methanotrophs when methane is added to cause the formation of TCE-epoxide, which will abiotically transform to dichloroacetic acid, TCE-diol, formic acid, and glyoxylic acid. Reduced dehalogenated intermediates often undergo rapid biodegradation by aerobic microorganisms in the presence of $O_2$ (7).

## Environmental Factors Affecting Biodegradation

Microbial ecologists have identified ranges of critical environmental conditions that affect the activity of soil microorganisms (Table 1). Many of these conditions are controllable and can be changed to enhance the biodegradation of organic constituents. A discussion of the factors identified below, including principles, status of the technology, secondary impacts, equipment, advantages and disadvantages, and references is provided in the document *Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils* (7).

Table 1. Critical Environmental Factors for Soil Microbial Activity (8).

| Environmental Factor | Optimum Levels |
|---|---|
| Oxygen | Aerobic metabolism: greater than 0.2 mg/L dissolved oxygen, minimum air-filled pore space of 10%<br>Anaerobic metabolism: less than 0.2 mg/L dissolved oxygen, $O_2$ concentration less than 1% air-filled pore space |
| Nutrients | Sufficient nitrogen, phosphorus, and other nutrients so not limiting microbial growth (suggested C:N:P ratio of 120:10:1) |
| Moisture | Unsaturated soil: 25-85% of water holding capacity, -0.01 MPa; will affect oxygen transfer into soil (aerobic status);<br>in saturated zone, water will affect transport rate of oxygen and therefore will affect rate of aerobic remediation |
| Environment (pH) | 5.5-8.5 |
| Environment (redox) | Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts |
| Environment (temperature) | 15-45°C (mesophilic) |

Oxygen diffuses into the soil from the air above it, and gases in the soil atmosphere diffuse into the air. Oxygen concentration in a soil may be much less than in air, however, while $CO_2$ concentrations in soil may be orders of magnitude higher than in air. A large fraction of the microbial population within the soil depends on oxygen as the terminal electron acceptor in metabolism. When soil pores become filled with water, the diffusion of gases through the soil is restricted since oxygen diffuses through air 10,000 times faster than through water. Oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anaerobic. Facultative anaerobic organisms, which can use oxygen when it is present or switch to alternative electron acceptors such as nitrate in the absence of oxygen (e.g., denitrifying

bacteria), and obligate anaerobic organisms become the dominant populations. Additional information concerning in situ anaerobic bioremediation can be found elsewhere (7).

Oxygen concentrations in soil systems may be increased by tilling and draining unsaturated soil, for example, in prepared-bed land treatment systems, in ex situ treatment (e.g., composting, biopiles, and fungal treatment) and in situ treatment systems, and through the application of bioventing systems, where air is forced through a soil system and carries oxygen to soil microorganisms to accomplish aerobic degradation. Hinchee (9) and Hinchee and Downey (10) successfully applied bioventing for enhancement of biodegradation of petroleum hydrocarbons in JP-4 jet fuel contaminated soil at Hill Air Force Base, Ogden, Utah, by increasing subsurface oxygen concentrations. Oxygen and $CO_2$ concentrations were monitored and correlated well with hydrocarbon biodegradation. A minimum criterion for aerobic biodegradation of PAH in creosote-contaminated soil was established at 2 percent $O_2$ in air (11).

Within saturated environments, oxygen transport is considered to be the rate-limiting step in aerobic bioremediation of contaminated hydrocarbons when adequate nutrients are present. At the Traverse City, Michigan, site contaminated with jet fuel (12), an increase in the oxygen concentration in water through addition of hydrogen peroxide and was observed to positively affect the rate of biodegradation of the jet fuel components benzene, xylene, and toluene.

Microbial metabolism and growth depend on adequate supplies of essential macro- and micronutrients. If the wastes present at a site are high in carbonaceous materials and low in nitrogen (N) and phosphorus (P), the subsurface may become depleted of available N and P required for biodegradation of the organic contaminants. Addition of nutrients may be required as a management technique to enhance microbial degradation, and can be used to treat water from a pump-and-treat system and applied through reinfiltration or irrigation (13). Recommended ratios for subsurface systems of carbon (C), N, and P are 120:10:1 on a weight basis. Nutrients have been added to enhance microbial degradation of hydrocarbon contaminants at many sites (14). At the Champion International Superfund Site in Libby, Montana (15), nutrients are added to enhance bioremediation in a prepared-bed land treatment system, in an aboveground reactor for treating extracted ground water, and in injection wells for in situ bioremediation of PAH and PCP.

Moisture content and the soil water matrix potential against which microorganisms must extract water from the soil regulate their activity. The soil matrix potential is the energy required to extract water from the soil pores to overcome capillary and adsorptive forces. Soil water also serves as the transport medium through which many nutrients and organic constituents diffuse to the microbial cell, and through which metabolic waste products are removed. Soil water also affects soil aeration status, nature, and amount of soluble materials; soil water osmotic pressure; and the pH of the soil solution (8). Generally, microbial activity measured as biodegradation rates and rates of detoxification of contaminants in soil have been found to be highest at soil moisture contents of 60 to 80 percent of field capacity (8). Field capacity is the amount of water held against the force of gravity, generally equal to 0.1 to 0.3 atmospheres of force.

Soil moisture can be increased using standard agricultural irrigation practices such as overhead sprinklers or subirrigation. To remove excess water or lower the water table to prevent water-logging, drainage or well point systems can be used. Also, the addition of vegetation to a site will increase evapotranspiration (ET) of water and will also retard the downward migration of water (i.e., leaching) (7, 16).

Other environmental factors, including pH, redox potential, and temperature, are important parameters that will affect the rate and extent of bioremediation in unsaturated and saturated subsurface systems. Outside the pH range of 5.5 to 8.5, microbial activity is generally decreased. Maintaining soils near neutral pH is most often recommended for enhanced bioremediation (7); however, acidic soils are known to become colonized by fungi over time. Conventional agricultural practices for increasing soil pH include adding lime periodically and mixing the lime with the acidic soil (7).

Redox potential of a subsurface environment has an influence on microbial metabolism and activity (5). For aerobic metabolism the redox potential should be greater than 50 millivolts, for anaerobic conditions less than 50 millivolts. At low redox potentials, alternative electron acceptors to oxygen (e.g., nitrate, iron, manganese, and sulfate) act as electron acceptors. A redox potential higher than 50 millivolts is conducive to biodegradation of hydrocarbons. A redox potential of less than 50 is condusive to degradation of chlorinated hydrocarbons (7).

Soil temperature has an important effect on microbial activity and has been correlated with biodegradation rates of specific organic compounds (12). Prepared-bed land treatment and in situ bioremediation should be planned to take advantage of the warm season in cooler climates. Vegetation can act as an insulator against heat loss and limit frost penetration. Application of mulches can help control heat loss at night and heat gain during the day (7, 12).

## Site Characterization

A contaminated site is a system generally consisting of four phases: 1) solid, which has an organic matter component and an inorganic mineral component composed of sand, silt, and clay, 2) oil (commonly referred to as nonaqueous phase liquid, or NAPL), 3) gas, and 4) aqueous (leachate or ground water). These phases and compartments need to be characterized with regard to extent and distribution of contamination as well as potential exposure to human and environmental receptors. Each phase affects bioavailability, i.e., interactions with microorganisms and exposure to human health and environmental receptors. Each phase can be a site for biological reactions that results in the transformation of a parent chemical to $CO_2$, $H_2O$, and other inorganic species through the process of mineralization, or transformation to intermediates that persist or that react with soil components to chemically bind to soil and therefore alter the bioavailability of the chemicals.

Evaluating the extent and distribution of contamination at a site will provide important information that can be used as a basis to select specific bioremediation technologies that are addressed in this seminar series, or to select a treatment train that represents a combination of physical/chemical and biological technologies. If contamination is widespread and low in concentration, then in situ treatment or natural attenuation may be feasible. Conversely, with high concentrations of contaminants, soil excavation and placement in a confined treatment facility (CTF) or a land treatment prepared-bed reactor may be advisable.

Distribution of contaminants at a site is determined by the physical and chemical properties of the contaminants and the properties of the site. Contaminant properties will affect whether contaminants are leachable, volatile, and/or adsorbable, and therefore will indicate which subsurface phases contain the contaminant(s). Physical phases containing the contaminants require evaluation of

bioremediation potential. When the physical and chemical properties are evaluated within the context of site characteristics, a site-based waste characterization can be used to identify the phases/compartments at the site and the chemicals associated with each phase. Additional information concerning practical aspects of site characterization for bioremediation of contaminated ground water is available in the document *In Situ Bioremediation of Contaminated Ground Water* (17).

## General Concept of Treatability Studies

Treatability studies are conducted in laboratory microcosms, at pilot scale, or in the field. EPA, through the Biosystems Field Initiative, and the Departments of Defense and Energy indicate an increased emphasis on field-scale evaluation of bioremediation, with a supportive role for laboratory-scale treatability testing. Parent compounds, intermediates, and electron acceptor utilization are evaluated. A mass balance conceptual framework for treatability studies, at any scale, refers to the characterization of the physcial phases in the soil and the determination of the influence of the phases on the bioavailability and bioremediation of associated target chemicals (18), as described in the "Site Characterization" section above.

While in the past the goal for bioremediation implied complete mineralization of chemicals to $CO_2$, $H_2O$, and inorganic chemicals, alternative endpoints that are protective of human health and the environment are currently being evaluated by the Department of Energy, EPA, the National Science Foundation, and the Office of Naval Research. Treatability studies that examine the bioavailability of contaminants in waste matrices, potential for toxic effects of intermediate metabolites during the degradation process, and interactions between waste chemicals and organisms are desired. The overall goal of treatability studies is to develop a better understanding of factors that threaten ecosystems and human health and of chemicals and their degradation products during bioremediation so that the regulatory community can take into consideration the possibility of alternatives to complete mineralization (19, 20).

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# Background Information for Bioremediation Applications

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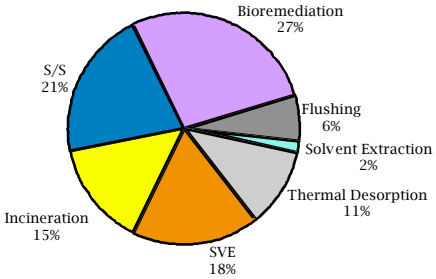
## Background Information for Bioremediation Applications

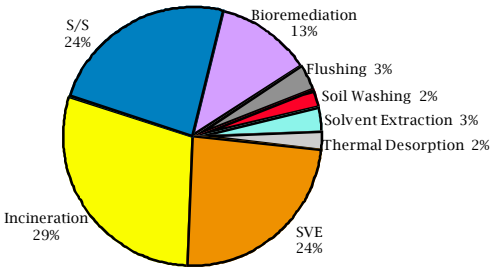
- National Status on Applications
- Biodegradation and Metabolism
- Environmental Factors Affecting Biodegradation
- Site Characterization
- General Concept of Treatability Studies

# National Status on Applications

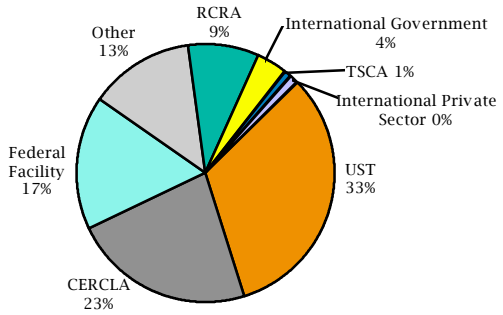
## Superfund Remedial Actions Technologies Selected in FY94



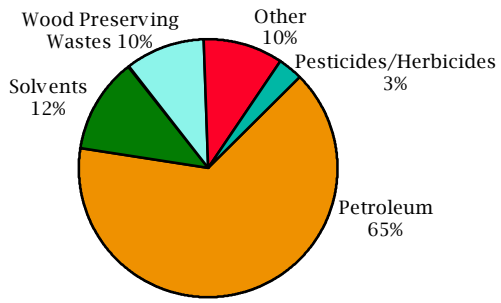

## Superfund Remedial Actions Technologies Selected in FY89



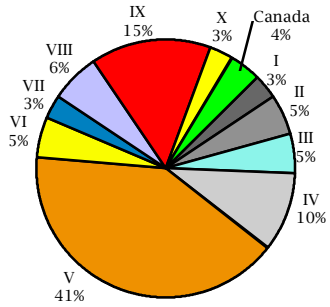

## Legislative Authority for Sites Using Bioremediation



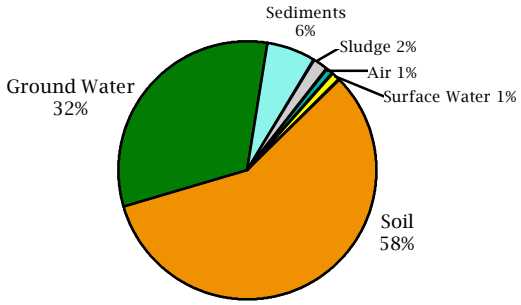
## Breakdown of Sites by Type of Contamination



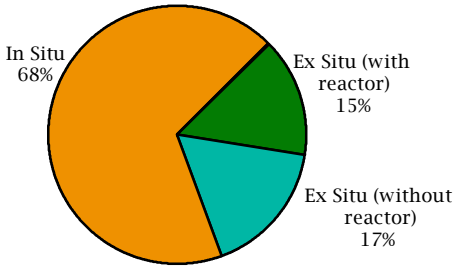

## Distribution of Bioremediation Projects by Region



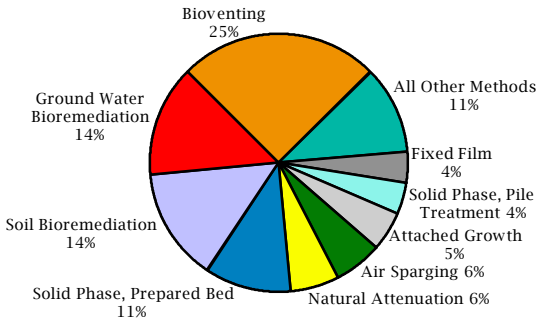

## Percentage of Sites Treating Each Medium



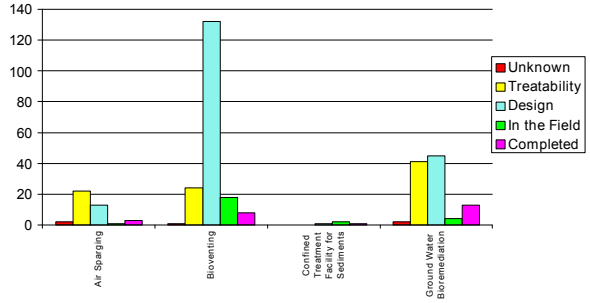

## Breakdown of Processes by Treatment Technology
(Includes Laboratory-, Pilot-, and Full-Scale)



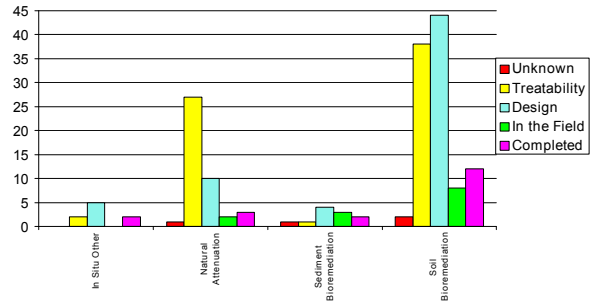

## Top 9 Bioremediation Methods




## In Situ Biotreatment Processes



## In Situ Biotreatment Processes
(continued)




# Biodegradation and Metabolism

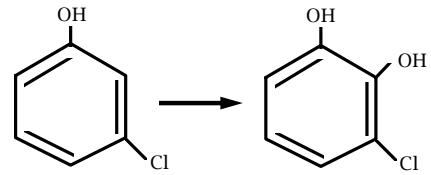
## Biodegradation and Metabolism

Chemical transformations mediated by microorganisms:

- Nutrition
- Energy
- Detoxification
- Fortuitous (co-metabolism)

## Biodegradation

- Biological transformation of an organic compound to another form without regard to extent

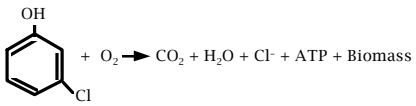



m-chlorophenol
3-chlorophenol

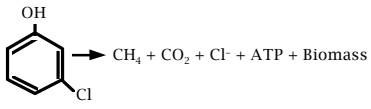
m-chlorocatechol
3-chlorocatechol

## Mineralization

- Conversion of an organic compound to carbon dioxide, water, methane, and other inorganic forms (e.g., $Cl^-$, $NH_4^+$)
  - Aerobic conditions




  - Anaerobic (methanogenic) conditions



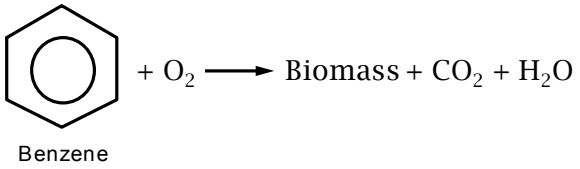

## Co-metabolism

$$CH_4 + O_2 \xrightarrow{MMO} CH_3OH + H_2O$$

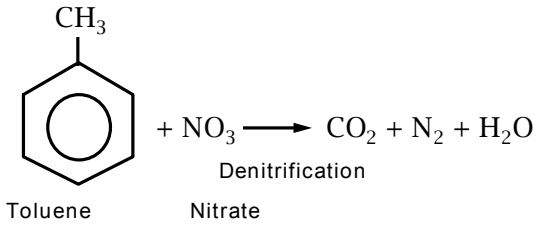
Methane — Methanotrophs — Methanol

$$TCE + O_2 \xrightarrow[Methanotrophs]{MMO} TCE\text{-}EPOXIDE + H_2O$$

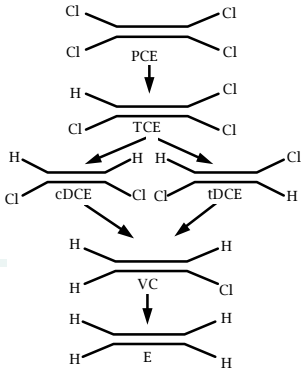
## Aerobic Biodegradation



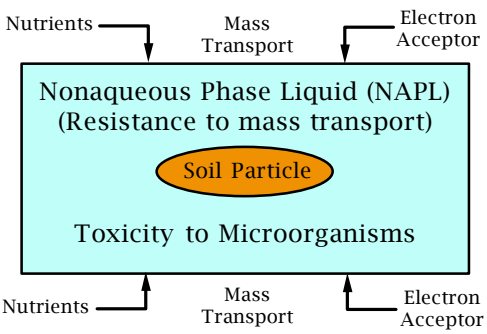

## Anaerobic Biodegradation




## Anaerobic Biodegradation (Reductive Dechlorination) of Chlorinated Alkenes




## Environmental Factors Affecting Biodegradation




Mass transport and toxicity limitations to bioremediation as a function of NAPL concentration

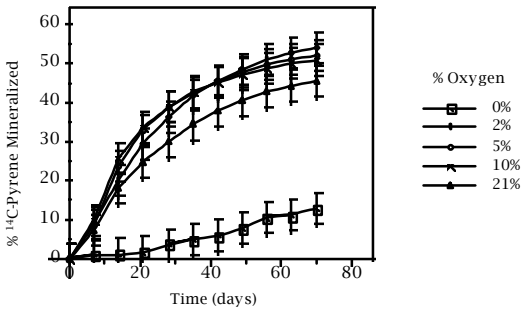
### Critical Environmental Factors for Soil Microbial Activity

| Environmental Factor | Effects |
|---|---|
| Oxygen | Metabolism: Aerobic/Anaerobic<br>Degradation Pathways |
| Nutrients | Nitrogen, Phosphorus Activity |
| Moisture | Unsaturated/Saturated Soil<br>Oxygen Transfer |
| Environment (pH) | 5.5–8.5<br>Activity |
| Environment (Redox) | Aerobes/Facultative Anaerobes: > 50 mV<br>Anaerobes: < 50 mV<br>Degradation Pathways |
| Environment (Temperature) | 15–45°C (Mesophilic)<br>Activity |

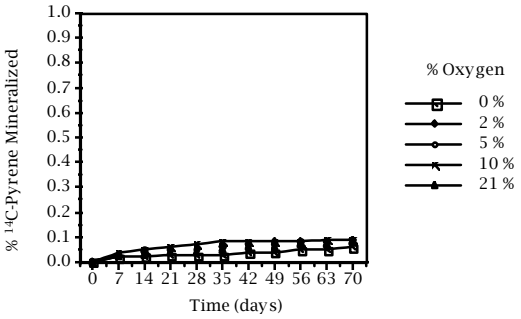
Reference: (9)

# Oxygen Supply

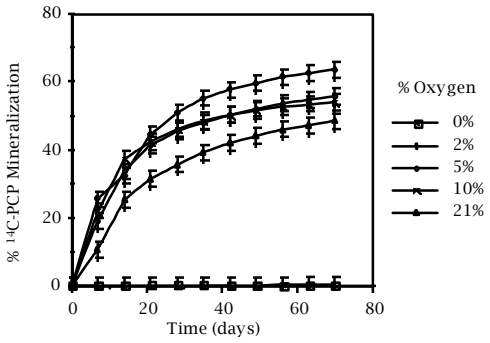
Oxygen diffuses through water at a rate that is 10,000 times less than oxygen diffuses through air



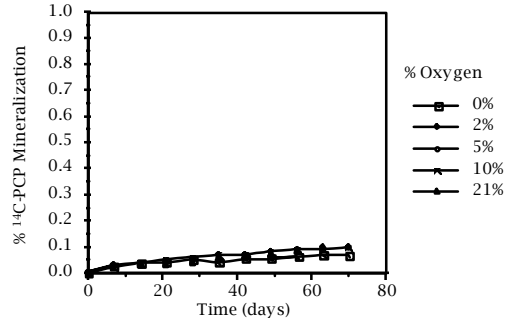

Mineralization of $^{14}$C-pyrene in non-poisoned soil microcosms as a function of time and oxygen concentration. Error bars represent the least significant difference of 7.94. Values are the means for triplicate reactors.
Reference: (12)




Mineralization of $^{14}$C-pyrene in poisoned soil microcosms as a function of time and oxygen concentration. Values are the means for triplicate reactors.
Reference: (12)




Mineralization of $^{14}$C-PCP in non-poisoned soil microcosms as a function of time and oxygen concentration. Error bars represent the least significant difference of 4.67%.



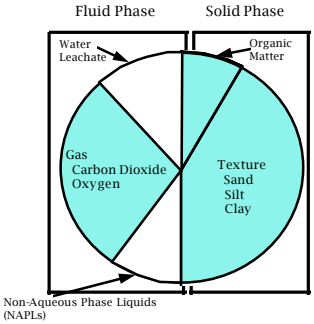

Mineralization of $^{14}$C-PCP in poisoned soil microcosms as a function of time and oxygen concentration. Values are the means for triplicate reactors.

# Environmental Factors

| | |
|---|---|
| Nutrients: | 100:10:1 Weight ratio |
| Moisture: | 60–80% Field capacity |
| pH: | 5.5–8.5 |
| Redox Potential: | >50 mV — Aerobic<br><35 mV — Dechlorination |
| Temperature: | Adaptation |

## Site Characterization

Physical Phases at a Site To Be Considered for Bioremediation Technologies

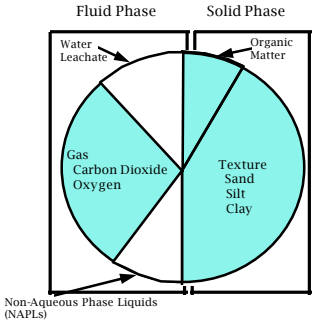



## General Concept of Treatability Studies

## Treatability Studies

- Field-scale — more emphasis
- Parent compounds
- Intermediates
- Electron acceptors

Physical Phases at a Site To Be Considered For Bioremediation Technologies




Mass Balance Framework

## Treatability Studies

- Alternative endpoints
  - DOE/EPA/NSF/ONR
  - Bioavailability
  - Intermediate metabolites
  - Interactions or chemicals and organisms
  - Risk impact

## Intermediate Metabolites

- 1-Hydroxy-2-Naphthoic acid
- 2,3-Dihydroxynaphthalene

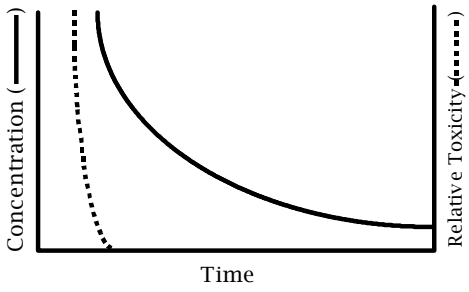
Reference: Ginn, J., W.J. Doucette, and R.C. Sims. 1994. Chemical mass balance approach for estimating fate and transport of polycyclic aromatic metabolites in the subsurface environment. Polycyclic Aromatic Compounds 5:225-234.

## Experimental Design

- Controls: sterile, no treatment, field background, number?
- Replicates: duplicate or triplicate? all time points? all controls?
- Treatments: what are the questions you want answered?
- How are you going to optimize the degradation process?

## Experimental Design (continued)

- Treatment time: how long should the study be performed?
- Types of analysis: bulk measurements? waste specific?
- Data reduction: raw data? massaged data? QC/QA?
- Cost considerations: how will it limit scope of test?




### Distribution of $^{14}C$ in Non-poisoned Microcosms Spiked With $^{14}C$-Pyrene

| Oxygen Conc. | % $^{14}C$ Mineralized | % $^{14}C$ Soil Bound | % $^{14}C$ Mass Recovered |
|---|---|---|---|
| 0% | 13 | 8 | 91 |
| 2% | 54 | 15 | 91 |
| 5% | 52 | 16 | 88 |
| 10% | 51 | 14 | 86 |
| 21% | 46 | 15 | 86 |

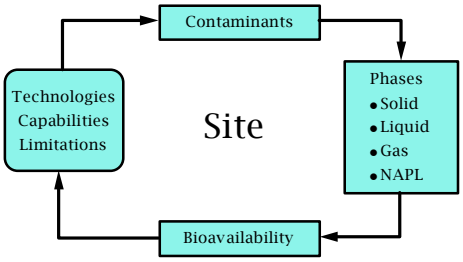
Reference: (12)

### Distribution of $^{14}C$ in Poisoned Microcosms Spiked With $^{14}C$-Pyrene

| Oxygen Conc. | % $^{14}C$ Mineralized | % $^{14}C$ Soil Bound | % $^{14}C$ Mass Recovered |
|---|---|---|---|
| 0% | <0.2 | 9 | 95 |
| 2% | <0.2 | 9 | 91 |
| 5% | <0.2 | 11 | 89 |
| 10% | <0.2 | 12 | 90 |
| 21% | <0.2 | 8 | 97 |

Reference: (12)

## Contaminated Site Characterization




Bioremediation Applications

# Bioventing

Gregory D. Sayles
Office of Research and Development, National Risk Management Research Laboratory,
U.S. Environmental Protection Agency, Cincinnati, OH

Research conducted in the mid to late 1980s by the U.S. Air Force (1, 2), researchers in the Netherlands (3-6), the Texas Research Institute (7, 8), Battelle Memorial Institute (2, 9-11), Utah State University (11), and the U.S. Environmental Protection Agency (EPA) (12), among others, suggests that delivering air to the vadose zone to promote biodegradation could be a low-cost means of cleaning fuel-contaminated vadose zone soils. This approach was motivated by attempting to solve two different remediation development problems: 1) soil vacuum extraction for treatment of contaminated vadose zones involved costly off-gas treatment and only removed the volatile fraction of the contamination, and 2) oxygen delivery to the vadose zone to promote aerobic biodegradation by using the approaches attempted in promoting biodegradation in ground water, namely delivering oxygen-saturated water or aqueous solutions of hydrogen peroxide or nitrate to the contaminated area, was not efficient or cost-effective.

A process was needed that could deliver oxygen by introducing air into the vadose at a rate that minimized volatilization of the contamination. Several groups simultaneously developed what is now known as bioventing.

EPA and the Air Force recognized the potential cost savings of such a technology over traditional remediation approaches and began an aggressive bioventing development program in 1990. To date, this program has demonstrated or is currently developing the use of bioventing for the following situations:

- With air injection (10-17)
- In cold climates (18-20)
- With soil warming (18-20)
- For jet fuel and other aviation fuels (10-20)
- For nonfuel contaminants such as acetone, toluene, polycyclic aromatic hydrocarbons (PAHs) (21), and trichloroethylene (TCE)

The cumulative knowledge of EPA, the Air Force, and Battelle Memorial Institute regarding bioventing of fuel contaminated sites was distilled in *Principles and Practices Manual for Bioventing*, released in 1996 (22). The manual outlines the physical, chemical, and biological principles used in bioventing, and accepted approaches to determining site-specific treatability using onsite tests, design and monitoring of bioventing systems, and site closure.

Many documents exist that provide valuable information on bioventing. The Army Corps of Engineers has also released a helpful manual (23). The most current collection of papers on bioventing research and development is available in the book *In Situ Aeration: Bioventing and Related Remediation Processes* (24). The next frontier for aerobic bioventing is the application of the process to sites contaminated with chlorinated solvents and PAHs. EPA is currently involved in two laboratory and field projects to develop co-metabolic bioventing. Co-metabolic bioventing is the promotion of the aerobic biodegradation of chlorinated solvents, such as TCE, in the vadose zone by delivering oxygen and, if necessary, a volatile co-metabolite to the contaminated site. The Air Force has developed cost estimates for bioventing of fuels (25). Calculations show that bioventing can range from $50 to $5 per cubic yard for soil volumes ranging from 2,000 to 20,000 cubic yards, respectively. These costs for bioventing are cheaper than costs estimated for other onsite remediation methods such as soil vapor extraction, land farming, and excavation followed by low-temperature thermal desorption.

The available information on bioventing (experimental, performance, cost) easily convince the reader that bioventing of fuels is probably the most successful in situ bioremediation technology developed to date. There are an estimated 1,000 sites in the United States that have used or are currently using bioventing, mostly for fuel-contamination remediation. In the future, expect the bioventing approach to be shown useful for the cleanup of almost any aerobically biodegradable contaminant.

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# Bioventing

## An Aerobic Bioprocess To Treat Vadose Zone Contaminated Soils

Presented by
Gregory Sayles or Dolloff F. Bishop

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U.S. Environmental Protection Agency
Cincinnati, Ohio

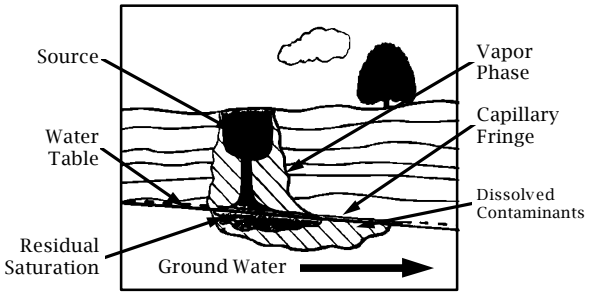
# Outline

- What is bioventing?
- Site characterization for bioventing
- Treatability for bioventing
- Full-scale design

# Outline (continued)

- Operation/Monitoring
- Field examples
- Costs
- Bioventing manual

## Hydrocarbon Distribution at a Contaminated Site

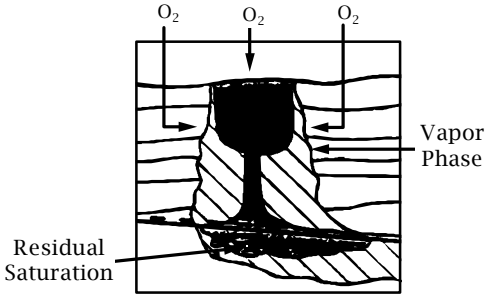



## Distribution of a 148,000 kg Spill (200 $m^3$)

| Phase | Concentration | Contaminate Volume ($m^3$) | % of Volume | Mass (kg) | % of Mass |
|---|---|---|---|---|---|
| Recoverable NAPL | 100% | 63 | 0.2 | 47,000 | 32 |
| Soil Gas | 1,000 ppm | 5,600 | 17.0 | 1.7 | .000011 |
| Ground Water | 100mg/L | 20,000 | 62.0 | 2.0 | .000014 |
| Residual Soil Sorbed | 10,000 mg/kg | 6,500 | 21.0 | 97,000 | 66 |

Courtesy of Rob Hinchee, Parsons Engineering Science Inc.

## Natural Oxygen Delivery Not Adequate



## Aerobic Biodegradation — Respiration

$$C_6H_6 + 7^1/_2\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$$

3.1 lb $O_2$/lb $C_6H_6$

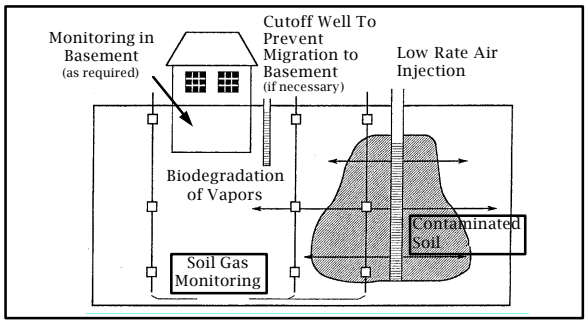
$$C_6H_{14} + 9^1/_2\ O_2 \longrightarrow 6\ CO_2 + 7\ H_2O$$

3.5 lb $O_2$/lb $C_6H_{14}$

## Oxygen Carrier Mass Requirements

| Oxygen Carrier | Carrier/Hydrocarbon (lb/lb) |
|---|---|
| Aqueous Solutions | |
| Air Saturated | 400,000 |
| Nitrate (50 mg/L) | 90,000 |
| $H_20_2$ (100 mg/L) | 65,000 |
| Air | 13 |

## Conceptual Layout of Bioventing Process With Air Injection Only

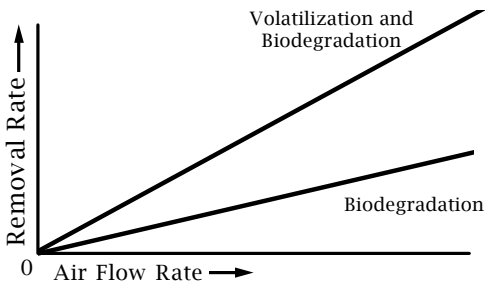



## What Is Bioventing?

### Definition

Forced air movement through contaminated vadose zone soils to supply the oxygen necessary for otherwise oxygen-limited in situ bioremediation

## Bioventing vs. SVE




## Aerobically Biodegradable

Rates vary from fast to slow:

| | |
|---|---|
| BTEX | Ketones (acetone) |
| Jet fuel | PAHs (naphthalene) |
| Gasoline | Alcohols |
| Diesel | Fuel oil |

Mono- or di-chlorinated benzenes, phenols

Mono- or di-chlorinated ethanes, ethylenes

## Site Characterization

- Historical data
- Soil gas survey
- Soil sampling

## Historical Data

Purpose: Initial evaluation of feasibility, help plan soil gas survey

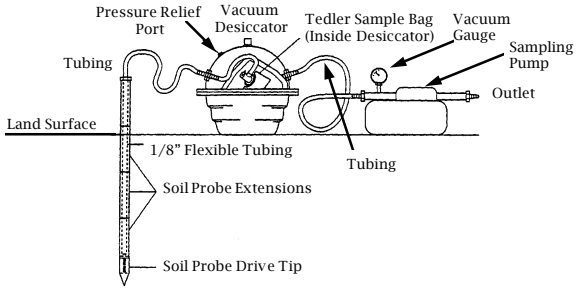
- Known spills, overfills, leaks
- Soil and GW data
- Location and levels

## Soil Gas Survey

Purpose: To locate areas where oxygen levels are low, minimize soil sampling

- Sample soil gas at various:
  - locations
  - depths
- Analyze gas for $O_2$, $CO_2$, TVH

## Schematic of a Soil Gas Sampling System




## Soil Gas Survey Results

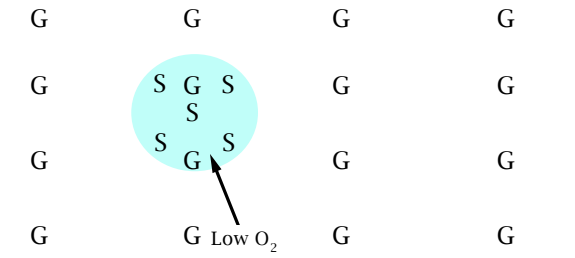
- Low $O_2$, high $CO_2$
  - Bioactivity present, but needs $O_2$
  - Candidate location for bioventing
- High $O_2$, low $CO_2$
  - Bioactivity low, something else is retarding biodegradation
  - Not a candidate site for bioventing

## Soil Sampling

Purpose: To confirm type and extent of contamination, estimate of cleanup time

- In region of low $O_2$, sample soil at various:
  - locations
  - depths
- Analyze for contaminants of regulatory concern (e.g., TPH, BTEX)

## Site Characterization-Aerial View




G = Gas samples

S = Soil samples

## Field Treatability Tests

Want to know the required:

- Air flow rate
- Well spacing
- Cleanup time estimate
- Cost estimate

## Treatability Test

- In situ respirometry test
- Soil gas permeability test

## In Situ Respiration Test

Purpose:

- To measure $O_2$ use rate for feasibility
- To calculate air flow rate for design
- To estimate cleanup time

## In Situ Respiration Test

Protocol:

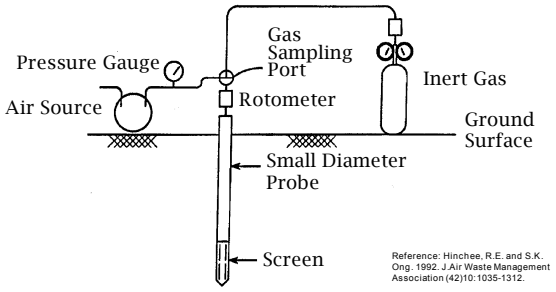
1. Install:
   - air injection tube
   - soil gas monitoring points

into contaminated area and background

## In Situ Respiration Test (continued)

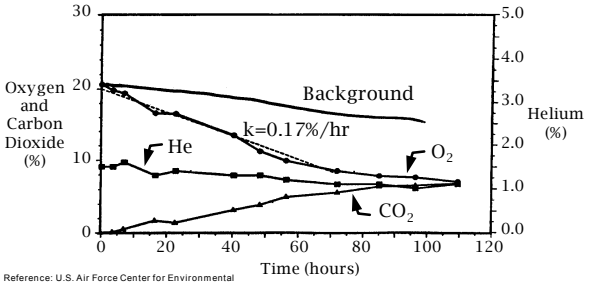
2. Aerate (air + helium) for 1-2 days, until soil gas levels steady
3. Shut off aeration
4. Monitor $O_2$, $CO_2$, and He with time

## In Situ Respiration Test Apparatus



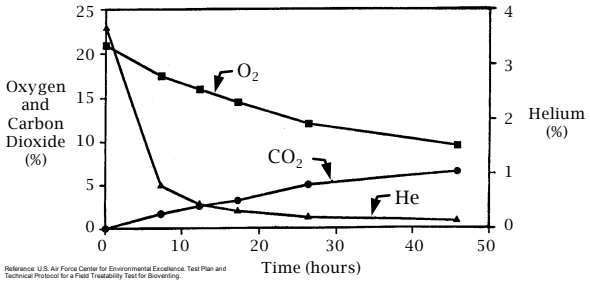

Reference: Hinchee, R.E. and S.K. Ong. 1992. J.Air Waste Management Association (42)10:1035-1312.

## In Situ Respiration Test Results for Tinker AFB, Oklahoma




Reference: U.S. Air Force Center for Environmental Excellence. Test Plan and Technical Protocol for a Field Treatability Test for Bioventing.

## In Situ Respiration Test Results for Kenai, Alaska



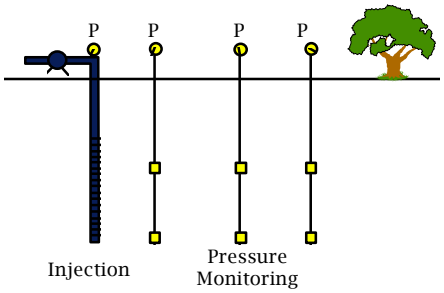

Reference: U.S. Air Force Center for Environmental Excellence. Test Plan and Technical Protocol for a Field Treatability Test for Bioventing.

## Soil Gas Permeability Test

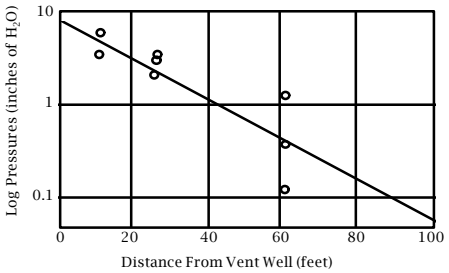
Purpose:

- Radius of influence of air injection
- Well-spacing
- Cost

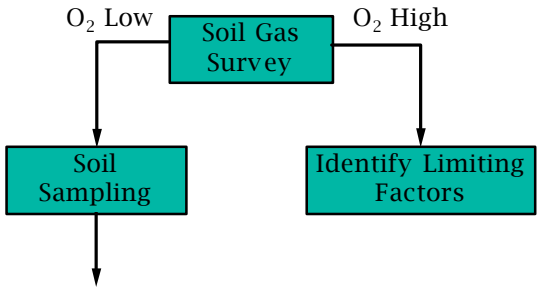
## Radius of Influence Test



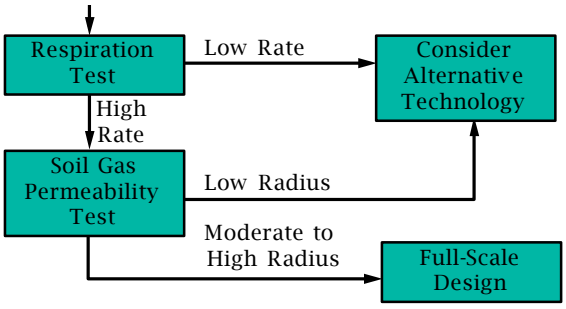

## Radius of Influence Data, Saddle Tank Farm, Galena AFS, Alaska



## Bioventing Decision Tree




## Bioventing Decision Tree (continued)




## Full-Scale Design

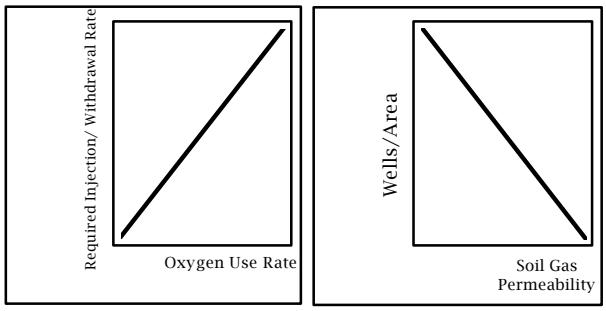
- Air flow rate
- Wells/Area
- Air injection vs. withdrawal
- Other well configurations

## Flow Rate and Wells

Using
- $O_2$ use rate
- Radius of influence

Calculate
- Total air flow rate
- Number of wells/area

## Design Approach

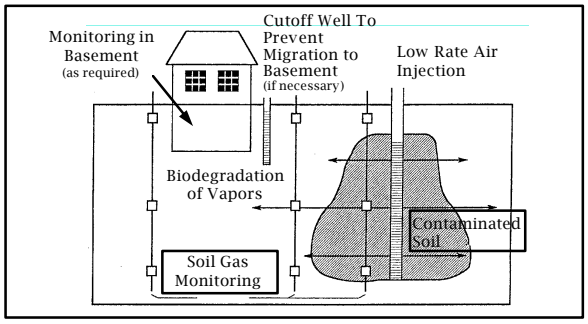



## Injection vs. Withdrawal

Injection usually preferred:
- Minimizes off-gas production
- Lowers water table—treats capillary fringe
- Vapor residence time greater

But, be careful of subsurface structures!

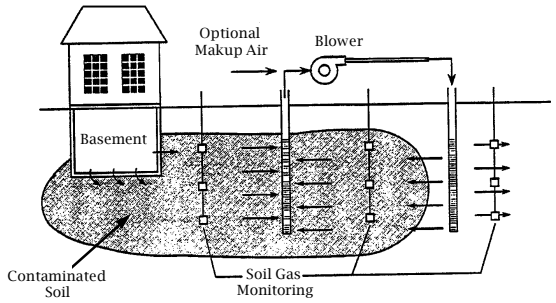
## Conceptual Layout for Bioventing Process with Air Injection Only



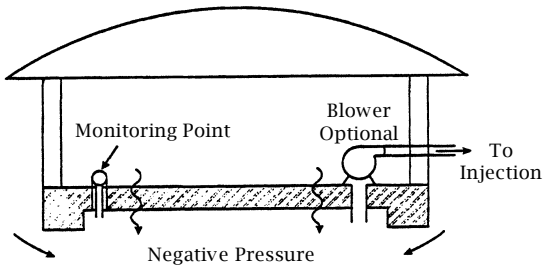

## Other Configurations

Use injection and withdrawal well combinations to meet special site requirements

## Air Injection System With Reinjection of Extracted Soil Gas




## Schematic of Bioventing Under Buildings




## Operation/Monitoring

- Soil sampling at selected time intervals
- $O_2$ gas measurements
- Soil temperature

## Operation/Monitoring (continued)

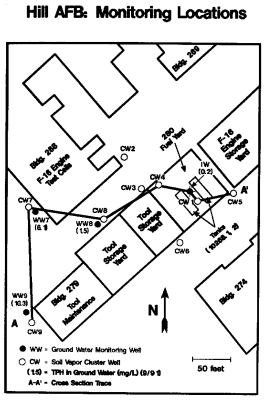
- Respiration tests at least semi-annually
- Operate year round
- t = end determined by rate → 0

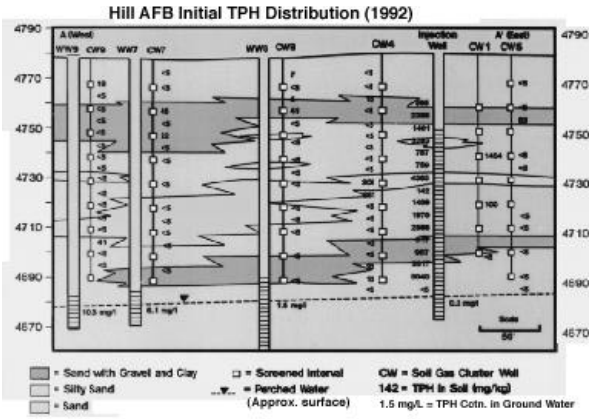
## Results From the Field

- Hill AFB Field Research Study
  - Arid soil, deep air injection
  - Jet fuel
- Greenwood Chemical Superfund site
  - Tight soil
  - Toluene, acetone, naphthalene

## Hill AFB, Utah, Bioventing Study

- Jet fuel contamination
- From overfills of old USTs
- Contamination to 95 ft deep
- Low moisture, high permeability soil
- Air injection operated for 3½ yrs



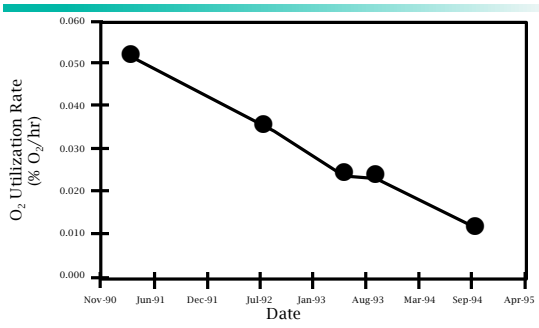

**HILL AFB Site 280 - Operations**

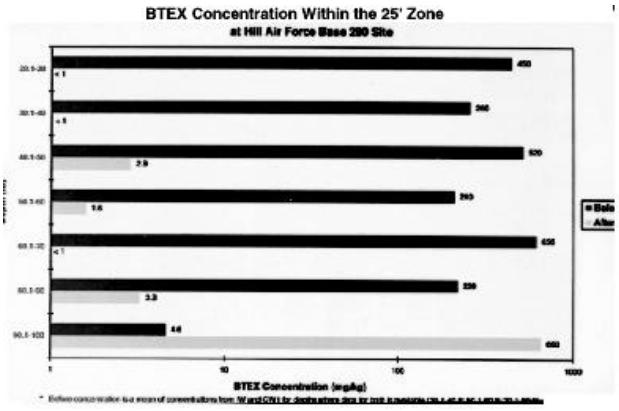
**Injection pressure = 0.8 psig**

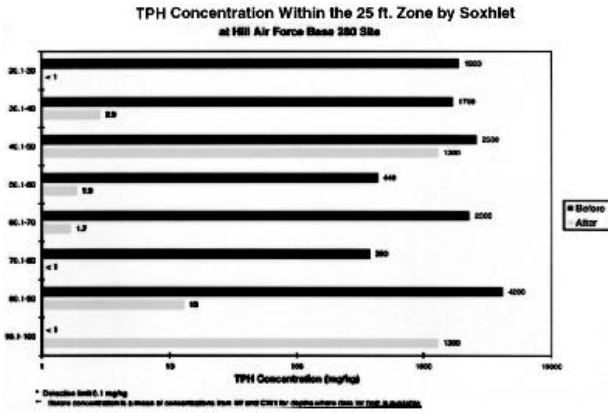
**Monthly soil gas monitoring**

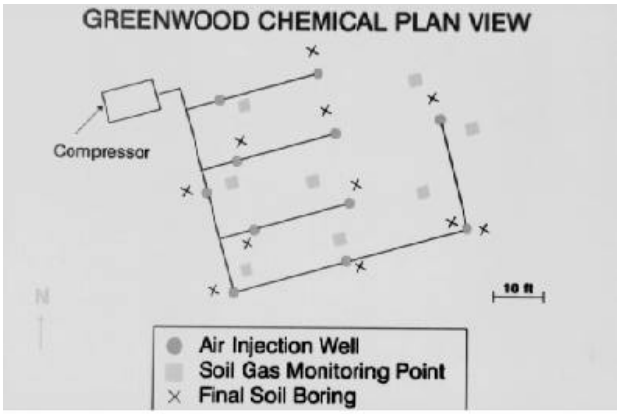
**Periodic in-situ respiration tests, surface emissions tests**

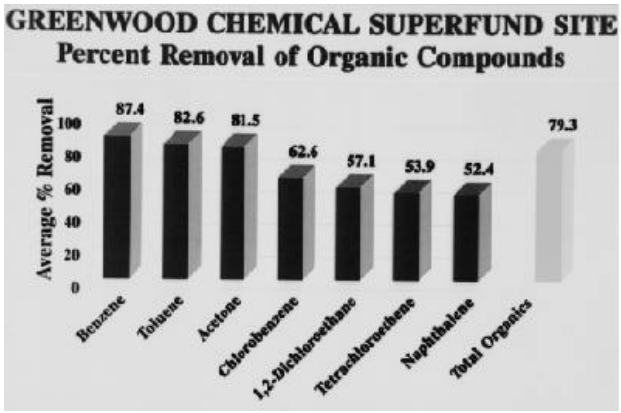
Mean Oxygen Utilization Rate vs. Time Within the IW 25-ft Zone at Hill Air Force Base 280 Site






## Greenwood Chemical Superfund Site, Virginia, Pilot Test

- Specialty chemical company
- Toluene, acetone, naphthalene, contamination
- Tight silty clay soils
- Air injection operated for 15 months

## Costs

Example calculation*

- 5,000 $yd^3$ jet-fuel contaminated soil
- 3,000 mg/kg TPH
- 4 injection wells
- Contamination, wells to 15 ft deep

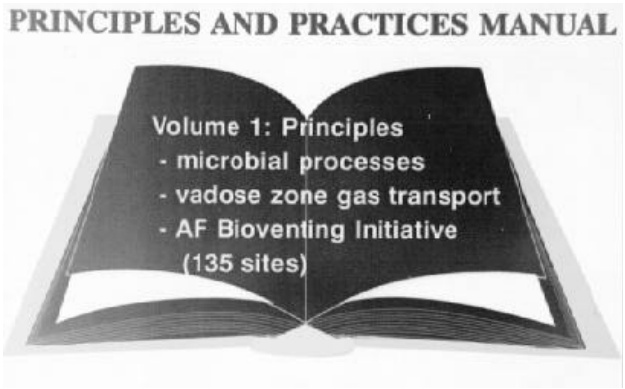
* "Bioventing Performance and Cost Summary," AFCEE, July 1994.

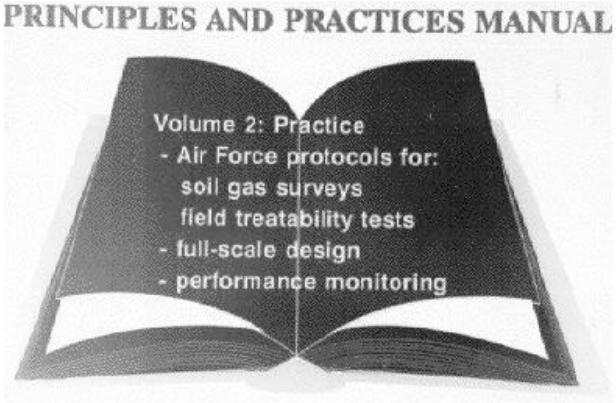
## Example (continued)

| Item | Cost |
|---|---|
| Project planning | $11,000 |
| Pilot testing | $27,000 |
| Regulatory approval | $3,000 |

## Example (continued)

| Item | Cost |
|---|---|
| Full-scale construction | $27,000 |
| Monitoring, 2 yrs | $6,500 |
| Power, 2 yrs | $2,800 |
| Final soil sampling | $13,500 |
| Total | $90,800 |
| Cost/yd$^3$ | $18 |




## Bioventing Manual

Available on the Internet

The Address is:
http://www.epa.gov/docs/ORD

## Summary

If your site:

- Has soil contamination
- Low $O_2$
- The contamination is aerobically biodegradable

Seriously consider bioventing

# Bioremediation of Sediments

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U.S. Environmental Protection Agency, Cincinnati, OH

## Introduction

Contaminated sediments in rivers, lakes, and harbors in the United States pose a potential risk to human health and the environment. Bioremediation (1-3), both through natural attenuation (intrinsic bioremediation) and through enhanced bioremediation, promises possible approaches for destruction of contaminants in sediments. Using natural processes involving microbial growth and enzymatic production, bioremediation can convert target contaminants ultimately to nontoxic end products. High molecular weight contaminants, however, such as polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), persist in sediments, biodegrading only slowly while strongly partitioning to the sediments and bioaccumulating up the food chain (4), ultimately reaching humans.

Both PCBs and PAHs are biodegradable under appropriate conditions in laboratory studies (1, 3). PAHs (5) are typically degraded under aerobic conditions. PCBs (1) are typically degraded under sequential anaerobic and aerobic conditions. Appropriate anaerobic conditions dehalogenate more highly chlorinated PCBs, usually the meta- and para-chlorines on the biphenyl structure. Aerobic conditions usually degrade the resulting lightly chlorinated PCBs with the chlorine atoms at the ortho position.

Reasons why the persistent contaminants in sediments (6) are resistant to microbial degradation include:

- Contaminant toxicity to the microorganisms
- Preferential feeding of microorganisms on other substrates
- Microorganisms' inability to use a compound as a source of carbon and energy
- Unfavorable environmental conditions in sediments for propagation of appropriate microorganisms
- Poor contaminant bioavailability to microorganisms

Indeed, while the intrinsic biodegradation of such recalcitrant compounds is not uncommon in nature, the degradation process can take many years.

The challenge for successful bioremediation of sediments involves combining appropriate microbial pathways, biochemistry, and the function of natural microbial communities with innovative engineering methods to overcome the recalcitrance of the compounds in sediments, thus increasing

bioremediation effectiveness. Successful acceleration of degradation rates in situ without a bioreactor would provide a method for preferred sediment remediation, but such approaches have exhibited limited effectiveness. Sediment dredging, usually to maintain open channels for shipping, however, also offers the opportunity for alternative ex situ treatment (6), such as biotreatment in confined treatment facilities (CTFs), slurry reactors, and composting land treatment applications. Slurry reactor technology has also been applied in situ to contaminated sediments in water bodies (5).

## Field Bioremediation of Sediments

This review examines two pilot field studies on contaminated sediments: one an ex situ CTF treatment of PCBs in sediments from the Sheboygan River in Wisconsin, the other an in situ slurry reactor treatment of PCBs in sediments in the upper Hudson River. The CTF study (6) was conducted for the U.S. Environmental Protection Agency's (EPA's) Region 5 and included a parallel laboratory study on the Sheboygan River sediments by EPA's Athens Laboratory. The in situ slurry reactor study (7) was conducted by the General Electric Company using caisson slurry bioreactors placed in PCB-contaminated sediments in the river.

The 14,000-square-foot aboveground CTF (Figure 1) used in the Sheboygan study was constructed of steel sheet piling with a containment capacity of approximately 2,500 cubic yards of sediment in four separate cells: two treatment and two control cells. Each cell (Table 1), lined with high-density polyethylene, was hydraulically independent. Water accumulating in each cell discharged through a permeable wall. The cells contained an underdrain system to add nutrients, oxygen, and other amendments which could also be used for leachate control. The cells were filled with dredged PCB-contaminated sediments (original source: Arochlor 1248 and 1254) obtained from the river in late 1989 and from March to August 1990. The study attempted to evaluate remediation under both anaerobic and aerobic conditions in the CTF. Two approaches for oxygenating the contained sediments in Cell 4 were use of oxygenated (saturated) water from a compressed air saturator (July 1992) and use of dilute hydrogen peroxide solutions (November 1993). Mineral nutrient were also added to the two treatment cells. Finally, laboratory studies were conducted to evaluate enhancing anaerobic dehalogenation in the Sheboygan sediments.

In the second field evaluation, six steel caisson slurry reactors (Figure 2) were driven into contaminated sediments in the upper Hudson River to isolate the natural bacteria and sediment from the river environment. The experimental design in the study (Table 2) featured a low-mix caisson and a high-mix caisson as unamended controls; two duplicate low-mix caissons with indigenous organisms amended with ammonium and phosphate nutrients, biphenyl, and hydrogen peroxide; and one high-mix and one low-mix caisson with indigenous organisms, both amended with ammonium phosphate nutrients, biphenyl, hydrogen peroxide, and a culture of PCB degraders, *A. eutrophus* H850.

The sediments were mixed using high-mix turbines turning at 40 revolutions per minute (rpm) and low-mix rakes turning at 3 rpm. The target dissolved oxygen level, automatically supported by addition of hydrogen peroxide solution, was maintained between 6.0 and 6.5 mg/L in four caissons. Other amendments were added to the four caissons as appropriate. The unamended high-mix

control became aerobic but was held to less than 2 mg/L liter by nitrogen purging while the low-mix control remained anaerobic.

## Sediment Remediation Performance

In the CTF study (Tables 3 and 4) at Sheboygan (8), the PCBs in the dredged sediments in the various cells had an average chlorine per molecule of biphenyl ranging from 2.79 to 3.12, indicating that only limited amounts of highly chlorinated congeners remained in the sediment. Heavy oxygen demand in the sediment on Cell 4 minimized the oxygen (less than 0.1 mg/L) available for degradation of lightly chlorinated PCBs. Attempts to aerobically degrade PCBs in the sediments in Cell 4 thus produced no increased PCB remediation in the sediments. The oxygenation attempts were unable to supply enough oxygen to overcome the oxygen demand in the sediment and the sediment in Cell 4 remained anaerobic. The sediments, loaded into the cells over an extended period, were dredged from various places in the river and were highly heterogenous with wide variability in PCB concentrations from sampling location to sampling location in each cell. The heterogeneity produced high variability in each cell's average concentration over the three sampling events, as shown in Table 5. Under anaerobic conditions in the other CTF cells, statistically valid increases in dehalogenation of the PCBs also did not occur.

Parallel laboratory studies at the Athens Laboratory (8) revealed (Figure 3) that addition of octachlorobiphenyl (octa-CB) substantially increased dehalogenation of the PCBs in the historical Sheboygan sediment. Sterile and live controls revealed no significant change in the PCBs in the sediment. Increased dechlorination in historical PCB mixtures in the sediment, induced by the added octa-CB, delayed the onset of transformation of the added octa-CB by 1 to 2 months.

The PCB homologs (Figure 4) revealed essentially no monohomolog and only modest dihomologs in the initial sediment. The largest homolog was the trihomolog, which accounted for approximately 50 percent of the PCBs. The control test after 30 weeks revealed insignificant changes in PCB homolog distribution. The amended system with 20 mg/L of octachlorobiphenyl exhibited significant dechlorination with major increases of mono- and dihomologs (Figure 5).

Three methods were used to examine PCB concentration changes within the slurry reactors in the Hudson River field study: direct concentration measurement and concentrations normalized to a recalcitrant reference congener (peak 61, 34-34-/236-34 chlorobiphenyl) and to sediment total organic carbon (9). The alternative methods were considered because of sampling variability in the caissons, reflecting the heterogeneity in PCB distribution and sampling in the field. The two normalizing methods were the most significant in quantifying PCB changes after 73 days of treatment in the caissons (Table 5).

The normalized analyses revealed statistically significant PCB losses of 38 to 55 percent in all amended caissons. The addition of the H850 culture produced no impact on the PCB changes, and the H850 cultures were not competitive. Congener homolog group analysis (Figure 6) revealed significant biodegradation of the mono- and dicongeners.

## Conclusions

The results of the Sheboygan River and the Hudson River studies reveal that partial bioremediation of PCBs in sediments is possible, even without active biotreatment. The remediation, however, is incomplete, even with active biotreatment. While sequential anaerobic/aerobic approaches may completely degrade PCBs in aqueous dispersions, portions of the PCBs in sediments are not available or only slowly available for biotreatment. Additional research is clearly needed to develop and evaluate improved approaches for sediment bioremediation. Alternative measurements (endpoints), based on toxicity, need to be evaluated on bioremediated sediments to assess the potential environmental and health impacts of the residual PCBs after intrinsic bioremediation (natural attenuation) and after active biotreatment.

## References


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# Bioremediation of Sediments

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W. J. Jones
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General Electric Company

# Bioremediaton of Contaminants in Sediments

- Natural attenuation (intrinsic bioremediation)
- Enhanced bioremediation using amendments
- Microbial growth and enzymatic production often limited by conditions in sediments
- PCBs and PAHs as common high molecular weight contaminants

# Conditions Limiting Bioremediation of Sediments

- Contaminant toxicity to microorganisms
- Preferential feeding of microorganisms on other substrates
- Inability of microorganisms to use contaminant as source of carbon and energy
- Sediment conditions unfavorable for appropriate microbial propagation
- Contaminants not bioavailable to microorganisms

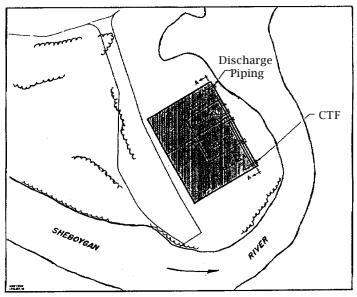
# Challenge for Sediment Bioremediation

- Combining appropriate microbial pathways, biochemistry, and function of natural microbial communities
- Developing innovative engineering methods in sediments to overcome contaminant recalcitrance to biodegradation
- Developing in situ biotreatment without reactors (preferred but has exhibited limited effectiveness)
- Developing in situ treatment of dredged sediments for enhanced bioremediation
- Developing in situ biotreatment with slurry reactors in water bodies

# Field Bioremediation of Sediments

- Ex situ treatment of PCBs in CTFs with supporting laboratory studies
- In situ aerobic slurry treatment of PCB in steel caissons

Figure 1. Confined Treatment Facility for Sheboygan River Sediments

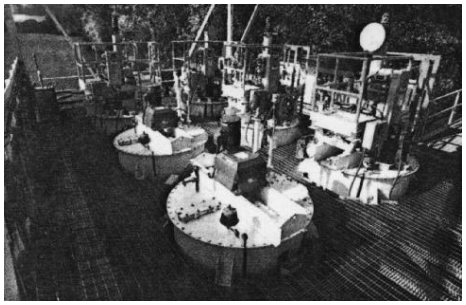


## Table 1. CTF Bioreactor Cells

| Cell No. | In Situ PCB mg/kg | Treatment Condition |
|---|---|---|
| 1 | 225 | Anaerobic with nutrients |
| 2 | 185 | Anaerobic control |
| 3 | 100 | Anaerobic control |
| 4* | 125 | Anaerobic with nutrients |

*Cell 4 was intended to be aerobic but D.O. never >0.1 mg/L

## Figure 2. In Situ Slurry Biodegradation of Hudson River Sediments



## Table 2. In Situ Slurry Reactor Experimental Design

| Caisson (mg/kg) | Treatment | Initial PCB Conc. |
|---|---|---|
| R101 | High-mix, control | 6.0 ± 1.9 |
| R102 | High-mix, amended H850 | 20.0 ± 11.0 |
| R103 | Low-mix, amended H850 | 30.2 ± 10.6 |
| R104 | Low-mix, control | 39.9 ± 15.6 |
| R105 | Low-mix, amended indig. | 49.7 ± 27.8 |
| R106 | Low-mix, amended indig. | 39.1 ± 17.5 |

## In Situ Slurry Reactor Design

- High-mix turbines turning at 40 rpm
- Low-mix rakes turning at 3 rpm
- Amended with ammonium and phosphate nutrients biphenyl, hydrogen peroxide (D.O. 6–6.5 mg/L)
- Indigenous organism or indigenous and H850 organisms
- Low-mix control-anaerobic; high-mix, <2 mg/L D.O.

## Table 3. Average CL Per Biphenyl*

| Sample date | Cell 1 | Cell 2 | Cell 3 | Cell 4 |
|---|---|---|---|---|
| 6-1-92 | 3.14 | 2.78 | 2.87 | 3.22 |
| 8-20-92 | 3.11 | 2.80 | 2.82 | 3.12 |
| 11-4-92 | 3.11 | 2.79 | 2.75 | 2.95 |
| Averages | 3.12 | 2.79 | 2.81 | 3.10 |

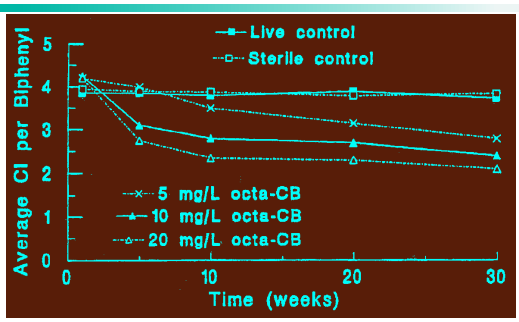
*Sheboygan River sediments in CTF

## Table 4. Average PCB Concentrations*, mg/kg

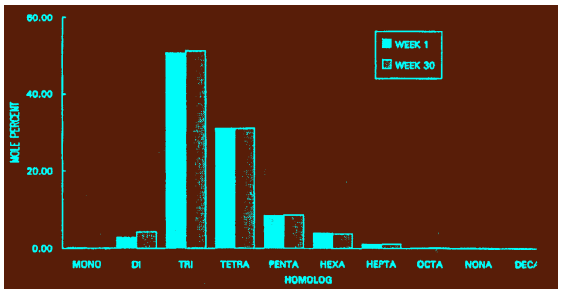
| Sample date | Cell 1 Anaerobic with nutrients | Cell 2 Anaerobic control | Cell 3 Anaerobic control | Cell 4** Anaerobic with nutrients |
|---|---|---|---|---|
| 6-1-92 | 200 | 115 | 91 | 134 |
| 8-20-92 | 273 | 132 | 109 | 230 |
| 11-4-92 | 323 | 165 | 180 | 236 |
| Averages | 265 | 137 | 127 | 200 |

*Sheboygan River sediments in CTF
**Cell 4 was intended to be aerobic but D.O. never >0.1 mg/L

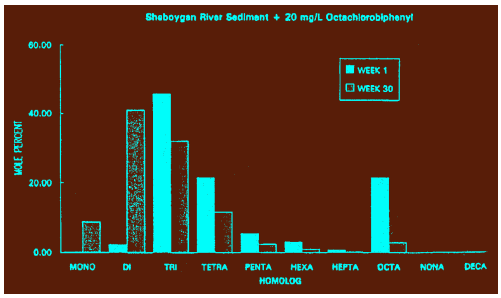
## Figure 3. Induced Dechlorination of Sheboygan Sediments




## Figure 4. Congener Homologs in Sheboygan River Sediments




## Figure 5. Congener Transformation by Octachlorobiphenyl Amendment

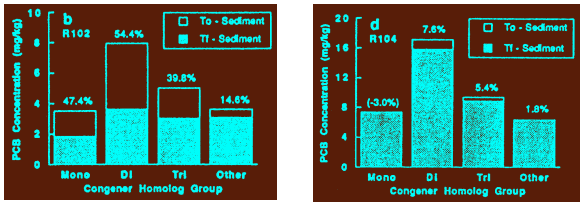



## Table 5. PCB Transformations in Hudson River Sediments

| | Percent Changed | | |
|---|---|---|---|
| Treatment | Direct Measure | Peak 61* | TOC** |
| High-mix control | +8.7 | -14.4 | -30.7 |
| High-mix, H850 | -41.0 | -42.4 | -44.7 |
| Low-mix, H850 | -36.8 | -37.8 | -55.5 |
| Low-mix, control | -41.8 | -4.3 | +8.4 |
| Low-mix, indig. | -72.6 | -40.5 | -53.1 |
| Low-mix, indig. | -68.5 | -38.7 | -46.0 |

*Normalized to congener 34-34/236-34 chlorobiphenyl
**Normalized to total TOC

## Figure 6. Transformation of PCB Homologs in Hudson River Sediments




To = Time zero.
Tf = Final time after 73 days.

# Conclusions

- Partial bioremediation of PCBs in sediments occurs even without active biotreatment
- Remediation is incomplete even with active biotreatment
- Portions of PCBs in sediment are not or only slowly available for biotreatment
- Alternative measurements (endpoints) based on toxicity need to be conducted on bioremediation sediments
- Research is needed to develop improved methods of sediment bioremediation

# Aerated Lagoons: A Case Study

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## Introduction

In the mid-1960s to the early 1970s, the French Limited Superfund site (Figure 1) was a state-licensed waste disposal site near Crosby, Texas. About 90 companies contributed petroleum and petrochemical wastes that were hauled to the site for disposal. At closure of the disposal site in 1971, about 70 million gallons of wastes were in the main waste lagoon. In late 1983, the potentially responsible parties (PRPs) formed the French Limited Task Group (FLTG) to consider site cleanup (1). In early 1987, the U.S. Environmental Protection Agency (EPA) issued a record of decision (ROD) for the site (2) calling for remediation by incineration, at estimated costs of $75 to $125 million.

Beginning in late 1985 and continuing through 1986, bench-scale bioremediation had already been successfully conducted on the contaminated sludges and soils in the lagoon. When the ROD selecting incineration was issued, FLTG began to explore, at field pilot scale, environmentally protective and less costly in situ bioremediation for French Limited cleanup. After the successful field pilot study, EPA in late 1987 modified the ROD to allow in situ bioremediation (2) as the preferred cleanup technology for the site. Full-scale site remediation, first in one biotreatment cell (one half of the lagoon) and then in a second cell, was initiated at the site in early 1992 and was completed by 1994.

## Cleanup Approach

Most contaminants were biodegradable and in a water matrix at a site with a warm climate. Practical bioremediation at the site needed to manage ambient air quality; mechanically mix microorganisms, nutrients, oxygen, sludge, soil, and mixed liquor to produce acceptable biodegradation rates in the 12-acre lagoon; and accurately measure cleanup effectiveness over time. The major design challenges that had to be met included providing oxygenation with minimum air emissions, effective mixing during reintroduction of lagoon sludges and soils into a suspended mixed liquor, and effective circulation (mixing) to distribute nutrients and dissolved oxygen throughout the biotreatment cell.

Several technologies (3) were considered for oxygenation, including fine bubble aeration and pure oxygen contacting. Dissolved pure oxygen (Table 1) provided the lowest air emissions. The Mixflo system (Figure 2), designed by Proxair Inc., was selected for the site by EPA, the FLTG, and ENSR Consulting and Engineering. Mixflo uses pure oxygen in a two-stage process. The system, with a maximum capacity of 25 tons of oxygen per day, is the largest oxygenation and sludge and soil mixing system in the world.

In the first stage, slurry pumped from the lagoon and pressurized in a pipeline was fed high-purity oxygen. The two-phase mixture flowed turbulently through the pipeline, substantially increasing oxygen solubility in the slurry under elevated pressure. In the second stage, the oxygen/slurry dispersion was reinjected into the lagoon using a liquid/liquid eductor (Figure 3) that mixed unoxygenated slurry with the oxygenated slurry and produced a fine bubble oxygen dispersion before dispersing the mixture throughout the lagoon.

The mixing of unoxygenated slurry with oxygenated slurry in the eductor before discharging the mixture reduced the dissolved oxygen concentration below atmospheric pressure saturation. Thus, dissolved oxygen did not come out of solution in the lagoon. The oxygen not dissolved in the pipeline contactor also was well distributed as fine bubbles with a low frequency of bubble coalescence in the lagoon. Further oxygen dissolution then occurred in the lagoon, minimizing air emissions and providing excellent (90 percent) oxygen dissolution efficiency. To ensure an effective circulation pattern in the lagoon biotreatment cell, nine 50,000-gallon-per-minute FLYGT banana mixers were placed on three rafts. The Mixflo system and the FLYGT mixers provided effective solutions to the engineering challenges. After completion of bioremediation, each biotreatment cell was subsequently filled with clean soil and planted in cover vegetation.

## Bioremediation Performance

In situ aerobic bioremediation met all sludge soil cleanup requirements (4, 5) for the lagoon. Using indicator contaminants (Table 2) as examples, residual arsenic had to be at or below 7 parts per million (ppm); benzene at or below 14 ppm; benzo(a)pyrene at or below 9 ppm; total polychlorinated biphenyls (PCBs) at or below 23 ppm; and vinyl chloride at or below 43 ppm. Actual concentrations of the indicator contaminants after bioremediation typically were 1 to 2 ppm arsenic, 0.5 to 10 ppm benzene, 1.8 to 10 ppm benzo(a)pyrene, 1 to 10 ppm PCBs, and 3 to 17 ppm vinyl chloride.

Ambient air monitoring during remediation (Table 3) revealed that air criteria concentrations to quantify maximum cumulative concentrations for each of 35 compounds of concern were also fully achieved. Finally, the direct costs (3) of the lagoon bioremediation (Table 4), including the field pilot demonstration, were $39 million. Total costs for bioremediation were $59 million, compared with the estimated $75 to $125 million, for incineration.

## Site Closure

A second bioremediation process (6), not presented here, was conducted at the site. The lagoon had contaminated the surrounding ground water. The ground-water bioremediation process was recently completed (January 1996). Full site closure with continued ground-water monitoring is nearly complete.

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# Aerated Lagoons

## A Case Study of the French Limited Superfund Site

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Acknowledgements

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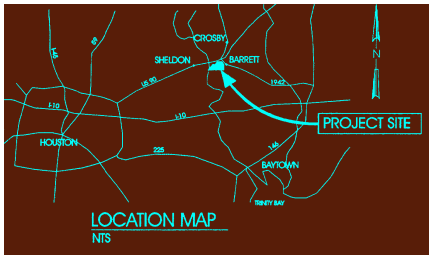
ARCO Chemical Company

## French Limited Waste Disposal Site

- Mid 1960 to 1971
- Petroleum and petrochemicals
- Incineration ROD in 1987 at estimated costs of $75–125 million
- ROD in late 1987 modified to permit in situ bioremediation

## Figure 1. French Limited Site Location



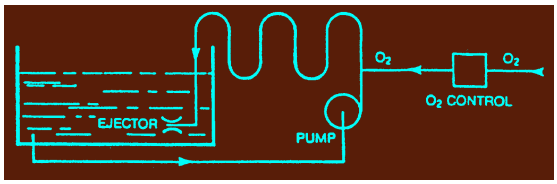

## Engineering Challenges in Lagoon Bioremediation

- Minimize air emissions
- Provide efficient shearing and introduction of sludge and soil into the lagoon's suspended mixed liquor
- Maintain mixing of suspended mixed liquor
- Provide efficient distribution of nutrients and oxygen

## Solutions to Engineering Challenges

- Pure oxygen dissolution using Mixflo
- Liquid/liquid eductor
- FLYGT banana mixers on rafts

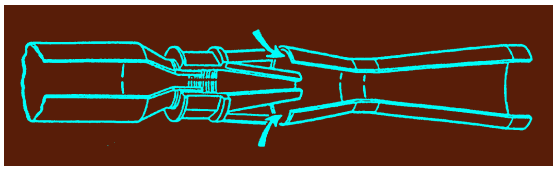
## Figure 2. Mixflo



## Table 1. Comparison of Mixflow and Fine Bubble Aeration

| | Mixflo | Fine Bubble |
|---|---|---|
| Oxygen transfer efficiency % | 90 | 14 |
| Gas volume, scfm | 112 | 3,418 |
| Off gas volume, scfm | 12 | 3,318 |

## Figure 3. Liquid/Liquid Eductor



## Table 2. Performance of Indicator Compounds

| | Cleanup Required PPM | Typical Residuals PPM |
|---|---|---|
| Arsenic | 7 | 1–2 |
| Benzene | 14 | 0.5–10 |
| Benzo(a)pyrene | 8 | 1.8–10 |
| Total PCBs | 23 | 1–10 |
| Vinyl Chloride | 43 | 3–17 |

## Table 3. Benzene Ambient Air Management ACC Ratios

| Subdivision | ACC* | Ratios** |
|---|---|---|
| | Cell E | Cell D/F |
| Riverdale | 0.2393 | 0.1872 |
| Rogge | 0.0597 | 0.0402 |
| Dreamland | 0.0368 | 0.0277 |

* Air Criteria Concentrations

** Requirement: ACC ratio must be less than 1.0 at end of 2 years.

## Table 4. Incineration and Bioremediation Costs

| | Incineration* $ Millions | Bioremediation $ Millions |
|---|---|---|
| General | 5 | 13** |
| Site Preparation | 7 | 7 |
| Remediation | 68 | 19 |
| Indirect Costs | 15 | 10 |
| Contingency | 30 | 5 |
| TOTALS | 125 | 54 |

* On site incineration

** Includes 10 million dollar cost for field pilot demonstration.

## Site Revegetation

# Oil-Contaminated Shorelines

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## Introduction

This case study is based on a field study conducted during the summer of 1994 by researchers from the U.S. Environmental Protection Agency's (EPA's) National Risk Management Research Laboratory and the University of Cincinnati, in cooperation with the Delaware Department of Natural Resources and Environmental Control (1).

Light crude oil was intentionally released onto plots to evaluate bioremediation. Past field studies involving bioremediation of oil-contaminated shores have concluded that bioremediation enhances the removal of crude oil several times more effectively than the intrinsic rate (2-9). Much skepticism remains in the field, however, because data from all of these investigations have been equivocal to some extent. The goals of this project were to quantify the effectiveness of natural attenuation due to levels of background nutrients already present in the Fowler Beach area of Delaware Bay; to demonstrate the effectiveness of biostimulation and/or bioaugmentation; to determine the extent of any resulting rate enhancement; and to provide guidelines that can be used by spill responders and on-scene coordinators for the effective bioremediation of oil-contaminated sandy shores. Biodegradation was tracked by gas chromatography/mass spectroscopy (GC/MS) analysis of selected components, and the measured concentrations were corrected for abiotic removal by hopane normalization. (Hopane is a nonbiodegradable compound that exists in all crude oils.) Five replicates of three treatments were evaluated: an oiled no-nutrient control, addition of water soluble nutrients, and addition of water soluble nutrients supplemented with a natural microbial inoculum from the site.

## Approach

Without full replication and random interspersion of treatments, it is impossible to ascribe statistically significant differences in the response variable(s) to the treatments. A randomized complete block design was used to assess treatment effects. Five areas (blocks) of beach were selected, each large enough to accommodate four experimental units or test plots. The blocks were positioned on the beach parallel to the shoreline. Three treatments were tested on oiled plots: a no-nutrient addition control, addition of water soluble nutrients (biostimulation), and addition of water soluble nutrients supplemented with a natural microbial inoculum from the site (bioaugmentation). A fourth treatment, an unoiled and untreated plot, served as a control for background biological measurements. The four treatments were randomized in each of the five blocks.

Previously weathered light crude oil from Nigeria (Bonny Light) was the source of crude oil. It was applied to the plots uniformly by spray nozzles connected to drums. Each plot received 36 gallons

of oil. Laboratory microcosms indicated that a concentration of 0.5 mg N/L and limited oxygen uptake and $CO_2$ production, whereas at concentrations greater than 2.5 mg N/L, maximum uptake was observed. Thus, the target nitrate-N was set at about 1.5 mg/L.

A lithium tracer experiment to determine how frequently fertilizer should be added to maintain the target nutrient level found that tracer diluted quickly as the plots became submerged by the incoming tides and waves. In fact, there was a direct correlation between plot submergence and the amount of tracer remaining in the bioremediation zone. Because the plots for the field study were positioned within the intertidal zone, nutrients had to be applied every day to maintain the desired 1.5 mg/L in the interstitial pore water.

The bioaugmentation treatment consisted of an inoculum of oil degraders isolated from the site, grown in batches on the same crude oil, and added back every week. The indigenous inoculum was grown for 2 weeks in two 55-gallon stainless steel drums. To allow weekly inoculation with fresh 2-week cultures, each drum was offset in time from the other by 1 week. The drums contained 40 gallons of seawater from Delaware Bay, the weathered Bonny Light crude oil (600 mL) as the sole carbon source, and the same nutrients used on the beach.

## Results

Nutrient Persistence. The control plots receiving only seawater with no nutrients had measurable concentrations of nitrate (mean of 0.82 mg/L), which were approximately half the 1.5 mg/L target level desired for maximum biodegradation. The concentrations in the nutrient and inoculum treated plots were substantially higher. The Fowler Beach area of Delaware Bay was close to farm land, where runoff could easily account for the high background levels found.

Physical Loss of Oil. To distinguish physical loss from biodegradative loss of oil, the concentration of hopane, a known nonbiodegradable biomarker in all crude oils, was quantified in each sand sample. Data from the three oiled treatments revealed a hopane half-life of 28 days. This was interpreted to represent physical loss of crude oil due to wave action and tidal inundation. A similar study of the temporal loss of total extractable organic material (EOM) from the plots revealed an EOM half-life of 21 days. The EOM first-order rate coefficient was significantly higher than the hopane disappearance rate. The difference in loss rates (and half-lives) between hopane and EOM was attributed to biodegradation because EOM includes both biodegradable and nonbiodegradable components. EOM, however, was not a sensitive enough indicator to discern treatment differences.

Results of Bioremediation. The bioremediation study revealed that, although substantial hydrocarbon biodegradation occurred in the untreated plots, statistically significant differences between treated and untreated plots were observed in the biodegradation rates of the hopane-normalized total alkane and total aromatic hydrocarbons. The rate enhancement was approximately two-fold for the alkanes and 50 percent for the aromatics. First-order rate constants for disappearance of individual hopane-normalized alkanes and polycyclic aromatic hydrocarbons (PAHs) were computed, and the patterns of loss were typical of biodegradation. As the number of alkyl-substituted groups increased on the aromatic ring structure, the rate of PAH disappearance decreased. This is known to be typical of biodegradation. In the field, the ratio of biodegradation rates of unsubstituted parent compounds and lower substituted compounds to the highest substituted

compound in a homologous series revealed strikingly close agreement with the same ratios computed from laboratory experiments (except for naphthalene and $C_1$-naphthalene, which are highly volatile). This signifies that the loss of hydrocarbons due to factors other than biodegradation (i.e., dissolution and volatilization) was negligible.

Significant differences were not observed between plots treated with nutrients alone and plots treated with nutrients and the indigenous inoculum. The high rate of oil biodegradation observed in the untreated plots was attributed to the relatively high background nitrogen concentrations that were measured at the site.

## Conclusions

Significant intrinsic biodegradation of petroleum hydrocarbons occurred naturally when sufficient nutrients already existed in the affected area. Statistically significant rate enhancement was demonstrated, even in the presence of an already high rate of natural attenuation, by supplementing natural nutrient levels with inorganic mineral nutrients; however, bioaugmentation did not significantly contribute to any further enhancement. Maintenance of a threshold concentration of about 2 mg nitrate-N/L interstitial pore water permits close to maximum hydrocarbon bioremediation. The incremental increase in biodegradation rate over the intrinsic rate (i.e., slightly greater than two-fold for the alkanes and 50 percent for the PAHs) might not have been high enough to warrant a recommendation to actively initiate a major, perhaps costly, bioremediation action in the event of a large crude oil spill in that area. Thus, the decision to apply nutrients should depend on the background concentrations available at the contaminated site, as well as the impact on ecological and health receptors.

The study showed that better hydrocarbon biodegradation takes place in the upper intertidal zone than in the lower intertidal zone due to the greater persistence of nutrients and highly aerobic conditions. Hopane was confirmed as a useful biomarker for tracking biodegradation success in the field.

For the first time, first-order biodegradation rate constants were developed from field data for the resolvable normal and branched alkanes and the important two- and three-ring PAH groups (and at least one four-ring PAH group) present in light crude oil. The relative biodegradation rates of homologous PAHs measured in the field were found to agree closely with those measured in the laboratory, thus corroborating the rates as being due to biodegradation and not physical washout or solubility differences.

## Lessons Learned

After a major spill has been beached, the first task is to measure the natural nutrient concentrations in that environment to determine if they are already high enough to sustain significant intrinsic biodegradation. Concentrations approaching 1.5 to 2.0 mg N/L in the interstitial pore water should support near-optimum hydrocarbon biodegradative activity. A determination should be made as to whether such nutrient levels are normal for the affected area for that time of the year. Oiled sandy

shorelines should only be treated with nutrients if concentrations are clearly limiting (i.e., well below 1 to 2 mg/L).

If the beach is treated with water-soluble nutrients applied by a spray irrigation system, they should be applied daily if the area gets completely submerged by tides and waves, even during neap tides. If the area is submerged only during spring tides, the intertidal coverage by water determines the frequency of nutrient addition. The Delaware study did not include evaluation of either oleophilic or slow release granular fertilizer for nutrient enhancement. For large expanses of contaminated shoreline or areas with difficult access and control (e.g., heavy wave action), oleophilic fertilizers may be more appropriate.

Degradation effectiveness should be monitored using specific analytes quantified by GC/MS and then only when analytes are normalized to a recalcitrant compound like hopane. Total petroleum hydrocarbon (TPH) measurements should not be used to monitor treatment effectiveness; they are too variable and too much affected by biogenic organic matter that has nothing to do with the hydrocarbons present.

Bioaugmentation is often unnecessary for accelerating biodegradation of an oil spill on a sandy beach. Quantifying the hydrocarbon degrader populations in the impact zone is useful, however. A treatment product should not be considered for use on a shoreline based only on results of bioremediation studies in a terrestrial environment. The abiotic loss mechanisms that act upon petroleum, nutrients, and microorganisms are substantially different on a beach than on dry land.

## Estimated Cost of Bioremediation

A rough estimate of the costs of an oil spill bioremediation project has been calculated, based on the Delaware study. The following assumptions have been made for this analysis:

- The spill has contaminated a 27-mile-wide intertidal zone of a long stretch of coarse sandy beach in an area that is easily accessible (unlike Prince William Sound), such as the Atlantic, Pacific, or Gulf coasts.
- Free product and heavy concentrations have already been removed by physical cleanup procedures.
- Pore water nutrient levels are well below the 1.5 to 2.0 mg N/L needed for optimum biodegradation effectiveness.
- Nutrients are added daily via a sprinkler or irrigation system to maximize bioremediation effectiveness.

Based on these assumptions, an estimated 2 person-years per kilometer (i.e., one supervisor and three laborers working full-time for approximately 3 months) would be required for cleanup. Assuming a supervisor salary (with benefits) of $100,000 per year and a laborer salary of $50,000 per year, the labor cost would be $62,500. Equipment needs are estimated to be about $75,000, chemicals $45,000, storage $2,500, and analytical needs $50,000. Total direct costs would thus

be approximately $235,000. Applying overhead at the rate of 100 percent yields a total cost of approximately $470,000 per kilometer of beach contaminated.

The above cost estimates are highly dependent on manpower for daily application of water-soluble fertilizer. If slow-release granular fertilizer is used (thus mitigating the need for daily application), and assuming target levels of nitrogen can be achieved for periods approaching a week, then the manpower and equipment needs will likely be significantly lower than those estimated above. Detailed economic analysis awaits data from further field evaluations.

## Protocol Development

As a result of the Oil Pollution Act of 1990 (OPA), EPA instituted a research program to develop an objective protocol assessing the bioremediation effectiveness and toxicity of commercial oil spill bioremediation agents. A tiered approach was developed in which a product is subjected first to a laboratory batch screening test and tested against a control for its ability to biodegrade crude oil (10, 11). An acute toxicity test is also performed to assess the product's ability to induce mortality in mysid shrimp species. The next tier involves further testing of the product compared with a control in a flow-through microcosm. The final tier consists of an actual field trial of the product. The laboratory screening test consists of shake flasks containing natural seawater, 5 g/L weathered Alaska North Slope crude oil, and the product. Two controls are set up: a no-nutrient, no-product control (i.e., natural seawater and weathered oil) and a nutrient control (natural seawater, weathered oil, and nitrate and phosphate salts as nutrients). Triplicate flasks are sacrificed at days 0, 7, and 28 to determine the extent of biodegradation of the crude oil components. Measurements are made by GC/MS. Alkane and aromatic hydrocarbon degraders are also measured by a most probable number technique (12). For a product to be deemed effective, it must demonstrate statistically significant removal of both alkane and aromatic hydrocarbons compared with the controls at the conclusion of the exposure period. EPA is currently attempting to refine the protocol by changing the natural seawater to a sterile artificial formulation and standardizing the microbial inoculum. Such refinements would make the test more reproducible. The inoculum would be used as a positive control for living products, whereas it would serve as the actual biodegrading population in the case of a non-living product. Products that successfully demonstrate the ability to biodegrade both the alkane and aromatic components of weathered crude oil are then placed on the National Contingency Plan product schedule, which makes them eligible for use in an oil spill.

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# Oil-Contaminated Shorelines

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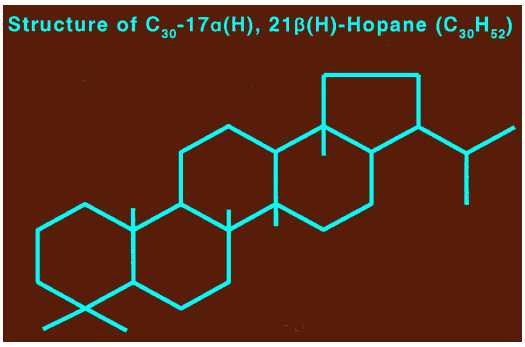
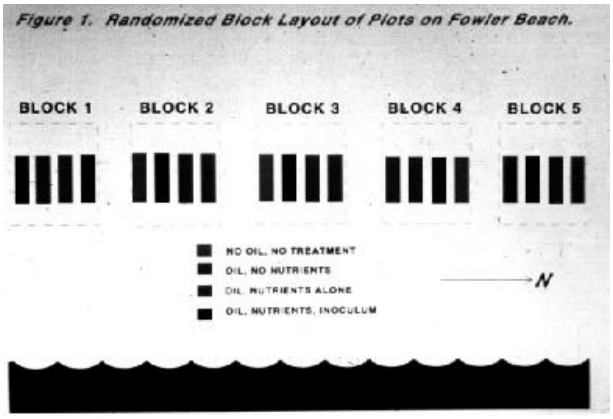
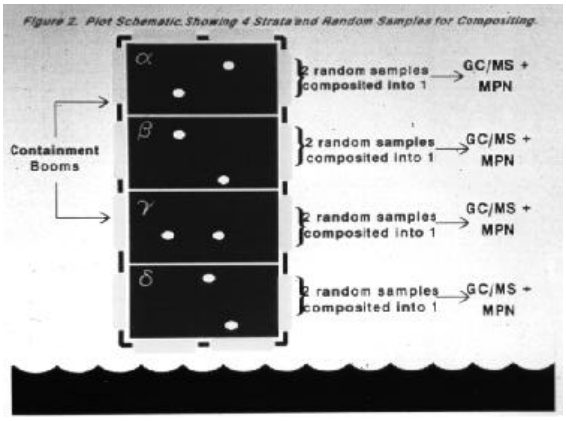
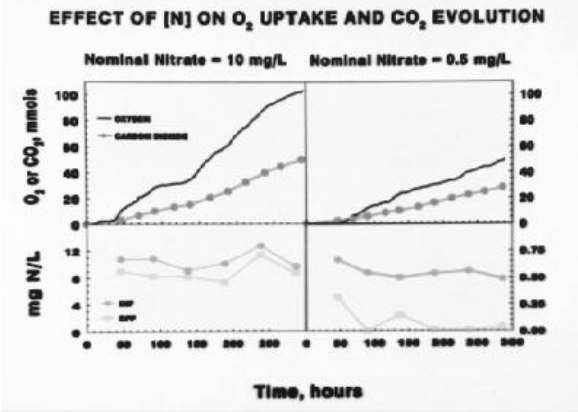
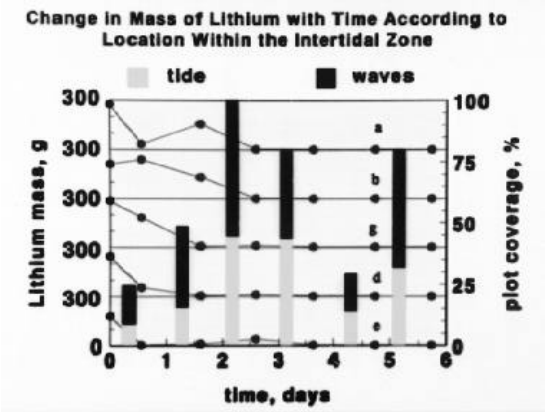
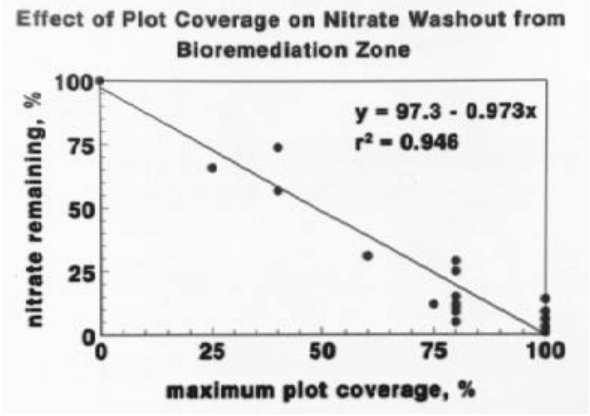


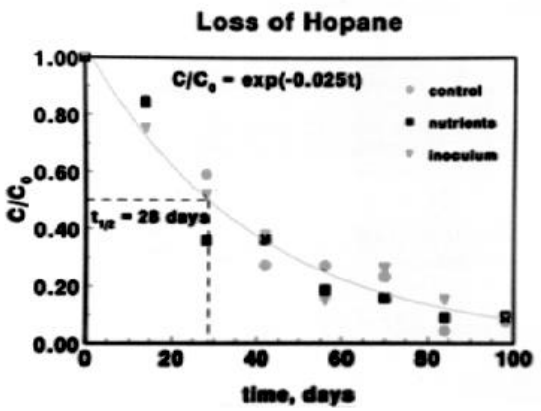



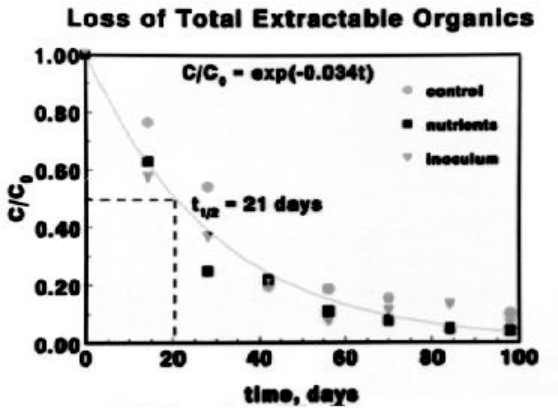



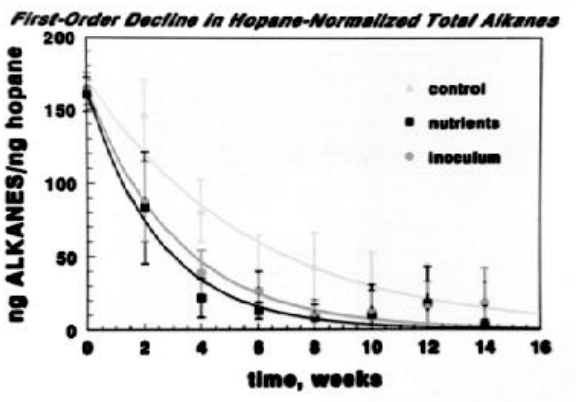


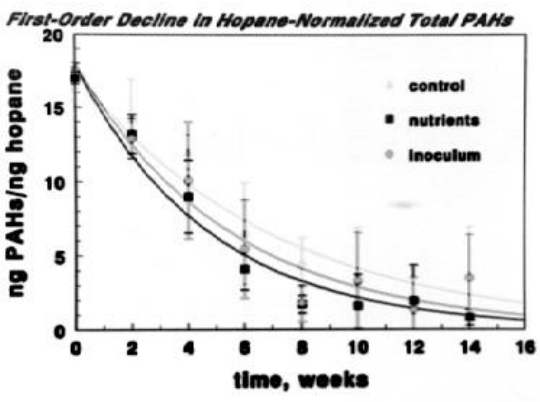

Average and Standard Deviation of Nitrate-N Concentrations for the 3 Treatments

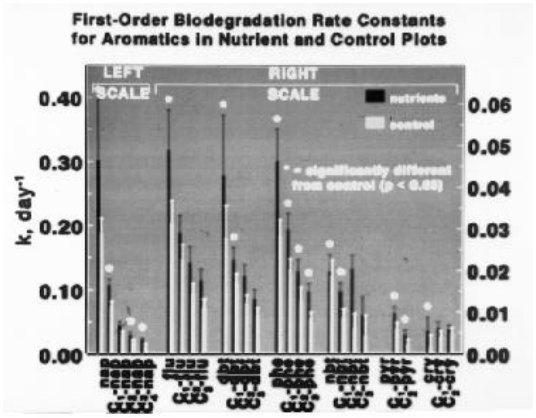
| Treatment | Avg., mg/L | SD, mg/L |
|---|---|---|
| Control | 0.8 | 0.3 |
| Nutrients | 6.4 | 2.7 |
| Inoculum | 3.5 | 1.7 |

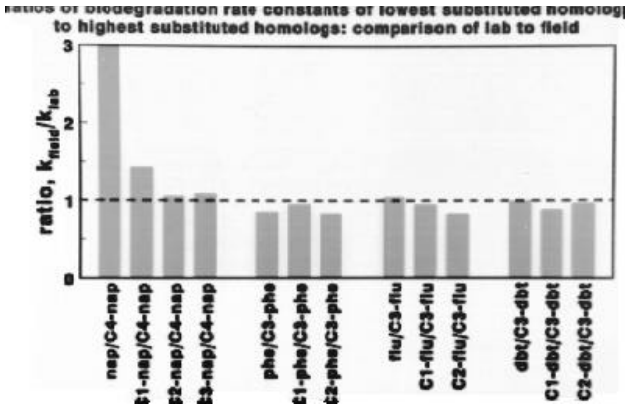



First-Order Biodegradation Rate Constants
for Aromatics in Nutrient and Control Plots
LEFT
SCALE
RIGHT
SCALE
nutrients
control
* = significantly different
from control (p < 0.05)
k, day-1
0.40
0.30
0.20
0.10
0.00
0.06
0.05
0.04
0.03
0.02
0.01
0.00


to highest substituted homologs: comparison of lab to field
ratio, k_field/k_lab
3
2
1
0
nap/C4-nap
C1-nap/C4-nap
C2-nap/C4-nap
C3-nap/C4-nap
phe/C3-phe
C1-phe/C3-phe
C2-phe/C3-phe
flu/C3-flu
C1-flu/C3-flu
C2-flu/C3-flu
dbt/C3-dbt
C1-dbt/C3-dbt
C2-dbt/C3-dbt

# Land Treatment

Daniel Pope
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## Definition of Land Treatment

Land treatment involves use of natural biological, chemical and physical processes in the soil to transform organic contaminants of concern. Biological activity apparently accounts for most of the transformation of organic contaminants in soil, although physical and chemical mechanisms may provide significant loss pathways for some compounds under some conditions. Degradation by ultraviolet light may serve as a loss pathway for certain hydrophobic compounds at the soil surface. Volatilization of some low molecular weight compounds also takes place at the soil surface and provides a significant loss pathway for such compounds. Certain chemical reactions such as hydrolysis can play an important role in transformation of some compounds. Humification, the addition of compounds to the humic materials in soil, can be an important route of transformation for some polynuclear aromatic compounds. The relative importance of these processes varies widely for different compounds under different circumstances. The land treatment concept serves as the basis for design and operation of soil bioremediation technologies at a large number of waste sites requiring cleanup.

## In Situ and Ex Situ Land Treatment

Land treatment techniques for bioremediation purposes most often are used for treatment of contaminated soil, but certain petroleum waste sludges have long been applied to soil for treatment. Ideally, the contaminated soil can be treated in place (in situ). Often, however, the soil must be excavated and moved to a location better suited to control of the land treatment process (ex situ).

In situ land treatment is limited by the depth of soil that can be effectively treated. In many soils, effective oxygen diffusion sufficient for desirable rates of bioremediation extends to a range of only a few inches to about 12 inches into the soil, although depths of 2 feet and greater have been effectively treated in some cases.

Ex situ treatment generally involves applications of lifts of contaminated soil to a prepared bed reactor. This reactor is usually lined with clay and/or plastic liners, provided with irrigation, drainage, and soil water monitoring systems, and surrounded with a berm. The lifts of contaminated soil are usually placed on a bed of relatively porous, noncontaminated soil.

The land treatment process may be severely limited in clayey soils, especially in areas of high rainfall. This limitation is primarily related to oxygen transfer limitations and substrate availability to the microorganisms. Clayey soils should be applied in shallower lifts than sandy soils. Tilth ("workability" of the soil) can often be improved by adding bulking agents.

After application to the land treatment unit, each lift should be tilled at intervals to enhance oxygen infiltration and contaminant mixing with the microorganisms. The soil should be near the lower end of the recommended soil moisture percentage range before tilling. Tilling very wet or saturated soil tends to destroy the soil structure, reduce oxygen and water intake, and cause reduced microbial activity. Tilling more than is necessary for enhanced oxygen infiltration and contaminant mixing may be counterproductive because tilling tends to destroy the soil structure and compact soil below the tilling zone.

Timing of application of succeeding lifts should be based on reduction to defined levels of particular compounds or categories of compounds in the preceding lift. For instance, the goal might be to reduce total petroleum hydrocarbons (TPH) to less than a regulatory or risk- calculated limit in the current lift before application of a new lift. Once desired target levels of compounds of interest are established, data obtained from land treatment unit (LTU) monitoring activities can be statistically analyzed to determine whether and when desired levels are reached and the LTU is ready for application of another lift.

## Nutrients, Carbon Sources, and Other Additives

Fertilizers can be used to supply nutrients, and wood chips, sawdust, or straw can supply carbon. Various animal manures are often used to supply both carbon sources and nutrients. High organic levels in manures, wood chips, and the other organic amendments increase sorptive properties of soil, thereby decreasing mobility of organic contaminants and possibly decreasing availability to the microorganisms. Organic amendments will also increase the water-holding capacity of soil, which can be desirable in sandy soils but can cause difficulty when land treatment is conducted in areas of high rainfall and poor drainage.

Agricultural fertilizer is usually supplied in prilled or pelleted form (the fertilizer compounds formed into pellets with a clay binder) suitable for easy application over large areas. Completely water-soluble fertilizers can be applied through irrigation systems, allowing application rates to be closely controlled, applications to be made as often as irrigation water is applied, and immediate availability to the microorganisms.

## Bioaugmentation

Microorganism cultures are often sold for addition to bioremediation units. Two factors limit use of these added microbial cultures in LTUs: 1) nonindigenous microorganisms rarely compete well enough with indigenous populations to develop and sustain useful population levels, and 2) most soils with long-term exposure to biodegradable wastes have indigenous microorganisms that are effective degraders if the LTU is managed properly.

Certain soil factors may interfere with microbiological activity in the LTU soil. High salt levels, indicated by high electrical conductivity (EC) readings, may reduce or stop useful microbiological activity. If levels are too high, it may be necessary to leach the soil with water to remove excess salts before biodegradation can occur. High levels of sodium may be detrimental to soil structure.

## Soil Moisture Control

Historically, it has been recommended that soil moisture be maintained at 40 to 70 percent of field capacity; however, recent experience indicates that 70 to 80 percent of field capacity may be optimum. A soil is at field capacity when soil micropores are filled with water and soil macropores are filled with air. This condition allows soil microorganisms to get air and water, both of which are necessary for aerobic biodegradation to occur. Maintaining soil at somewhat less than 100 percent of field capacity allows more rapid movement of air into the soil, thus facilitating aerobic metabolism without seriously reducing the supply of water to microorganisms. If soils are allowed to dry excessively, microbial activity can be inhibited or stopped; if the wilting point is reached, cells may lyse or rupture. Continuous maintenance of soil moisture at adequate levels is of utmost importance. Either too little or too much soil moisture is deleterious to microbial activity. Surface drainage of the LTU can be critical in high rainfall areas. If soil is saturated more than an hour or two, aerobic microbial action is reduced.

Underdrainage is generally provided by a sand layer or a geotextile/drainage net layer under the LTU. The system should be designed so that excess water quickly drains away and thus microbial activity is not inhibited. The interface between the lift and the drainage layer underneath should be composed of well-graded materials so that the transition from the (usually) relatively fine soil texture of the lift to the relatively coarse texture of the drainage layer is gradual rather than sudden. Grading of the materials reduces the tendency for the soil lift to become saturated before drainage occurs, which inhibits aerobic biological activity.

## Types and Concentrations of Contaminants Remediable by Land Treatment

The types of contaminants most commonly treated in LTUs are petroleum compounds and organic wood preservatives. Historically, petroleum refineries have used land treatment to dispose of waste sludges. Although waste petroleum sludges currently are not often applied to soil for treatment, the technology has been applied to remediation of soil contaminated with many types of petroleum products, including fuel, lubricating oil, and used petroleum products. Land treatment has historically been used to remediate contaminated process waters from wood preserving operations. This technology currently is not used for this purpose but is currently used to remediate soil contaminated with wood preserving wastes.

Other applications for land treatment technology include remediation of soil contaminated with coal tar wastes, pesticides, and explosives. Since coal tar wastes are similar to creosote wastes (wood preserving creosote is made from coal tar), such wastes are considered amenable to land treatment. Land treatment appears to be potentially useful for certain pesticides, but the evidence for applicability of this technology to explosives-contaminated soil is inconclusive.

## Levels of Contamination Susceptible to Land Treatment

The levels of petroleum product contamination amenable to land treatment vary by waste type and site conditions. In many cases, soils with higher levels of contaminants than are recommended for

land treatment can be mixed with less contaminated soils to bring contamination levels down to recommended starting levels for treatment. Levels of petroleum product contamination as high as 25 percent by weight of soil have been reported as treatable, although experience indicates that levels 5 to 8 percent by weight or less are more readily treated.

Soils contaminated with 15,000 to 20,000 mg/kg dry weight creosote wastes have been treated in soil systems, although more usual starting levels are in the 5,000 to 10,000 mg/kg range. Pentachlorophenol wastes are rarely treated at more than 1,000 mg/kg starting levels since pentachlorophenol is quite toxic to microorganisms at the higher levels.

The final levels attainable also vary by waste and site conditions. Generally, once total contaminant levels are below 50 to 200 mg/kg polynuclear aromatic hydrocarbons, remediation by land treatment is slow, and further treatment by conventional land treatment techniques may be ineffective. For instance, land treatment of creosote wastes is generally considered successful if total carcinogenic polynuclear aromatic hydrocarbons are reduced to below 50 to 100 mg/kg, and specific components are reduced to their "land ban" levels (for instance, pyrene to 7 mg/kg). Laboratory treatability studies may be used to assess the "best case" potential for final contaminant levels, with the assumption that actual final levels in the field would rarely if ever be lower than those found in laboratory study.

Costs for land treatment are estimated at between $20 to $200 per cubic yard.

# Land Treatment

Daniel Pope
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## Land Treatment

Biological, chemical, physical processes transform contaminants

## Degradation by Biological Activity

- Most transformation of organic contaminants
- Physical, chemical mechanisms also involved

## Degradation by Ultraviolet Light

- Soil surface
- Higher PAHs

## Volatilization – Low Molecular Weight Compounds

- BTEX
- Naphthalene
- Methyl naphthalenes

## Hydrolysis – Pesticides

- Amides
- Triazines
- Carbamates
- Thiocarbamates
- Nitriles
- Esters
- Phenylureas

## Humification

- Polymerization of contaminants
- PAHs known to humify

## Know Thy Waste

Relative importance of processes varies widely for different compounds under different circumstances

## Compounds Amenable to Land Treatment – PAHs

- 2-ring PAHs – readily degraded, volatile, leachable
- 3-ring PAHS – degradable, leachable
- 4-ring PAHS – fairly degradable, leachable
- 5–6-ring PAHs – difficult to degrade

## Compounds Amenable to Land Treatment – Phenols

- Penta & Tetrachlorophenol
  - Difficult over 1,000 ppm
- Other phenolics

## Compounds Amenable to Land Treatment – Hydrocarbons

- Aliphatics 1–8 C chains
  - Degradable
  - Volatile

## Compounds Amenable to Land Treatment – Hydrocarbons

- Most 12–15+ C chains
  - Slower degradation
  - Relatively immobile
  - Relatively nontoxic

## Compounds Amenable to Land Treatment – BTEX

- Degradable
- Volatile

## Compounds Amenable to Land Treatment

- Energetics – more often composted
- Phthalates
- Pesticides

## Bioremediation— What Is It?

- Two fundamental aspects of bioremediation . . .
- Developing large populations of microorganisms that can transform pollutants
- Bringing microorganisms into intimate contact with pollutants

## Land Treatment Technology

- Contaminated soil
- Sludge application to soil

## In Situ – Ex Situ Land Treatment

- The issue is control
- Control of runoff, leachate, volatiles

## In Situ – Practical Soil Depth

- Based on effective oxygen diffusion
- Bioventing for greater depths

## In Situ

- Treat surface soil, remove
- Treat surface soil, deep till

## Semi In Situ

- Remove soil to depth
- Add lifts back to excavation for treatment

## Tillage Depth

- Most tractor-mounted tilling devices till down to one foot
- Large tractors, specialized equipment till to three feet or more
- Large augers move soil from 50-100 feet to surface, but practicality not fully shown

## Ex Situ

- Application of lifts of contaminated soil to prepared-bed reactor
- Clay and/or plastic liners
- Bed of porous soil
- Irrigation, drainage, and soil water monitoring systems
- Berm

## Land Treatment – Lift Depth

- Generally limited to 6–24 inches of soil
- Usually 12 inches or less lift depth
- Refinery LTU 36 inches or more

## Soil Type

- Limited in heavy clay soils, especially in high rainfall areas
- Oxygen transfer limitations
- Substrate availability

## Soil Type – Working With Heavy Soils

- Shallow lifts for easier tilling, better diffusion
- Improve tilth with bulking agents

## Improving Tilth – Bulking Agents

- Organic matter (sawdust, compost, manures, etc.)
- Add gypsum if soil has high sodium content

## Preparing Soil for Application

- Screen to remove debris greater than 1 in. diameter
- Remove large debris that may adsorb waste compounds

## Tilling

- Enhances oxygen infiltration
- Mixes contaminants with microorganisms
- Disperses contaminants

## Tilling

- Lower end of soil moisture percentage range before tilling
- Tilling very wet or saturated soil tends to destroy soil structure, reduce microbial activity
- Wait 24 hours after irrigation or a significant rainfall event

## Tilling Schedule

- Compromise of several antagonistic factors
- Loosens soil for oxygen access
- Destroys soil structure
- Dries soil
- Mixes contaminants and bugs
- Equipment compacts soil

## Tilling – Mixing

- Mostly along line of travel
- Till in varying directions

## Tilling Equipment

- Rotary tiller for tilling, mixing purposes
- Disk harrow often used, may not mix soil well
- Subsoil plow, chisel plow to break up zone of compaction

## Tilling

- Subsequent lifts tilled into top 2 in. or 3 in. of previous lift
- To mix populations of well acclimated microorganisms
- Avoids sudden transition in permeabilities if different soil types being remediated

## Lift Application Timing

- Based on reduction to defined levels of particular compounds or categories of compounds
- Usually more detailed sampling to determine finish

## Nutrients, Carbon Sources, and Other Additives

## Carbonaceous (Organic) Amendments

- Animal manures
- Wood chips, sawdust
- Straw, hay

## Carbonaceous Amendments

- Supply carbon and some nutrients
- Act as bulking agent, adsorbent

## Carbonaceous Adsorbents

- Slow migration
- May sequester contaminants
- Increase permeability—Increased oxygen, water flux
- Increase oxygen demand due to microbes breaking down
- Increase water holding capacity

## Carbonaceous Amendments—Application Rates

- Must be balanced with nutrients
- 3–4% by weight of soil

## Carbonaceous Amendments

- Manures often mixed with bedding—straw, sawdust, rice hulls
- Bedding acts as bulking agent, but also has a nutrient demand

## Carbonaceous Amendments

- Should have moderately small particle size
- Thoroughly mixed with soil

## Fertilizers

- Can cause pH to drop
- Acid forming equivalent indicated on bag

## Fertilizers – Soluble Forms

- Can be applied through irrigation systems
- Application rates may be closely controlled
- Applications can easily be made as often as irrigation water is applied
- Immediately available to microorganisms
- Equipment meters concentrated nutrient solutions into irrigation system on demand

## Soil Nutrient Levels

- Nutrient requirements not thoroughly studied
- Detailed information not available to indicate optimal levels
- Difficult to show response in field

## Soil Nutrient Levels

Desired levels based on concentration in soil, or concentration ratio of several nutrients

## Micronutrients

- Carbonaceous amendments may contain some micronutrients
- Trace amounts in many packaged inorganic fertilizers
- Commercially available as micronutrient blends
- Apply specific micronutrients only if treatability studies show response

## Proprietary Micronutrients

- Usually expensive compared with horticultural fertilizer sources
- Generally easily supplied with readily available horticultural fertilizers

## Complex Nutrients

- Vitamins, growth factors
- Need easily shown in lab culture, with defined media
- Difficult to show effectiveness in field

## Bioaugmentation

- Indigenous microorganisms isolated, cultured
- Nonindigenous microorganisms
- Genetically engineered microorganisms

## Bioaugmentation

- Nonindigenous microbes rarely compete well enough to develop, sustain useful population
- Most soils with long-term exposure to biodegradable wastes have indigenous microorganisms that are effective degraders given proper management of the LTU
- Little data from well-designed experiments to show efficacy
- Perhaps more useful as understanding increases

## Soil Moisture Control

- 40–80% of field capacity
- Usually at high end of range

## Field Capacity

- Soil micropores filled with water
- Soil macropores filled with air
- Microorganisms get air and water

## Soil Moisture

Maintaining 40–80% of FC allows more rapid movement of air into soil, facilitating aerobic metabolism without seriously reducing supply of water to microorganisms

## Soil Moisture

- Some evidence that continuous maintenance at high levels better
- Some evidence that low end of range good for some compounds
- Requires careful management to maintain any given level

## Soil Moisture

- If soils dry excessively, microbial activity seriously inhibited, stopped
- Maintenance at proper level is not trivial

## Measuring Soil Moisture

- Gravimetric—simple, accurate, slow
- Tensiometer—simple, fairly accurate for many soils
- Gypsum blocks—good for undisturbed soil
- Capacitance effect—accuracy questionable
- Neutron probe—accurate, but uses radioactive material, expensive eqipment

## Surface Drainage

- Critical in high rainfall areas
- Saturation greater than one hour greatly reduces microbial action
- Surface should be sloped 0.5–1.0%
- Greater slopes—erosion hazard
- Design to allow collection, return of eroded soil

## Internal Drainage

- Sand/gravel layer
- Geotextile/drainage net layer

## Internal Drainage

Initial lifts usually placed on bed of sand, other porous soil, which causes a perched water table to develop

## Perched Water Table

- Lift takes up water until field capacity achieved
- Then begins to drain excess water
- Lower part of lift layer may remain overly wet

## Internal Drainage

- The interface between lift & drainage layer should have well-graded materials
- The psoil particle size transition from lift to drainage layer should be gradual
- Water movement through interface enhanced with gradual transition

## Internal Drainage

- Good internal drainage reduces tendency for soil lift to become saturated
- Interface may be graded by tilling lift into top of drainage layer

## LTU Leachate and Runoff

- Recycled onto LTU
  - With or without treatment
- Treated (biological or adsorption) and discharged

## Disposal of Treated Soil

- Replace in excavation
- Disposal cell

## LT as Part of a Treatment Train

High organics (bulking agents, contaminants) in soil may inhibit subsequent solidification/stabilization for metals treatment

## LT Disadvantages

- Slow—takes a long time for treatment
- High contaminant concentrations may be hard to treat
- Low contaminant concentrations may not show significant reduction
- Final levels may not be achievable depending on the requirements
- Space requirements are high
- Volatiles/dust/leachate control may be difficult

## LT Costs

- Earthmoving—$1–2+ per yard
- Containment—berm
- Monitoring—usually major part of expense
- Operations
- Volatiles control can be very expensive

# Land Treatment Unit Case Study: Champion International Superfund Site

Daniel Pope
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## Introduction

The Champion International Superfund Site at Libby, Montana (referred to as the "Libby Site"), is an operating lumber mill where wood preserving operations using creosote and pentachlorophenol (PCP) were conducted from 1946 to 1969. Soil, sediments, and ground water at the site were contaminated with creosote and PCP wood treating solutions and wastes.

Champion International uses three biological processes for environmental remediation at the Libby site: 1) a prepared-bed, lined land treatment unit (LTU) for treatment of excavated soil; 2) an abovegrade, fixed-film bioreactor for treatment of extracted ground water, and 3) an oxygen and nutrient enhanced bioremediation system for in situ treatment of the upper aquifer. As part of the U.S. Environmental Protection Agency's (EPA's) Bioremediation Field Initiative, a team consisting of Utah State University, EPA's National Risk Management Research Laboratory (Ada, Oklahoma), and Dynamac Corporation conducted a performance evaluation of bioremediation systems used by Champion International at the Libby site.

Objectives of the LTU performance evaluation were to:

- Describe and summarize previous and current remediation activities.
- Develop an evaluation plan, including statistical requirements for the number, timing, and location of samples.
- Perform a laboratory evaluation of the potential for soil microorganisms to bioremediate soil contaminants under site conditions of temperature and soil moisture.
- Conduct a comprehensive field evaluation to assess treatment effectiveness, treatment rate, and detoxification of contaminated soil in the LTU.

## SUMMARY OF REMEDIATION AND MONITORING ACTIVITIES CONDUCTED BY CHAMPION INTERNATIONAL

When full-scale soil remediation began, approximately 75,000 cubic yards of contaminated soil and sediment at the site was excavated down to the water table from the three primary source areas at

the site: a former tank farm, an unlined butt-dip area, and an unlined waste pit. Rocks larger than 1 inch in diameter were removed from the excavated material and used to construct subgrade infiltration galleries upgradient from the waste pit area where substantial residual contamination remained in the subsurface. Effluent from the abovegrade fixed-film bioreactor was applied to the infiltration galleries to stimulate biodegradation of any contamination adhering to the rocks, and to allow infiltration of treated water from the bioreactor back into the subsurface to stimulate subsurface bioremediation. The excavated soil remaining after rocks were removed (about 45,000 cubic yards) was placed into the waste pit excavation, where it is pretreated by land treatment (tilling, irrigation, nutrient addition) prior to placement in the LTU.
The geometric means of initial soil concentrations from all three contaminated sites are as follows:

| | |
|---|---|
| Total carcinogenic polynuclear aromatic hydrocarbons (TCPAHs) | 189.0 mg/kg |
| PCP | 29.0 mg/kg |
| Note: Maximum concentrations greater than geometric mean by factors of 6 to 90. | |

Target remediation levels as specified in the record of decision for soil treated in the two LTUs are as follows:

| | |
|---|---|
| Naphthalene | 8.0 mg/kg |
| Phenanthrene | 8.0 mg/kg |
| Pyrene | 7.3 mg/kg |
| TCPAHs | 88.0 mg/kg |
| PCP | 37.0 mg/kg |

## LTU Cell Design

The lined, prepared-bed LTU is composed of two cells with a total area inside the outer berm perimeter of both cells of 2 acres. The berms allow containment, treatment, and ultimate disposal of additional contaminated soils, if required.

The bottom of the LTU cells are sloped to a central gravel drain (2 percent slope), which is sloped to a collection sump (1 percent slope) so drainage water can be removed as needed. Leachate is removed from the collection sump by means of an automated pump and piping system. Beneath the drainage system is a geotextile filter underlain by a high-density polyethylene liner, which in turn is supported by a base layer of compacted soil.

## Monitoring

Monitoring, conducted by Champion International, involves periodic collection and analysis of leachate, soil, ground-water, and air samples both inside and outside treatment cells during operation and closure periods.

Leachate monitoring involves sampling from LTU sumps on a quarterly basis and during rainfall events. Monitoring of LTU soil involves operational, confirmation, and compliance sampling. Operational sampling consists of onsite laboratory analysis of contaminants during lift treatment as well as assessing nutrient and soil moisture requirements. After operational samples indicate contaminant target levels have been met in a lift, confirmation samples are analyzed by an offsite laboratory to confirm attainment of contaminant target levels. Compliance samples may include previously collected confirmation samples or additional samples, if required, to fully demonstrate that target levels have been reached.

Ground-water monitoring includes six wells (four downgradient and two upgradient). Monitoring of the ground-water wells around the LTU is performed semiannually.

Ambient air is monitored for polynuclear aromatic hydrocarbons (PAHs) and PCP by an upwind and downwind station to characterize concentrations due to unit operations and to protect workers' health. Moisture is applied to LTU for dust control during operation.

## Land Treatment Operations

Contaminated soils are placed in the LTU cells in 6- to 12-inch lifts for treatment during the summer. Water is applied to the LTU to maintain adequate moisture levels (approximately 40 to 70 percent of field capacity) in the treatment zone and for dust control.

Nutrients (nitrogen and phosphorus) are added to the LTU dissolved in irrigation water or as solid fertilizers applied directly to the LTU. The nutrient requirement selected was a carbon:nitrogen ratio in the soils of approximately 12-30:1 and a nitrogen:phosphorus ratio of approximately 10:1. Nutrients are added as frequently as every other day, depending on soil moisture and nutrient needs.

The LTU is tilled at least weekly, using a tractor-mounted rototiller. Tilling is suspended if the LTU contains ponded water.

# LAND TREATMENT PERFORMANCE EVALUATION

Introduction . Utah State University conducted a field and laboratory performance evaluation of the LTUs. During the performance evaluation, soil in the two LTU cells was sampled at several depths over a 2-year period. Concentrations of the 16 priority pollutant PAH compounds and PCP were determined. The performance evaluation was based on: 1) the changes in concentration of soil contaminants over time to evaluate the effectiveness of remediation, 2) changes in the concentration of soil contaminants in a lift after application of additional lifts to evaluate downward migration of

contaminants, 3) changes in soil toxicity as determined by bioassays to evaluate toxicity reduction, and 4) a laboratory study of chemical, physical, and biological processes affecting soil contaminant concentrations to determine the mechanisms responsible for remediation.

Results. Soil sampling indicated that land treatment was able to meet the treatment goals for reduction of contaminant concentrations in the contaminated soil, and there was no evidence of downward migration of target PAH compounds and PCP through the LTUs. In addition, pyrene, PCP, and TCPAH concentrations continued to decrease with time after placement of lifts in both LTUs.

## Laboratory Assessment

Two laboratory evaluations of soil microbial metabolic potential were conducted to add information concerning biodegradation versus physical/chemical mechanisms for disappearance of phenanthrene and PCP, e.g., volatilization and mineralization. The first laboratory evaluation was designed to determine rates of biological mineralization and volatilization as affected by contaminant concentration, temperature, and soil moisture. The second evaluation was designed to provide information addressing a mass balance of radiolabeled carbon that was used to evaluate humification of the two chemicals.

Results. The laboratory studies demonstrated that both PCP and phenanthrene were partially metabolized to carbon dioxide in the contaminated soil matrix at the site. Both were also mineralized with the indigenous soil microorganisms at temperatures and moisture levels representative of site conditions. It appears that significant volatilization of PCP or phenanthrene at the full-scale site is unlikely. The laboratory evaluation corroborates the interpretation that decreases in target chemical concentrations are due to biological processes rather than physical/ chemical processes.

Laboratory evaluations demonstrated that not all of the parent compounds were mineralized within soil in the laboratory microcosms. Rather, carbon in the parent compounds also became distributed among air, solvent extract, and soil-bound phases. A major pathway for $^{14}C$ for phenanthrene and PCP was humification (binding to soil), such that the compound is not solvent-extractable from soil. A significant fraction of $^{14}C$ was solvent-extractable from the soil, either in the form of the parent compound or intermediates. Mineralization represented the third most important fraction for $^{14}C$ in this laboratory study. Volatilization of phenanthrene and PCP over the 45-day evaluation was less than 1 percent and therefore not considered to be an important route of compound removal from soil.

Soil Toxicity Testing. The Microtox assay was used to measure general physiological toxicity, and the Ames assay was used to measure mutagenicity of soil solvent extracts. Toxicity assays indicated that soil within the LTUs was detoxified to background soil levels. Average Microtox toxicity decreased from an $EC_{50}$ value of 6.6 initially to nontoxic (greater than 100) for all soil samples tested. The initial mutagenic potential of soil applied to LTU 1 was considered to be approximately 330 revertants per gram of soil (weighted activity). Results of mutagenicity testing for Lift 1 sampled 3 months after application and biological treatment indicated detoxification to soil background levels (less than 150 revertants per gram of soil).

## Conclusions

The field performance evaluation of two full-scale LTUs at the Libby, Montana, Superfund site indicated that enhanced land treatment of soil contaminated with wood preservative chemicals was effective and resulted in the treated soil meeting target remediation levels for target contaminants as specified in the record of decision. Downward migration of target chemicals as a result of the application of additional lifts was not observed. The contaminated soil was detoxified to background levels as a result of the treatment, based on the results of toxicity and mutagenicity assays.

In summary, results of the field performance of the LTUs at the Champion International Superfund site in Libby, Montana, indicated that bioremediation using indigenous microorganisms was the process that accomplished soil treatment. Soil treatment included degradation of target PAH compounds and PCP in contaminated soil to target remediation levels and detoxification of soil.

# Land Treatment Case Study: Libby Superfund Site

Daniel Pope
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Ada, OK

## Land Treatment Case Study: Champion International Superfund Site

- Currently an operating lumber mill
- Creosote/pentachlorophenol wood preserving from 1946 to 1969
- Soil, sediments, & ground water contaminated with creosote and PCP wood treating solutions, wastes

## Biological Processes For Remediation

- Prepared-bed, lined land treatment unit (LTU) for soil
- Above grade, fixed-film bioreactor for extracted GW
- Oxygen/nutrient enhanced bioremediation for in situ treatment of the upper aquifer

## U.S. EPA Bioremediation Field Initiative Performance Evaluation

- Utah State University
- Dynamac Corporation
- NRMRL Ada Division (RSKERL)
- Champion International

## LTU Performance Evaluation Objectives

- Document remediation activities
- Laboratory evaluation of bioremediation
- Field evaluation: treatment effectiveness and rate, detoxification of soil

## Remediation/Monitoring Activities Summary

As conducted by Champion International

## Full-Scale Soil Remediation

- 75,000 yards contaminated soil/sediment excavated
- Rocks >1 inch diameter removed
- Remaining soil (~45,000 yards) replaced in excavation
- Pretreated by "in situ" LT prior to placement in LTU

## LTU Cell Design

- Lined, prepared-bed land treatment unit
- Two cells ~1.0 acre each

## Monitoring (Champion International)

- LTU soil
- LTU leachate
- Ground water (6 wells)
- LTU air emissions

## Land Treatment Operations

- 6- to 12-inch lifts
- Water ~40 to 70% FC
- Weekly tilling
- Discontinued during winter

## Nutrients

- Applied in irrigation water or as solids
- C:N ratio 12-30:1
- N:P ratio 10:1
- Based on TOC, TKN, total phosphorus

## LTU Performance Evaluation Utah State

- LTU cells sampled over two-year period
- Concentrations of 16 priority pollutant PAHs and PCP

## Performance Evaluation: Contaminant Concentrations

- Contaminant concentration changes over time
- Concentration changes in a lift after application of additional lifts

## Performance Evaluation: Toxicity Reduction

- Microtox assay – general physiological toxicity
- Ames assay – mutagenicity

## Performance Evaluation: Contaminant Fate

Lab studies of chemical, physical, and biological processes to determine mechanisms responsible for remediation

## Field Evaluation Results

- Contaminant reduction goals met
- No evidence of downward migration of PAHs, PCP
- Pyrene, PCP, TCPAH, decreased after lifts covered in both LTUs

## Laboratory Study Objectives

Determine fate of $^{14}C$-phenanthrene and $^{14}C$-PCP in LTU soil, as affected by soil moisture, temperature

## Laboratory Study Results

PCP, phenanthrene partially metabolized with indigenous soil microorganisms at temperatures and moisture levels representative of site conditions

## Laboratory Study Results

Significant volatilization of PCP or phenanthrene in lab study did not occur

## Laboratory Study Results

- Not all of parent compounds were mineralized within soil in laboratory microcosms
- Carbon in parent compounds became distributed among air, solvent extract, and soil-bound phases

## Laboratory Study Results

- Major pathway for phenanthrene, PCP was humification
- Next significant pathway was solvent-extractable from soil parent compound or intermediates
- Mineralization was third most important pathway
- Volatilization was less than 1%

## Soil Toxicity Testing

- Microtox – general physiological toxicity
- Ames assay – mutagenicity of soil solvent extracts

## Average Microtox Toxicity

- Initial $EC_{50}$ value of 6.6
- After treatment, $EC_{50}$ value >100 (nontoxic) for all soil samples tested

## Ames Test

- Initial mutagenic potential of applied soil ~330 revertants per gram of soil
- Lift 1 sampled after 3 months treatment indicated detoxification to soil background levels (less than 150 revertants per gram of soil)

## Conclusions: Field Performance Evaluation

Land treatment of soil contaminated with wood preservatives was effective and resulted in the treated soil meeting target remediation levels for target contaminants as specified in the Record of Decision (ROD)

## Conclusions: Field Performance Evaluation

Downward migration of target chemicals as a result of the application of additional lifts was not observed

## Conclusions: Field Performance Evaluation

Contaminated soil was detoxified to background levels as a result of the treatment, based on results of toxicity and mutagenicity assays

# Phytoremediation

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Phytoremediation is the use of higher plants to bioremediate contamination in soil, water, or sediments. Variations of phytoremediation that have been used in the past include wetlands to treat municipal sewage or neutralize acidic mine drainage. Currently, phytoremediation is proposed for remediation of both organic and inorganic contaminants in soil, sediments and water.

Phytoremediation, as with bioremediation using microorganisms, involves the use of natural processes to change the form or location of contaminants. Roots of higher plants take up water, nutrients, and other compounds from soil. Water moves throughout the plant, eventually going to the leaves and out into the atmosphere in the process of transpiration. Ongoing processes of plant metabolism use water, nutrients, carbon dioxide, and sunlight to synthesize organic compounds, which are moved throughout the plant for use in growth and for storage of reserves. A large community of microorganisms thrives in contact with the plant (particularly on the root system) and is supported to a greater or lesser degree by products of the plant. Plants may transport oxygen down to the root system and release some of the oxygen to the soil. As the roots grow through the soil, they form channels that can increase soil aeration, particularly as the roots die and decay, leaving voids. As with bioremediation using natural microbial processes, it is possible to use these natural plant processes to remediate contaminants.

Much of the biodegradation associated with certain kinds of phytoremediation occurs in a zone around the root system called the rhizosphere (Figure 1). The rhizosphere is a zone of enhanced microbial activity at the interface between the root and the soil. The rhizosphere supports larger microbial populations than surrounding soil and has different types of microorganisms than surrounding soil. The enhanced microbial activity in the rhizosphere is thought to be responsible for degradation of certain contaminants, particularly of some organic contaminants.

The rhizosphere is a narrow zone, with a depth from a few millimeters to perhaps a centimeter. The actual depth of the rhizosphere is hard to measure, but the "rhizosphere effect" of enhanced microbial activity appears to diminish rapidly with distance. Since the rhizosphere is closely involved with phytoremediation, the degree of contact that the root system has with the soil is important. Plant root systems vary considerably, but in general most root systems can be divided into two classes: tap root systems, with large main roots emerging from the plant base and branching to smaller and smaller roots; and fibrous root systems, with many small roots emerging from the plant base and also branching to smaller and smaller roots. Fibrous root systems generally have more surface area per length of root than taproot systems. Some plants, notably grasses, have very fine, fibrous root systems that are highly ramified throughout the soil volume they occupy. This should

mean that the plant roots actually contact more of the soil, and therefore their affect on remediation should be more uniform throughout the soil volume occupied.

Plants may transport oxygen into the subsurface; lower the water table by transpiration, thereby pulling oxygen into the soil from the atmosphere; and increase hydraulic conductivity of the soil as roots produce channels in soil. Flood-tolerant and wetland plants are especially efficient at transporting oxygen into the subsurface. These processes are thought to enhance aerobic biodegradation by increasing oxygen in the subsurface.

As plants transpire, the movement of water through the plant also carries along dissolved components (Figure 2). Dissolved contaminants such as chlorinated solvents can be removed from the soil in the transpiration stream and emitted to the atmosphere through the plant leaves. This type of "remediation" could be undesirable, obviously.

Many plants transpire significant quantities of water under the right conditions, but certain plants, called phreatophytes, which ordinarily grow their roots down to the water table, can transport relatively large quantities of water from the soil to the atmosphere. Willow and poplar species are well known examples. Many plants, particularly the phreatophytes, can significantly influence ground-water levels, especially in soils of low permeability. Such plants could not only remediate the ground water by the various mechanism already discussed but also could help protect ground water by lowering the water table below contaminated zones.

Most plants grow roots down to about 2 meters deep or less, but some plants can reach far deeper under good conditions. Obviously it might be desirable for phytoremediation to have plants that grow dense, highly ramified, fibrous root systems down very deep. Research is needed to determine the depth of influence of plant root systems, and ways to encourage deeper rooting and greater soil volume coverage.

The community of microorganisms in the rhizosphere has been shown to be involved in degradation of numerous contaminants, including pesticides, polynuclear aromatic hydrocarbons, petroleum compounds, volatile organic chemicals, and inorganics. Also, plants can degrade contaminants during plant metabolic activities; for instance, 2,4,6-trinitrotoluene has been shown to be degraded by plant enzymes. Plants can use contaminants as nutrients; nitrate contamination of ground water can serve as a nitrogen source for plants.

Plants can adsorb or take up and accumulate contaminants either in their roots and other belowground parts or in aboveground parts including stems, leaves, and fruits. Plants are not able to take up all types of contaminants; small, low molecular weight polar compounds are favored for uptake into the plant, but large, high molecular weight lipophilic compounds tend to be excluded. Plants may extract metals from soil and accumulate them in tissues. Accumulators of lead, cadmium, chromium, nickel, cobalt, copper, zinc, and selenium have been found (Table 1). Location of the accumulation site in the plant is important. Accumulation of contaminants in the root may pose problems with removal of the contaminant from the site, since it may be impractical to harvest the root systems and separate them from the soil. Ideally, the plant would efficiently extract the contaminant from the soil down to very low levels and accumulate the contaminant to high concentrations in an aboveground plant part that could be easily harvested without harming the plant.

## Applications and Examples

In general, phytoremediation appears to be best suited for cleanups over a wide area, with fairly shallow contaminants in low to medium concentrations. Using plants to remediate a site can be much less expensive than conventional cleanup options because installation and maintenance costs are typically very low. Public acceptance of phytoremediation can be very high, in part because of the added benefits of parklike aesthetics, including providing bird and wildlife habitat. A planted wetland or interceptor barrier of poplar trees can remediate a chronic problem for years with little or no attention. The cleanup time can be longer than with some physical or chemical processes, and like most bioremediation is typically measured in months and years.

Phytoremediation has been shown to reduce concentrations of hydrocarbons from spills and leaking underground storage tanks; polychlorinated biphenyls from transformers; pentachlorophenol and creosote from wood preserving sites; nitrates, pesticides, and herbicides from agricultural runoff; and chlorinated solvents like trichloroethylene from industrial processes. Some plants can extract heavy metals such as lead, chromium, and uranium. Study in this field is relatively new, with much of the work done on the laboratory and pilot scale, though some field work is now under way.

Wetlands constructed with reeds and cattails are used to prevent acid mine drainage from polluting streams. The biological processes in a wetland neutralize the acidity of the water and decrease the mobility of the metals. Poplar and willow trees are planted as interceptor barriers to remediate ground-water contamination or to protect surface water from agricultural runoff. The roots of these trees can "pump and treat" hundreds of gallons of water each day. Contaminants may be degraded by the microbial community that is supported by the trees or by the tree itself. Plants such as mustard may be used for extraction of heavy metals by taking up the contaminants into the roots, then translocating them to the shoots and leaves. Some plants may sequester metals in the root structure but not move them further into the plant. Alfalfa, ryegrass, and other plants are used for in situ soil remediation. These plants encourage biodegradation of organic contaminants by microbes by providing oxygen, nutrients, enzymes, and other key elements in the root zone of influence or rhizosphere.

Plants are limited as to the depths that they can effectively treat. Mustard plants grow down 12 to 18 inches. Ryegrass and fescue can extend roots a few feet. Alfalfa has been found with roots down to 20 feet. Poplar tree roots can tap a water source 10 to 20 feet down, and some claim much deeper root depth.

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# Phytoremediation

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Ada, OK

Growing plants to clean contamination from soil, water, or sediments

## Early Indications of Phytoremediation Potential

- Plants have been used for prospecting for minerals—Geobotany
- Wetlands have been found to neutralize acidic mine drainage

Certain plants can help degrade contaminants, others can take up contaminants

Figure 1. Hypothetical Mechanism

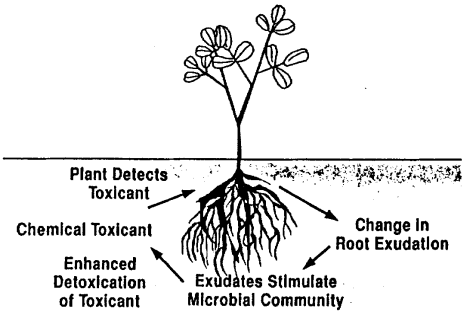
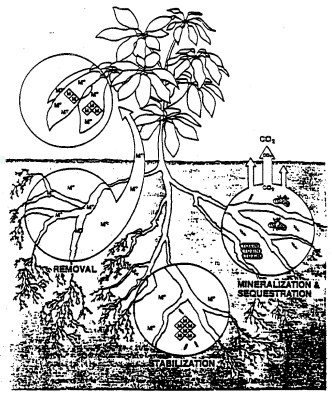



Figure 2. Diagram of Phyto-remediation



## Table 1. Examples of Metal Hyperaccumulators

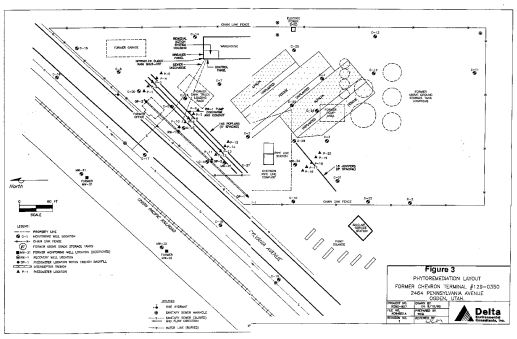
| Metal | Plant Species | Metal in Dry Weight of Leaves (%) | Original Location |
|---|---|---|---|
| ZN | Thlaspi calaminare | <3 | Germany |
| | Viola species | 1 | Europe |
| Cu | Aeolanthus biformifolius | 1 | Zaire |
| Ni | Phyllanthus serpentinus | 3.8 | New Caledonia |
| | Alyssum bertoloni and 50 other alyssum species | >3 | Southern Europe and Turkey |
| | Sebertia acuminata | 25 (in latex) | New Caledonia |
| | Stackhousia tryonii | 4.1 | Australia |
| Pb | Brassuca juncea | <3.5 | India |
| Co | Haumaniastrum robertii | 1 | Zaire |

Mature cottonwood or poplar will pump and treat 25 to 300 gallons of water per day

## Phytoremediation Project for the Chevron Ogden Terminal by Phytokinetics

Treating TPH in soil with grass and alfalfa; Treating TPH in ground water with poplar and juniper

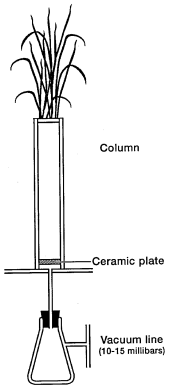
## Site Map




Phytoremediation uses slightly modified standard agronomic practices

## Treatability study in greenhouse to determine best species for site

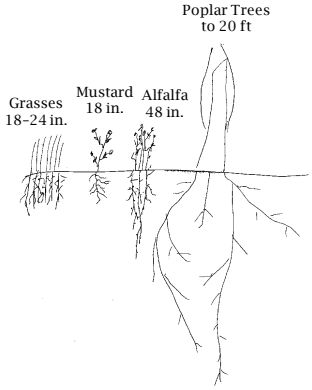
## Schematic of Soil Column




## Phytoremediation in Soil Is Best Applied to:

- Soil: widespread, fairly shallow, low to medium concentration contamination
- Ground water: shallow (to 20' easily, some claim deeper)

## Treatment Depth




## Advantages of Phytoremediation

- Less expensive with low installation and maintenance cost
- High public acceptance
- Can clean chronic pollution sources (i.e., acid mine seeps)

## Disadvantages of Phytoremediation

- At least 2–3 years for cleanup
- Most contaminants not tested extensively except for hydrocarbons, pesticides, and agricultural nutrients

## Field Experience

Field-scale demonstrations on hazardous waste are underway in:

Oregon Utah California

Texas Ohio Virginia Maryland

# Development and Application of Composting Techniques for Treatment of Soils Contaminated With Hazardous Waste

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## Introduction

Historically, composting has been used to degrade solid waste materials such as leaf litter, sewage sludge, and food wastes. More recently, composting has been investigated as a remediation technology for hazardous wastes (1). Laboratory and field-scale work has been conducted to determine the fate of polycyclic aromatic hydrocarbons (2) and explosives (3) in the composting environment. Composting is not generally employed to treat heavy metals or other inorganics, although it may be applicable to inorganic cyanides. Other studies have indicated that composting is potentially effective in degrading or transforming petroleum hydrocarbons (4, 5) and pesticides (6) to environmentally acceptable or less mobile compounds.

## Process Description

Optimum conditions for composting may vary depending on a number of factors, but generally 40 to 60 percent moisture content, a carbon-to-nitrogen ratio of 20:1 to 30:1, and aerobic conditions are considered best. Bulking agents may consist of sawdust, corn cobs, straw, hay, alfalfa, peanut hulls, or other organic materials.

The aerobic compost process passes through four major microbiological phases, identified by temperature: mesophilic (35° to 55°C), thermophilic (55° to 75°C), cooling, and maturation. The greatest microbial diversity has been observed in the mesophilic phase. Microbes found in the thermophilic phase have been spore-forming bacteria (*Bacillus* spp.) (7) and thermophilic fungi (8, 9). Microbial recolonization during the cooling phase brings the appearance of mesophilic fungi whose spores withstood the high temperatures of the thermophilic phase. Composting can be anaerobic, but most methods use aerobic conditions.

Composting can be performed in windrows, where material is put into rows and periodically turned; aerated static piles, where perforated pipes within the pile supply air; and vessels, where material is periodically mixed inside an aerated containment vessel.

## Future Research

Despite promising studies, the ability of composting to completely degrade synthetic organic compounds has not been fully demonstrated. Although composting systems have been used to biodegrade some hazardous compound, few studies (mostly bench-scale) have provided mass balance closures or fully investigated all of the intermediate products, final products, and byproducts of the composting process. The lack of mass balance closure and conclusive evidence of the fate of contaminants in field-scale applications is not unique to composting. Many other technologies (both ex situ and in situ) lack conclusive evidence of contaminant fate in field-scale applications.

Future investigations will include technical developments necessary to improve composting applications for degradation of hazardous waste. This will involve increased application of pilot-scale composting systems in addition to ongoing research in bench-top composters. Emphasis will be placed on developing techniques for trapping volatile organic compounds from pilot-scale systems, determining mass balance of contaminant degradation in the compost, and identifying microbial species responsible for biodegradation of contaminants.

Future studies will also attempt to validate extrapolation of results from bench-top to pilot-scale and field demonstration levels. Maintaining a bench-top system at optimum conditions is relatively easy compared with a large-scale composter where optimum conditions will not prevail at all times. The degree of variance from optimal conditions requires investigation and approximation in small-scale systems.

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# Composting

Presented by
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## COMPOSTING

### Definition

**... method of solid waste management whereby the organic component of the solid waste stream is biologically decomposed under controlled conditions to a state in which it can be handled, stored, and/or applied to the land without adversely affecting the environment.**

**Golueke, 1977**

## COMPOSTING PROCESS

**MIX SOIL WITH:**

- **Bulking Agent (Sawdust corn cobs, straw)**
- **Moisture**
- **Nutrients (Manure, Sludge, Food Scraps)**

## WASTE STREAMS

- **Wood Treating Waste**
- **Oil Separator Sludge**
- **Pesticides**
- **Halogenated Aromatic Hydrocarbons**
- **Munitions Wastes**

## COMPOSTING PRINCIPLES

- **Operation can be conducted under both aerobic and anerobic conditions**
- **A wide variety of cheap bulking agents are available**
- **Desired biological activities can be selected by process mainipulation**
- **Can operate under mesophilic and thermophilic conditions**
- **Inoculation with nonindigenous microorganisms is possible**

## LIMITATIONS OF COMPOSTING

- **Metals May be Toxic to Microorganisms**
- **Metals Cannot be eliminated by Microorganisms**
- **Some Organic Compounds May Not be Metabolized**

## GENERAL ECONOMIC CONSIDERATIONS

- Cost of Bulking Agents and Nutrients
- Cost of Excavation
- Time Factor (Slow Process)
- Cost of Handling Finished Product
  - Disposal
  - Further Remediation

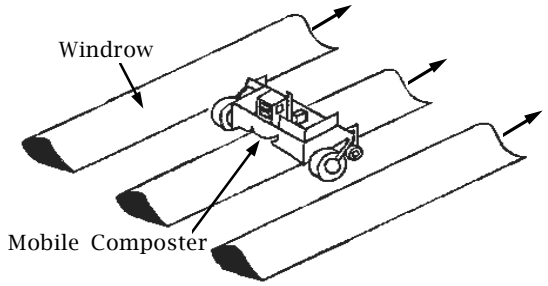
## TYPES OF COMPOST OPERATIONS

**Static Pile**
- Forced air

**Windrow (Turned Pile)**
- Turn pile periodically to aerate

**In-Vessel**
- Forced air
- Regular mixing
- Climate control

## Windrow Compost System



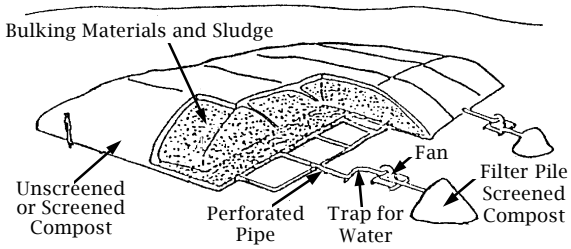

## ADVANTAGES Windrow Systems

- Capacity to handle high volume of material
- Relatives low capital investment
  - pad for piles
  - windrow machine
  - front-end loader
- Good oxygen transfer
- Intermediate stage of mixing

## DISADVANTAGES Windrow Systems

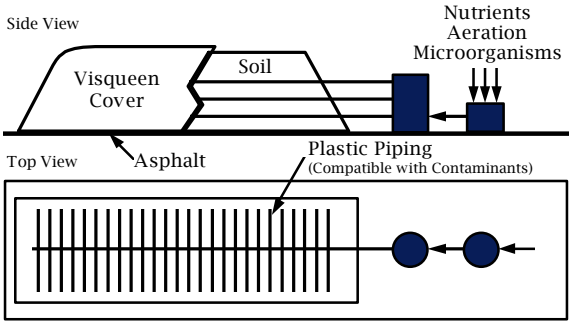
- Not space efficient
- Equipment maintenance cost can be significant
- Aeration is highly dependent on operator skill
- Subject to changing climate conditions unless covered
- Demands significant moisture control
- Requires large volume of bulking agent
- Poor control of pollutant treatment rate in system

## Schematic Diagram of Extended Aerated Pile




Composting Extended Piles with Forced Aeration

## Static Pile Composter

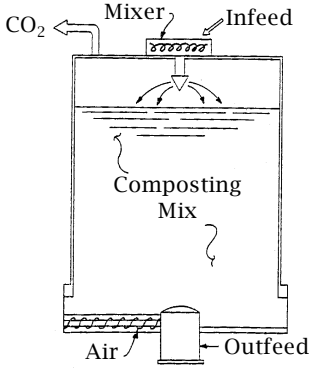



## ADVANTAGES
## Static Pile Systems

- **Low capital costs**
- **More space efficient than windrow**
- **Process control may be partly automated**
- **Downflow system can be interfaced with a biofilter to control VOCs**

## DISADVANTAGES
## Static Pile Systems

- **Requires more land than in-vessel option**
- **Requires higher energy input than windrow**
- **Subject to the influence of climate conditions**
- **Poor control of pollutant fate in treatment system**




## In-Vessel Composter

## ADVANTAGES
## In-Vessel Systems

- **Space efficiency**
- **Improved process control over open systems**
- **Process control may be automated**
- **Independent of climate**
- **Facilitates mass balance monitoring**

## DISADVANTAGES
## In-Vessel Systems

- **High capital investment**
- **General lack of operating data**
- **Process susceptible to mechanical disruption**
- **Compost compaction may confound results**
- **Low operational flexibility**

# METHODS

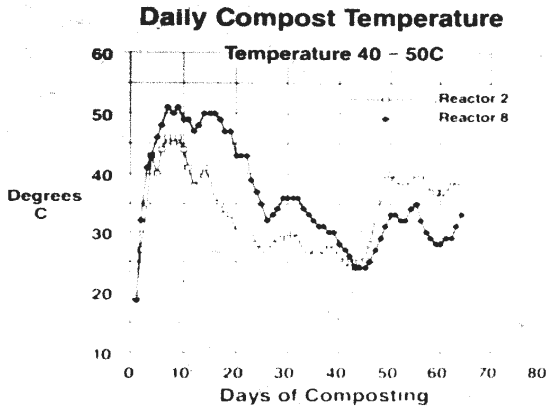
**PAH contaminated soil from Reilly Tar Pit Superfund Site, St. Louis Park, MN**

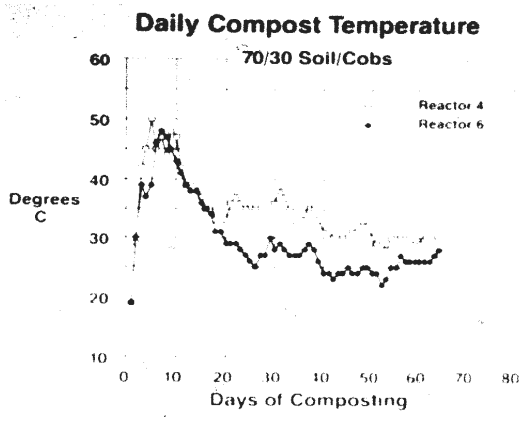
**Soil blended with ground corn cobs (bulking)**

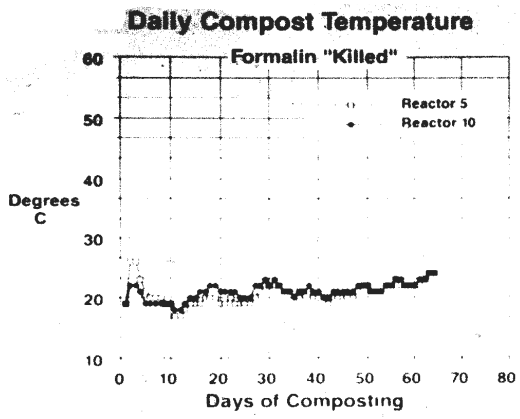
**Reactor contents mixed daily**

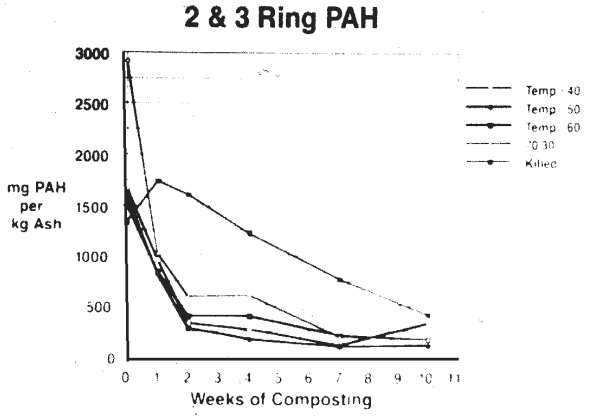
**Moisture: 40% – 50%**

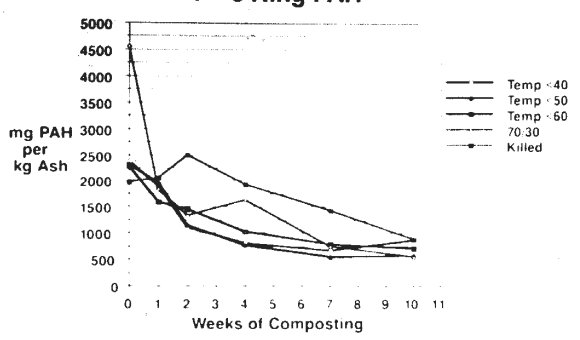
**Air flow:**
**Regular: 5 l/min**
**High: 50 l/min (for cooling)**

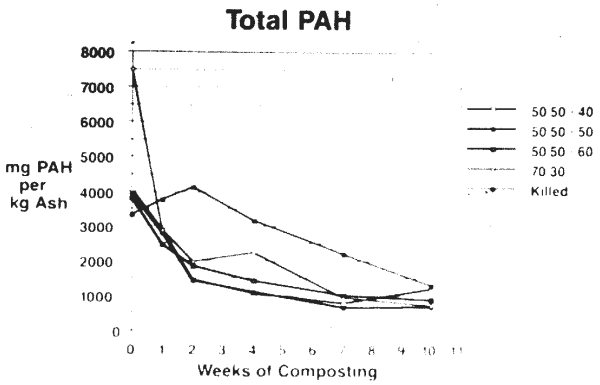





# Conclusions

- Composting reduced soil concentrations of PAHs over a 10-week treatment period
- 30% bulking as effective as 50% for remediation of PAH during first 10 weeks
- PAH degraders withstood temperature as high as 56°C

# Field Example
## Indiana Woodtreating Corp. Site

- 22,000 tons of PAH-contaminated soil
- Soil screened to remove rocks >3 inches

# Indiana Woodtreating Corp. Site

- Each 100 tons mixed with:
  - 5 rolls straw
  - 5 bails horse manure
  - 200 lbs. urea fertilizer
  - 100 lbs. ammonium nitrate fertilizer (34-0-0)
- Soil treated in 9 piles

# Indiana Woodtreating Corp. Site

- Initial total soil PAH (TPAH): 20,410 mg/kg
- Action levels:

| | |
|---|---|
| TPAH | 500 mg/kg |
| Each carcinogenic PAH | 100 |

# Indiana Woodtreating Corp. Site

Results of Test

- After 1 year of composting: TPAH <500 mg/kg
- Additional 1 year of treatment using land farming: TPAH <100 mg/kg

# Biopile Treatment of Soils Contaminated With Hazardous Waste

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## Introduction

Biopile systems offer the potential for cost-effective treatment of contaminated soils. Like composting, biopiles provide favorable environments for indigenous microorganisms to degrade contaminants present in the soil matrix. Although similar to compost piles, these systems differ in that lesser quantities of bulking agents are used in biopile units. Air is supplied to the biopile system through a system of piping and pumps that either forces air into the pile under positive pressure or draws air through the pile under negative pressure (1). Depending on the contaminants in the soil, conditions are established in the biopile to favor either anaerobic or aerobic microorganisms. In some cases, exogenous microbes, such as fungi, may be added to the biopile to enhance contaminant degradation.

Field studies have indicated biopile successes in remediation of soils contaminated with pentachlorophenol (2) and petroleum hydrocarbons (3). Costs of soil bioremediation using biopiles range from $30 to $100 per ton of soil, depending on soil conditions and the biodegradability of contaminants.

## Process Description

Biopile structure resembles a static pile compost system. Conceptually, one may think of a biopile as an ex situ bioventing system in that aeration usually involves forcing air through the soil by injection or extraction through perforated pipes. Volatile organic compound emissions can be controlled by aerating the pile with negative pressure and venting off gases into a small compost pile or biofilter (1).

Optimum conditions for biopiles vary depending on the type of soil, climate conditions, and the chemical and biological attributes of the soil. Because biopile treatment is an ex situ technology, most conditions can be controlled to achieve an acceptable range of conditions. Generally, moisture content between 40 and 85 percent of soil field capacity, a carbon-to-nitrogen ratio of 10:1 to 100:1, and pH between 6 and 8 are acceptable depending on soil conditions. Organic amendments can be used to increase the water-holding capacity of poor soils.

Wood chips may be added as bulking agents to increase soil porosity and promote aeration and irrigation. Sawdust or straw can be added to supply carbon. Animal manure (1 to 4 percent w/w) can supply both carbon and nutrients.

## Future Studies

Future studies are needed to evaluate the applicability of biopile technology and to optimize systems for treating an increased variety of contaminants. Alternating between anaerobic and aerobic conditions may provide a mechanism for degrading heavily chlorinated organic compounds via reductive dehalogenation combined with oxidative mineralization (4).

Also, soil microbiology and fungal treatment will receive increased focus in the future. Fungal technology appears promising for biodegradation of recalcitrant contaminants (5). Fungi do not generally metabolize contaminants; degradation occurs extracellularly by enzymes excreted by the fungi. Much research remains to be done to identify the fungal strains most capable of degrading specific contaminants.

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# Biopiles

## Aerated Static Soil Piles for Treatment of Shallow Contaminated Soil

Presented by
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U.S. Environmental Protection Agency
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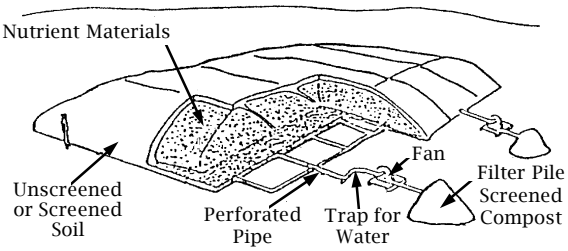
## Schematic Diagram of Extended Aerated Pile




Extended Soil Piles With Forced Aeration

## Biopile Systems

- Potential to provide cost-effective treatment
- Provide a favorable environment for indigenous aerobic or anaerobic microorganisms
- Similar to compost piles
- Air delivery system
- Nutrient enhanced

## Biopile Design

Pile Size

- Height = 3 to 10 feet
- Width is unrestrited unless pile is turned
  - 6 to 8 feet if turned

Land Requirements

- Amount of soil treated/Pile height
- Additional land required for:
  - Berms
  - Access
  - Sloping terrain

## Biopile Design (continued)

Aeration Equipment

- Blowers or fans
- Aeration piping in pile lifts
- Turning equipment if pile is turned

Biopile Construction

- Site preparation
  - Clearing and grading
- Berms, liners, and covers (if needed)
- Piping
  - Moisture addition
  - Nutrient addition
  - Aeration (if forced air)

## Biopile Design (continued)

Leachate Management

- Collection
- Treatment

Soil Pretreatment

- Shredding
- Blending
  - Amendments
  - Bulking agents (increase porosity)
  - pH adjustment

## Biopile Soil Conditions

| | |
|---|---|
| Moisture | 40% ≤ Field capacity ≤ 85% |
| pH | 6 ≤ pH ≤ 8 |
| Temperature | 10°C ≤ Temperature ≤ 45°C |
| C:N:P | 10:1:0.5 ≤ C:N:P ≤ 100:10:1 |
| Heavy metals | <2,500 ppm |

## Economic Considerations

Electricity input
- 2 hp blower running at 2 psi
- $50–$75 per month per pile

Analytical Monitoring
- Chemical
- Biological

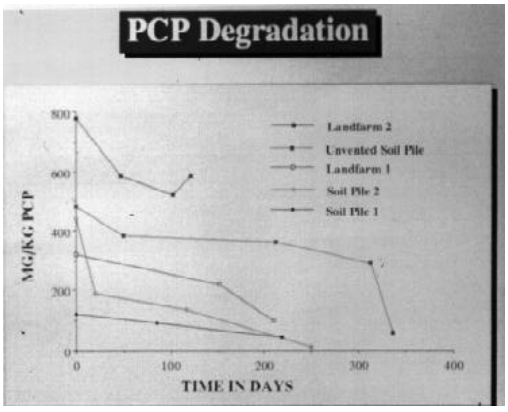
Bioremediation Cost
- Type of contaminants (biodegradability)
- Contaminant concentrations (time required)
- Typically $50 to $100/ton of soil

## Advantages of Biopiles

- Simple to design and implement
- Low cost ($50–$100/ton)
- Require less land area than land farming
- VOC emissions can be controlled

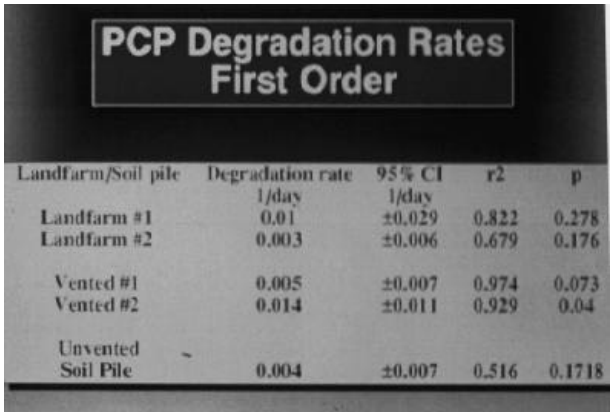
## Field Example

- Former wood treating site in southeastern U.S.
- PCP-contaminated soil
- Biopiles compared to land treatment in an effort to save space on site




**Field Soil Experiment Characteristics**

| Soil pile | Initial PCP mg/kg | Final PCP mg/kg | Elapsed time in days | #Sampling events | Size (m3) |
|---|---|---|---|---|---|
| land farm #1 | 319 | 101 | 182 | 3 | 1408 |
| land farm #2 | 780 | 586 | 186 | 4 | 2753 |
| Vented #1 | 122 | 45 | 239 | 3 | 1408 |
| Vented #2 | 443 | 11 | 242 | 4 | 2753 |
| Unvented soil pile | 484 | 61 | 339 | 5 | 646 |




## Conclusion

Vented soil piles are as effective if not more effective than landfarms

# Effective Treatment of Hazardous Waste Constituents in Soil by Lignin-Degrading Fungi

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## Introduction

The diversity of fungi and their remarkable ability to degrade complex and persistent natural materials (Table 1) such as lignin exemplify the host of useful features (1) found with these organisms. In contrast to bacteria, fungi are able to extend the location of their biomass through hyphal growth in search of growth substrates. Lignin-degrading fungi have been investigated for their enzymatic activity to degrade aromatic organic chemicals, which are structurally related to the composition of lignin. Enzymes involved in lignin breakdown are extracellular and have low substrate specificity. Fungi can thoroughly colonize soil and show exceptional tolerance to high concentrations of toxic pollutants. Chemical structural similarities and expected reactivities between lignin and organic pollutants have fostered the consideration of these fungi as potential pollutant degraders.

White rot fungi are unique in their ability to transform all components of native lignin to carbon dioxide and water. Lignin is constructed of an amorphous polymeric network that resists attack by many microbes. Three major classes of oxidative enzymes designated, lignin peroxidases (LIPs), manganese-dependent peroxidases (MnPs), and laccases, play an important role in the fungal degradation of lignin. All three enzymes can oxidize phenolic compounds, thereby creating phenoxy radicals. Nonphenolic aromatic compounds, however, are oxidized via cation radicals. Laccase can oxidize nonphenolic compounds with relatively low ionization potential, while nonphenolics with high oxidation potential are readily oxidized by LIPs and MnPs.

## Pollutant Degradation

Extensive lists of xenobiotic organic chemicals currently considered degradable by lignin-degrading fungi have been compiled. Contaminant categories to which lignin-degrading fungi have been applied are wood-treating/town gas chemicals, munitions, and pesticides and other chlorinated organic chemicals. Fungal bioremediation is an emerging technology that has been applied in the field only to wood treating wastes (pentachlorophenol and creosote). Application to other contaminants requires field evaluation.

## Field-Scale Evaluation

Application of fungal treatment in beds of contaminated soil (2) was studied at an Oshkosh, Wisconsin site (Figure 1). The contamination was a wood preservative formulation composed of 5

percent pentachlorophenol (PCP) in mineral spirits. Soil concentrations of 1 to 4,435 mg/kg to depths of 30 cm were determined through extensive sampling. Blended soil, with the larger stones and rocks removed, was added to each soil bed. Two fungi *(Phanerochaete chrysosporium* and *P. sordida)* were selected as candidate treatment species (Table 2) for the evaluation. The fungi were added to the contaminated area using spore inoculated/infested wood chips with the appropriate fungal strain. The pentachlorophenol concentration (Table 3) was depleted by 82 percent for *P. chrysosporium* and 85 percent for *P. sordida*, after 56 days of treatment, despite temperatures that dipped below the temperature range considered optimal for these fungi. *P. sordida* is a known soil inhabitant and can tolerate lower soil temperatures than *P. chrysosporium*. *P. sordida* is known to have a lower optimum temperature (30°C) than *P. chrysosporium* (40°C).

Some of the decrease in PCP is by methylation-producing pentachloroanisole (PCA), the methyl ether of PCP (Table 4). PCA accumulation in the treatment plots was monitored and did not increase with time, suggesting that degradation of PCA occurs in the inoculated soil. Transformation of PCP to PCA is evident in both liquid and soil cultures and seems to compete with other PCP transformation reactions (i.e., oxidation). In laboratory soil cultures (3) inoculated with *P. chrysosporium,* the amount of soil-bound versus an organic extractable PCP-transformation product, later identified as PCA, was greatly influenced by soil type. PCP oxidation may be enhanced further by identifying the soil conditions that favor oxidation over transformation to PCA.

Another treatment effectiveness study (Figure 2) for fungal treatment of PCP-contaminated soil (Table 5) was conducted at an abandoned wood treating site at Brookhaven, Mississippi. The field study (Figure 3) was a two-phase field assessment. The first phase (4) was designed (Table 6) to evaluate the ability of three different fungal species to deplete PCP in soil. *P. sordida* was superior in its ability to deplete PCP in soil. The results for depletion of PCP by *P. sordida* paralleled the results of the Wisconsin study, where the inoculation with either *P. chrysosporium* or *P. sordida* was applied to soil contaminated with 250 to 400 $\mu$g/g PCP. In the Brookhaven study, *P. sordida* treatment (Figure 4) resulted in an overall decrease of 88 to 91 percent at PCP concentrations of 672 mg/kg in 6.5 weeks. *P. chrysosporium* treatment reduced PCP by 67 to 72 percent in multiple soil beds at PCP concentrations greater than 1,000 mg/kg.

The Brookhaven site was also contaminated with 4,017 $\mu$g/g of total polynuclear aromatic hydrocarbons (PAHs), other components of creosote. The effects of solid-phase bioremediation with *P. sordida* (with two control treatments) on soil concentrations of 14 priority pollutant PAHs (5) were determined over a 56-day period.

Depletion of both three- and four-ring PAH analyses (Table 7) in *P. sordida*-treated soil was greater than in the controls. Concentrations of the three-ring analyses decreased by an average of 31 percent after 7 days and by an average of 911 after 56 days. Four-ring analyses were more persistent; losses first became apparent between 14 and 28 days of treatment, and an average of 45 percent was depleted after 56 days. Five- and six-ring analyses were the most recalcitrant species, persisting at original levels throughout the course of the study. The persistence of these compounds in soil is due to their low bioavailability when bound to soil particles. Depletion of five-ring analyses of PAHs, however, have been reported by some researchers under conditions providing a higher fungus:contaminant ratio than that used in this evaluation.

A larger scale demonstration (Figure 5) of the *P. sordida* treatment (6) was conducted as the second phase of the study. Inoculation of the soil with a 10-percent dry weight inoculum consisting of fungal hyphae and growth substrate reduced PCP soil concentrations of greater than 1,000 mg/kg by 64 percent after 20 months of treatment (Figure 6). The two control soil beds showed reductions of 18 and 26 percent of the PCP soil concentration.

Low initial amounts (Table 8) of fungal biomass, measured by ergosterol analysis, may have contributed to the reduced performance. Heavy rains and weather-related modification to the tilling schedule may also have limited the performance of the *P. sordida* treatment.

*P. chrysosporium* ATCC 24725-based treatment was applied to 6,000 cubic meters of soil contaminated with a mixture of chlorophenols, known as KY-5, at a site in Finland (7, 8). Initial concentrations of total chlorinated phenols decreased with depth of excavated soil layers ranging from 203 to 38 mg/kg. Contaminant composition of the constructed fungal treatment piles varied with the order of excavation. Soil contaminant reduction depended on the initial contaminant concentration. Concentrations of total chlorinated phenols between 173 and 203 mg/kg were reduced by 85 and 90 percent after 20 months of treatment (Table 9). After only 12 weeks, chlorophenol concentrations of 38 to 84 mg/kg were reduced by 80 to 90 percent to target endpoints of less than 10 mg/kg. One of the piles produced poor contaminant depletion kinetics, which was attributed to soil processing and pile construction.

## Conclusions

Removal of PCP has now been demonstrated (Table 6) in a strongly acidic (pH 3.8) Mississippi clay soil and in alkaline (pH 9.6) Wisconsin sandy gravel soil. This strongly supports the potential of fungi for treating organic pollutants in a wide range of soils having varied physical and chemical characteristics.

In the Mississippi test, *P. sordida* was capable of reducing an initial soil PCP concentration of 672 mg/kg by 89 percent using a 101 inoculum loading level by dry weight. The depletion of three-ring and four-ring analyses of PAHs (total measured PAHs, 4,017 ppm) by *P. sordida* was also promising, with reductions of 85 to 95 percent and 24 to 72 percent, respectively. *These percentage depletions for PCP and the PAH analyses were, in the Mississippi test, obtained after only 56 days of experimentation*.

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# Effective Treatment of Hazardous Waste Constituents in Soil by Lignin-Degrading Fungi

Presented by
Gregory Sayles or Dolloff F. Bishop

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National Risk Management Research Laboratory
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## Table 1. Rationale for Fungal Biotreatment

- Enzyme systems capable of degrading complex natural aromatic polymers
- Chemical structure of natural polymers resemble many organic pollutants
- Fungi have the ability to reach remote areas of the soil by extension of hyphae

## Selection Criteria

- Powerful oxidizing enzymes
  - Extracellular
  - Broad range substrate specificity
  - Multiplicity of isoenzymes
- Ability to move throughout the soil
- Genetic Stability

## Classes of Oxidative Enzymes

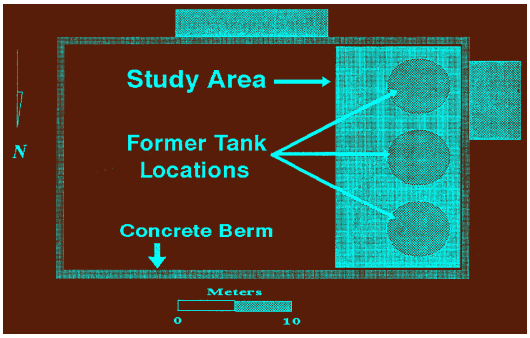
- Lignin peroxidases (LIPS)
- Manganeses-dependent peroxidases (Mn Ps)
- Laccases

## Contaminant Categories Where Lignin-Degrading Fungi Applied

- Wood treating wastes*
- Town gas chemicals
- Munitions
- Pesticides and other chlorinated organics

* Only waste having significant field testing

## Figure 1. Wisconsin Site Layout



## Wisconsin Soil Characteristics

| Characteristic | Value |
|---|---|
| Texture | Gravel/sand |
| pH | 9.6 |
| Pollutant conc. | 250–400 mg/kg |
| CEC | 17.22 |
| Total carbon (%) | 8.95 |
| Sulfur (%) | 0.14 |

## Table 2. Wisconsin Treatment Systems

| Conditions | | Inocula: P. chrysosp. | Inocula: P. sordida | Sterile chips | Organic matter |
|---|---|---|---|---|---|
| Treatment | A1 | + | – | + | + |
| | A2 | – | + | + | + |
| Controls | B | – | – | + | + |
| | C | – | – | + | – |
| | D | – | – | – | + |
| | E | – | – | – | – |

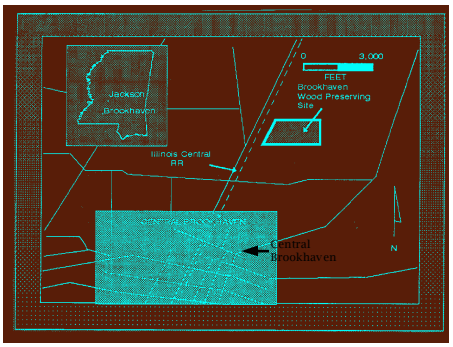
## Table 3. Wisconsin PCP Decrease

| Conditions | Percent PCP Decrease: Day 8 | Day 15 | Day 29 | Day 46 |
|---|---|---|---|---|
| A1 | 9.1 | 33.3 | 70.6 | 82.3 |
| A2 | 9.7 | 42.2 | 75.9 | 85.8 |
| B | 4.9 | 13.7 | 20.9 | 27.5 |
| C | 0.5 | -10.0 | 7.1 | 16.2 |
| D | 15.3 | 26.1 | 10.7 | 3.0 |
| E | 10.9 | 13.8 | 23.8 | 19.1 |

## Table 4. Wisconsin PCA Conversion

| Conditions | Percent PCP Converted to PCA: Day 1 | Day 15 | Day 29 | Day 46 |
|---|---|---|---|---|
| A1 | 1.3 | 13.1 | 13.0 | 14.1 |
| A2 | 0.8 | 6.6 | 9.4 | 9.1 |
| B | 0.8 | 1.4 | 1.1 | 0.7 |
| C | 1.3 | 2.3 | 1.4 | 1.5 |
| D | 0.5 | 0.9 | 0.6 | 0.6 |
| E | 0.6 | 0.9 | 0.8 | 0.7 |

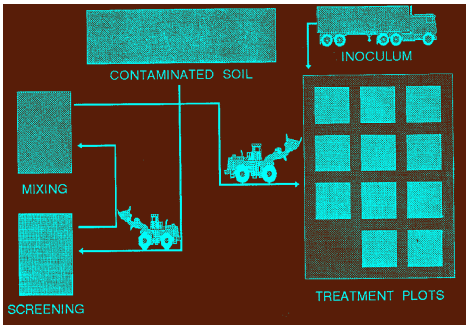
## Figure 2. Brookhaven Site Location




## Table 5. Mississippi Soil Characteristics

| Characteristic | Value |
|---|---|
| Texture | Sandy Clay |
| pH | 3.8 |
| Pollutant conc. | PCP 429-5,200 mg/kg (ave.) 2,355 mg/kg |
| Total carbon (%) | 2.2 |
| Total nitrogen (%) | 0.04 |

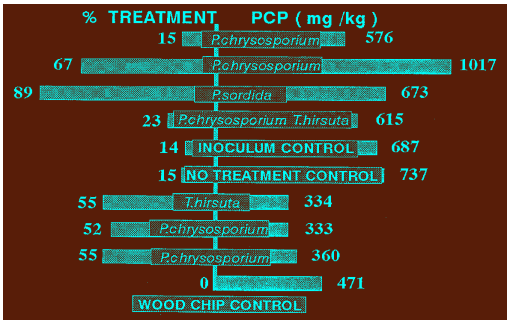
## Figure 3. Unit Processes in Site Preparation




## Table 6. Mississippi Experimental Design

| Amendment | Quantity (dry wt) |
|---|---|
| P. chrysosporium | 5.0% and 10.0% |
| P. sordida | 10.0% |
| P. chrysosp./T. hirsuta | 5.0% each |
| T. hirsuta | 10.0% |
| P. chrysosporium | 13.0% |
| P. chrysosporium | 10.0%; 3.0% (day 14) |
| No treatment, wood chip, and inoculum controls | —, —, 10.0% |

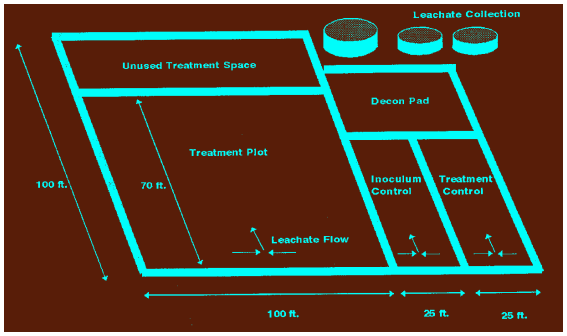
## Figure 4. Treatment Performance



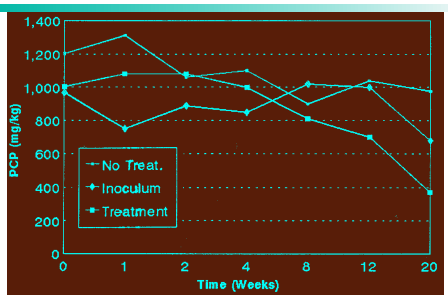

## Table 7. Transformation of PAHs

| Compound | Init. Conc. (mg/kg) | % Decrease: No Treatment Control | % Decrease: Carrier Control | % Decrease: P. sordida Treatment |
|---|---|---|---|---|
| Acenapthene | 429 | 49 | 68 | 95 |
| Phenanthrene | 941 | 69 | 49 | 90 |
| Anthracene | 684 | 57 | 48 | 285 |
| Fluoranthene | 972 | 23 | 42 | 72 |
| Chrysene | 90 | 6 | 14 | 233 |

## Figure 5. Demo Treatment Plot Perspective




## Figure 6. Pentachlorophenol Depletion




Demonstration Study

## Table 8. Ergosterol Evaluation

| | Conc. (mg/kg) | |
|---|---|---|
| | Found | Expected |
| Inoculum | 241 | — |
| Raw soil | 0.2 | — |
| Inoculated soil | 4 | 24 |

## Table 9. Transformation of Chlorinated Phenols

Finland Field Application (20 Month Treatment)

| Treatment Bed | Init. TOLX Conc.* (mg/kg) | Init. TCP Conc.* (mg/kg) | Pile pH | P. chrysosporium Treatment Removal |
|---|---|---|---|---|
| A | 2,727 | 203 | 7.1 | 85% |
| B | — | 173 | — | 94% |
| C | — | 84 | — | — |
| D | 816 | 38 | 7.7 | — |

*TOLX = Toluene extract; TCP = Total Chlorophenols

## Fungal Treatment Summary

- Treatment of pentachlorophenol occurred for concentrations greater than 1,000 mg/kg
- Consistent transformations values for PCP of 80 to 90% occurred for the Wisconsin and Mississippi sites
- Soil pH does not apparently affect the fungal treatment because pH values for the sites ranged from 3.5 to 9.2
- Fungal treatment in 56 days efficiently transformed three-ring PAHs by 85-95%; four-ring PAHs by 24-72%

# Slurry Bioreactors for Treatment of Contaminated Soils, Sludges, and Sediments

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## Introduction

A slurry bioreactor may be defined as a containment vessel and apparatus used to create a three-phase (solid, liquid, and gas) mixing condition to hasten the biodegradation of soil-bound and water-soluble contamination as a water slurry of the contaminated soil, sediment, or sludge and biomass (usually indigenous bacteria) capable of degrading targeted contaminants.

## Advantages and Limitations

Bioremediation of contaminated soils, sludges, and sediments using slurry bioreactors offers several advantages over other remediation technologies:

- Intimate contact between microbiota and contaminants combined with process controls such as (but not limited to) pH, temperature, and nutrients provide conditions favorable for rapid remediation of targeted contaminants.

- Since most reactor vessels fully contain the contaminated solid and liquid fractions, they offer almost unlimited treatment flexibility. Nutrient amendments, which in some cases may not be permitted in situ (such as ammonium and nitrate), may be used in a slurry bioreactor. Other amendments that can be used in slurry bioreactors include designer bacteria, surfactants, and enzyme inducers. Slurry bioreactors may be fitted to provide sequential anaerobic/aerobic treatment conditions. Slurry bioreactors may fit into various treatment trains, which must include particle size separation (most slurry bioreactors do not accept particles larger than ¼ inch in diameter) and commonly include soil washing. Slurry bioreactors can be operated in batch mode (at least 10 percent of the slurry should be reserved for seeding subsequent batches), or several bioreactors can be sequentially linked for continuous or semicontinuous operation.

- Most bioreactor vessels fully contain the contaminated solid and liquid fractions and can be designed to contain volatile contaminants; they offer a high degree of safety as related to contaminant containment.

- Slurry bioreactors require a relatively small space compared to technologies such as land treatment, biopiles, and composting. Many slurry bioreactors may be mounted on trailers and transported for use at several sites.

Slurry bioreactors also have limitations:

- Bioslurry is an ex situ process, which by definition requires excavation and transport (even if only a few feet) of the contaminated waste.
- Reactor mixers consume energy.
- Slurry bioreactors generally will not accept particles larger than ¼ inch in diameter, requiring soil sieving or some other type of particle size separation. Sand particles are highly abrasive in slurry bioreactors, shorten their operating life, and generally contain a small fraction of the contamination. Operators often choose hydrocycloning for sand fraction rejection.
- Bioslurrys require dewatering after remediation is terminated.
- There is a limited history of full-scale bioslurry operations. Although there are many pilot studies, slurry bioreactors are not easily scaled upward in size. Some investigation or experimentation may be required to achieve optimal operating conditions in a full-scale operation. These limitations will increase the cost of remediation by slurry bioreactors.

## Waste Streams

Contaminants that have been successfully remediated using slurry bioreactors include wood treating waste, oil separator sludge, munitions, pesticides (not including highly chlorinated pesticides), and halogenated aromatic hydrocarbons. Slurry bioreactors have been used most frequently to remediate creosote.

## Case Study

OHM, Inc., conducted large-scale slurry bioreactor remediation of creosote-contaminated lagoon solids stabilized with fly ash (total polycyclic aromatic hydrocarbons [PAHs] of 11 g/kg). Extensive classification of contaminated solids was accomplished and included screening and hydrocycloning. Slurry bioreactors with a 750,000-liter operating capacity were used to treat a 20-percent slurry. The results were mixed with 82 to 99 percent remediation of the three- to four-ring PAHs and 34 to 78 percent remediation of the five- to six-ring PAHs.

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# Slurry Bioreactors

Presented by
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National Risk Management Research Laboratory
U.S. Environmental Protection Agency
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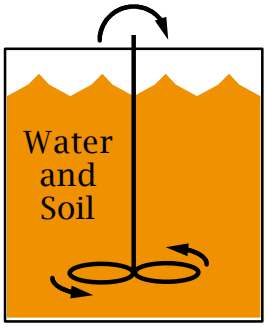
## Slurry Bioreactors

For the treatment of contaminated soils, sludges, and sediments

## A Slurry Bioreactor




## Advantages of Slurry Bioremediation

1. Enhanced process control
2. Faster rates of biodegradation of contaminants are possible
3. Better physical contact between pollutants and microorganisms
4. Distribution of nutrients, gases (air, oxygen), and other materials for support of biological process is greatly improved
5. Optimal soil, sediment, or sludge particle size distribution can be selected
6. Liquid phase organic solubilities may be enhanced by surfactant application

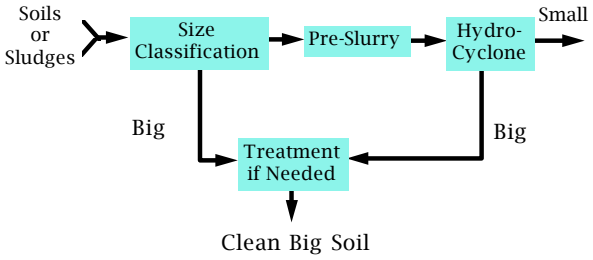
## Bioreactor Feed Characteristics

- Solids particle size: <200 mesh
- Solids content in slurry: 10-30% (w/w)
- Total organics: <10% (w/w), i.e., no free product
- pH 4.5–9.0

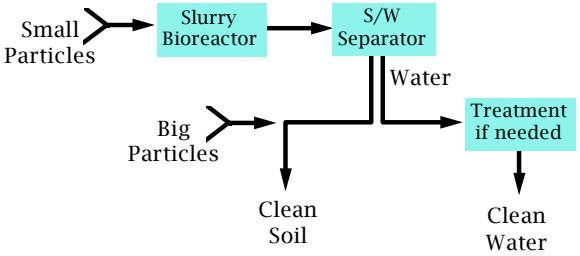
## Contaminated Soil Characterization Requirements

1. Particle size distribution
2. Texture/composition (silt, clay, sand)
3. Soil nutrients (nitrogen, phosphorous)
4. pH
5. Cation exchange capacity (CEC)
6. Metals (speciated)
7. Total organic carbon

## Process Components




## Process Components (continued)



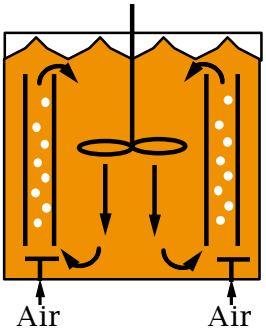

## Reactor Configurations

- Batch (most common)
- Sequenced batch
  - Anaerobic—aerobic
  - Long-short residence time

## Types of In-Vessel Mixing

- Impeller
- Airlift (rising air bubbles induce slurry circulation)
- Combination of above

## Slurry Bioreactor Mixing




## Candidate Waste Streams

- Soils, sediments, and sludges associated with:
  - Wood treating waste (PAHs, PCP)
  - Oil/water separators
  - Munitions
  - Pesticides
  - Halogenated aromatic hydrocarbons

## Examples of Slurry Bioreactor Use in the U.S.

| Site | Contamination | Status |
|---|---|---|
| Cape Fear Wood Preserving Fayetteville, NC | Creosote Contaminated Soils and Sludges | Full Scale Predesign |
| Fennema Excavating Byron Center, MI | Soil Contaminated With Fuel Hydrocarbons (PAHs) | Full Scale Underway |
| Pri Mart #7 Buchanan, MT | Soil Contaminated With Fuel Hydrocarbons (PAHs) | Full Scale Underway |

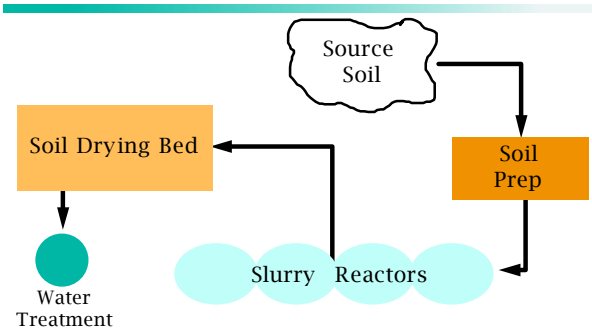
## Examples of Slurry Bioreactor Use in the U.S. (continued)

| Site | Contamination | Status |
|---|---|---|
| Wseco Oil #37 Muskegon, MI | Soil Contaminated With Fuel Hydrocarbons (PAHs) | Full Scale Underway |
| Moss-American Milwaukee, WI | Creosote Contaminated Soils and Sludges | Full Scale Predesign |
| Lone Star Army Ammunition Plant Texarkana, TX | TNT, TPHs | Full Scale Predesign |
| Sheridan Disposal Services Hempstead, TX | PCBs and Other Assorted Organic Pollutants | Full Scale Predesign |

## Field Example: Southern Wood Preserving, Canton, MS

- Creosote contaminated lagoon solids, stabilized with fly ash
- pH 6–8
- Used extensive size classification
- Bioreactor uses impeller and airlift mixing

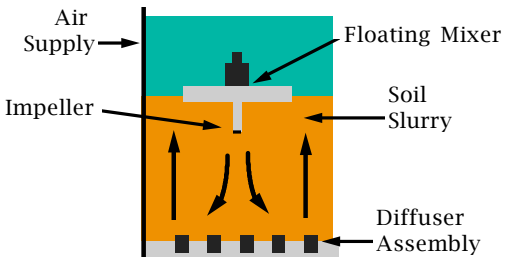
## Canton Site Layout



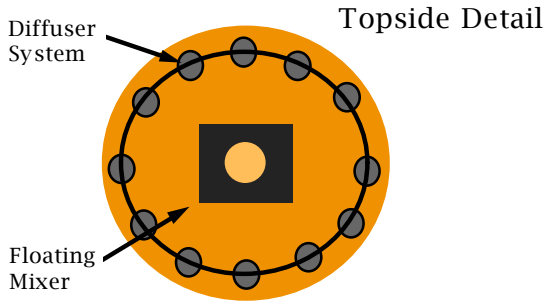

## Contaminated Material Size Fractions

| Fraction | Size | Quantity ($yd^3$) | Quantity Tons |
|---|---|---|---|
| Large Debris | + 6 inch | 150 | 165 |
| Power Screen Rejects | -6 + 1/2 inch | 300 | 330 |
| Shaker Screen Rejects | -1/2 + 12 mesh | 1,500 | 1,825 |
| Hydrocyclone Rejects | -12 + 200 mesh | 1,500 | 1,825 |
| Material for Treatment | -200 mesh | 7,050 | 9,995 |
| TOTAL | | 10,500 | 14,140 |

## OHM Canton Site Reactor



## OHM Canton Site Reactor




## Reactor Operating Conditions

| | |
|---|---|
| Volume (L) | 750,000 |
| Impeller Speed (RPM) | 900 |
| Air Flow Rate (Scfm) | 350+/-100 |
| Solids Loading % | 20 |

## Reactor Operating Conditions (continued)

| | |
|---|---|
| Temperature (C) | 30+/-10 |
| pH (S.U.) | 7.2+/-1.0 |
| DO (mg/L) | >2.0 |
| Ammonia Nitrogen (mg/L) | 60+/-20 |
| Phosphorous (mg/L) | 20+/-10 |
| Retention Time | ? |

## Canton Site Treatment Results
### PAH Treatment

| | Initial | Final | Treatment Effectiveness |
|---|---|---|---|
| 3 RING | | | |
| Acenaphthene | 909 ± 230 | 6 ± 3 | 99 |
| Acenalthylene | 93 ± 81d | 15 ± 5 | 82 |
| Anthracene | 1,950 ± 530 | 121 ± 59 | 94 |
| Fluorene | 630 ± 283 | 14 ± 6 | 97 |
| Phenanthrene | 1,031 ± 661 | 34 ± 23 | 96 |

## Canton Site Treatment Results (continued)

| | Initial | Final | Treatment Effectiveness |
|---|---|---|---|
| 4 RING | | | |
| Benzo(a)anthracene | 280 ± 51 | 12 ± 5 | 95 |
| Chrysene | 296 ± 59 | 36 ± 11 | 90 |
| Fluoranthene | 1,708 ± 395 | 32 ± 7 | 98 |
| Pyrene | 1,148 ± 252 | 33 ± 12 | 97 |

## Canton Site Treatment Results
### PAH Treatment

| | Initial | Final | Treatment Effectiveness |
|---|---|---|---|
| 5 & 6 RING | | | |
| Benzo(b)fluoranthene | 321 ± 34 | 208 ± 54 | 52 |
| Benzo(k)fluoranthene | Combined with Benzo(b)fluoranthene | | |
| Benzo(g,h,i)perylene | 92 ± 82 | 18 ± 12 | 43 |
| Benzo(a)pyrene | 130 ± 52 | 79 ± 15 | 34 |
| Dibenzo(a,h)anthracene | 92 ± 82 | 9 ± 6 | 78 |
| Indeno(2,3-cd)pyrene | 94 ± 79 | 31 ± 5 | 46 |

## Canton Site: Cost of Operation Only

Cost for Full-Scale Slurry-Phase Bioremediation of RCRA K001 Waste Per Ton of Contaminated Soil

| Cost Category | Soil Preparation | Slurry Treatment |
|---|---|---|
| Labor/Equipment | $30–35 | $10–15 |
| Supplies/Utilities | $20–25 | $25–30 |
| Analytical Support | <$5 | $5–10 |
| TOTAL | $50–60 | $40–55 |

## Canton Site: Cost of Project Components

Project Costs for Full-Scale Application of Slurry Treatment to K001 Contaminated Soil

| Unit Task | Cost* |
|---|---|
| Treatability Testing | $200,000 |
| Predesign Engineering | $100,000 |
| Slurry Treatment | $800,000 |
| Slurry Dewatering | $700,000 |
| Site Preparation and Closure | $400,000 |
| Administration and Support | $500,000 |
| TOTAL (Price per ton) | $190–200 |

*Cost rounded to nearest $100,000.

# Fixed Film Bioreactors

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## Introduction

Fixed film bioreactors have become conventional technology for treating biodegradable contaminants in air and water. Principal fixed film bioreactor applications include treatment of industrial wastewaters, leachates or ground water, and air emissions of volatile organic compounds (VOCs). In the reactors, biological activity usually converts contaminants to innocuous end products such as carbon dioxide, methane, and water. Conventional fixed film reactor approaches involve aerobic, aerobic co-metabolic (with aliphatic and aromatic organic inducers), and anaerobic metabolism. Emerging reactor approaches also include sequential anaerobic/aerobic metabolism.

Fixed film bioreactors use either fixed, expanded, or fluidized beds of inert or adsorptive media to support the biofilm's biodegradation of contaminants. Practical inert media include plastic, stone, sand, wood, and ceramics. Contaminant removal from the air or water is achieved through biofilm sorption. Adsorptive media, typically peat or granular activated carbon (GAC), remove contaminants from the air or water through both biosorption and physical adsorption. While highly efficient adsorptive media such as GAC are expensive, the high adsorptive capacity provides improved protection to the biofilms by limiting microbial inhibition from toxic contaminants while increasing contaminant removal efficiencies, especially during treatment startup. GAC media also improve biosystem response to widely varying contaminant concentrations.

## Representative Reactor Systems

Many contaminants can be biodegraded using aerobic metabolic or co-metabolic pathways. A few, however, require anaerobic conditions for efficient biodegradation. Selection and design of reactor systems depend on several factors: contaminant biodegradation kinetics, contaminant sorptive properties, metabolic or co-metabolic pathways of the individual contaminants, contaminant concentration(s), and reactor system temperature and pH. Representative reactor systems include aerobic fluidized-bed GAC filters (1, 2), anaerobic expanded- or fluidized-bed GAC filters (3-5) for aqueous streams, and biofilters (6-8) for contaminated air.

Aerobic fluidized-bed GAC filters (Figure 1) are best suited for low to moderate concentrations of contaminants such as typically found in ground water and leachates. These filters can treat slowly aerobically degradable, poorly biosorbable, or inhibitory contaminants. Some contaminants will require the addition of appropriate co-metabolites for efficient biodegradation. Where only aerobically degradable (metabolic and co-metabolic) and noninhibitory contaminants are found in the aqueous stream, however, fixed film bioreactors with inert media may be used.

Envirex Ltd. and Envirogen Ltd. employ, before the inlet to the bioreactor, efficient pure oxygen contacting approaches, with oxygen recycle that limits stripping of VOCs into the gas phase and prevents difficult-to-control three-phase flow in the bioreactor. With aqueous stream recycle, transferred dissolved oxygen is sufficient to meet the biological oxygen demand (BOD) of ground-water contaminants.

Anaerobic expanded- or fluidized-bed GAC filters (Figure 2) are best applied to moderate to high-strength aqueous waste streams such as leachates and industrial wastewaters. In these waste streams, most contaminants are at least slowly anaerobically biodegradable. Highly halogenated contaminants and aromatic contaminants with multiple nitro groups (munitions), however, are recalcitrant or require a co-metabolite for aerobic degradation. The presence of these compounds requires or favors anaerobic biotreatment. A significant advantage of anaerobic fixed film bioreactors is that oxygen does not have to be transferred to the aqueous stream, producing substantial operating cost savings, especially for high BOD streams. A major disadvantage is that slow anaerobic degradation rates for many compounds mean bigger reactors are required.

Air biofilters use two alternative reactor approaches: biofilters (Figure 3) with natural media (e.g., peat, compost, wood bark) and trickling biofilters (Figure 4) with inert or adsorptive media and continuous recycling of nutrients and buffer solutions. Commercial peat and compost biofilters require efficient air humification to maintain biofilm activity and to prevent irreversible channeling of the bed, which causes bypassing of VOCs into the filter's effluent air stream. High contaminant concentrations (greater than 100 parts per million volume) at ambient temperatures produce plugging of commercial biofilters by excess biomass. Periodic (1- to 5-year) media replacement in commercial biofilters is also required because of consumption of available nutrients and deterioration of media structure.

Trickling biofilters, an emerging technology, use recycling of nutrient and buffer solutions to support metabolic activity and maintain desired reactor pH. These biofilters can treat higher loadings (800 to 1,000 parts per million volume) but require media cleaning at the high loadings to prevent filter plugging and excessive pressure loss. Cleaning of ceramic pellet media through regular hydraulic backwashing has been successfully demonstrated at pilot scale. Cleaning of complex media structures is under study.

Novel media designs (Figure 5) to permit treatment of all VOCs have also been evaluated, typically at bench scale. Carbon coating of inert media or carbon pellets produces improved filter performance for slightly soluble VOCs. VOC permeable silica gel pellets with retarded oxygen transport and with encapsulated biomass produce sequential anaerobic/aerobic treatment. Partial dehalogenation of perchloroethylene (PCE) and trichlorethylene (TCE) occurs in the pellet core. Then, aerobic degradation of the daughter products (e.g., vinyl chloride) occurs in the outer zone of the pellet. Sodium formate is added to the nutrient and buffer solution to provide an energy source for the dehalogenation.

## Performance and Costs

Aerobic fluidized-bed GAC bioreactors treating typical contaminant concentrations in ground water efficiently remove most contaminants. As an example, in a reactor (Table 1) with a 5-minute hydraulic residence time (HRT), concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) were reduced (1) from 5,420 to 64 parts per billion (98.9 percent removal). Benzene removal exceeded 99.9 percent (less than 1 part per billion residual benzene). Anaerobic fluidized-bed GAC bioreactors (5) treating moderate- to high-strength leachate (Table 2) produced highly efficient removals (98 to 99 percent of chlorinated aliphatic VOCs, 85 to 97 percent of aromatic and ketone VOCs, and 97 to 99 percent removal of semivolatile organic compounds) at HRTs of 3 to 12 hours.

Commercial biofilters (Table 3) with natural media (6) very efficiently remove soluble aerobically degradable VOCs, such as alcohols, ketones, and phenols; efficiently remove moderately soluble aerobically degradable VOCs, such as BTEX; and minimally remove slightly soluble or aerobically recalcitrant VOCs, such as pentane, cyclohexane, PCE, and TCE. Trickling biofilters with adequate retention time and appropriate media very efficiently treat all types of VOCs (Table 4). Examples of performance with hydraulic backwashing to control pressure losses are shown in Figures 6 through 8.

The costs of these fixed film systems (Figures 9 through 12) vary depending on the application characteristics. Capital costs are generally competitive with alternative technologies such as activated carbon adsorption, but operating costs, especially long term, are substantially lower than those of alternative technologies.

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# Fixed Film Bioreactors

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## Fixed Film Bioreactors for Air and Water

- Fixed, expanded, and fluidized beds
- Aerobic metabolism
- Aerobic co-metabolic metabolism
- Anaerobic metabolism
- Sequential anaerobic/aerobic metabolism

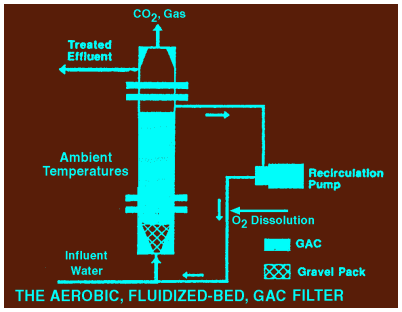
## Fixed Film Support Media

- Inert media – plastic, stone, sand, wood, ceramics, and glass
- Adsorptive media – granular activated carbon, peat compost, resins
- Contaminant removal – inert media by biosorption and biodegradation, adsorptive media by biosorption, physical adsorption and biodegradation

## Bioreactor Selection and Design Criteria

- Contaminant biodegradation kinetics
- Contaminant sorptive properties
- Contaminant metabolic pathways
- Contaminant concentrations
- Reactor system temperature and pH

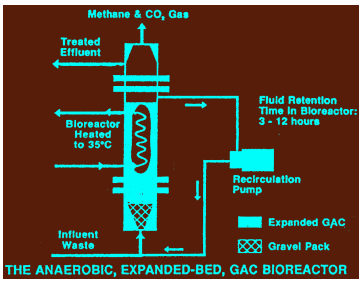
## Figure 1. Aerobic Fluidized-Bed GAC Filter



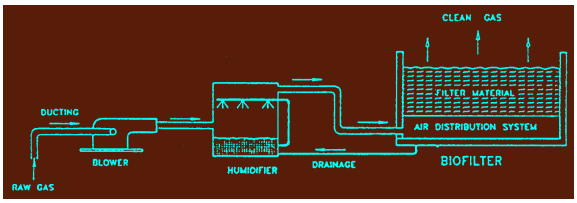

## GAC-Fluid Bed Advantages

- Low ppb residuals in effluents
- Small size
- No off gas
- Good stability
- No carbon regeneration

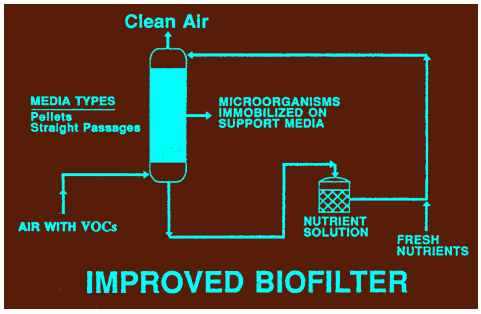
## Figure 2. Anaerobic Expanded or Fluidized-Bed GAC Filter




## Figure 3. Commercial Biofilters




## Figure 4. Trickling Biofilters




## Commercial Biofilter Characteristics

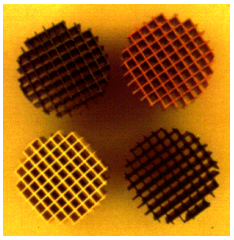
- VOC destruction unlike some control technologies
- Some VOC poorly removed
- Low energy usage
- Efficient moisture control essential
- Plugging at high VOC loading
- Periodic media replacement

## Trickling Biofilter Characteristics

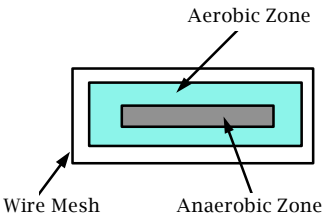
- Destruction of all VOCs
- Recycling of nutrient and buffer solution
- Low energy usage
- Media cleaning at high VOC loadings
- No media replacement

## Figure 5. Novel Media Designs

Porous Ceramic and Carbon Coated Media



Silica Gel Pellets



## Table 1. BTEX Removal in a Fluidized-Bed GAC Reactor

| Compound | Influent (ppb) | Effluent (ppb) | % Removal |
|---|---|---|---|
| Benzene | 1,100 | >1 | >99.9 |
| Ethylbenzene | 137 | >1 | >99.9 |
| Toluene | 1,079 | 1.3 | 99.9 |
| P,M Xylenes | 751 | 5.1 | 99.3 |
| O-Xylenes | 234 | 0.7 | 99.7 |

## Table 2. Anaerobic GAC Bioreactor Performance

| Compound | Influent Conc (mg/L) | % Removal |
|---|---|---|
| Perchloroethylene | 20 | >99 |
| Chlorobenzene | 1.1–20 | >85 |
| Penta chlorophenol | 1.3–20 | >99 |
| Methyl Isobutyl-Ketone | 10 | >94 |
| Naphthelene | 30 | >99 |

## Table 3. Commercial Biofilter Performance

| Compound | Removal* |
|---|---|
| Aliphatic hydrocarbons | Low-moderate |
| Aromatic hydrocarbons | Moderate-high |
| Alcohols, aldehyeds, and ketones | High |
| Sulfur compounds | Moderate-high |
| Chlorinated hydrocarbons (low concentrations) | Low-moderate |

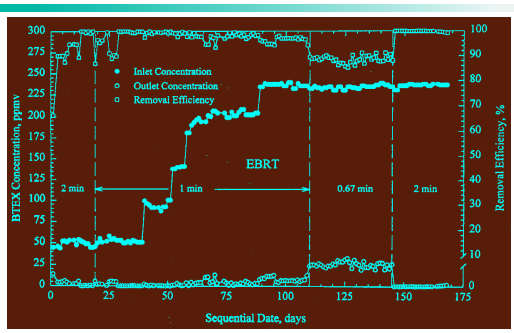
*High = >95%, Moderate = 85-95%, and Low = >85%

## Table 4. Trickling Biofilter Performance

| Compound | Influent Conc. (ppmv) | % Removal |
|---|---|---|
| Toluene | 430 | >99 |
| Methylene Chloride | 150 | >99 |
| Trichloroethylene | 25 | ~35 (>99)* |
| Ethylbenzene | 20 | >99 |
| Chlorobenzene | 40 | >95 |

*Addition of co-metabolite phenol to nutrient and buffer solution.

## Figure 6. Biofilter Performance on BTEX Removal




## Figure 7. Biofilter Performance on Individual BTEX Components

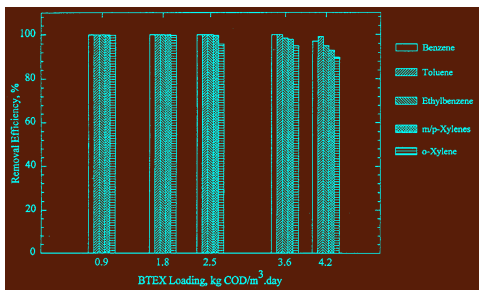


Figure 8. Typical Toluene Removal Recovery Following Biofilter Backwashing Cycle

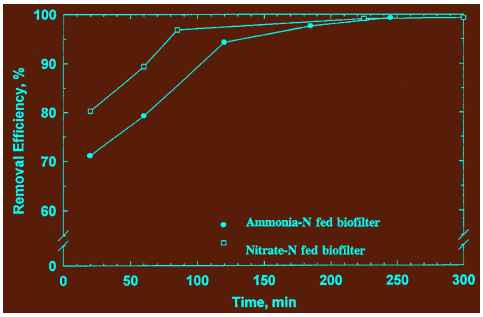



Figure 9. Life Cycle Cost Comparison

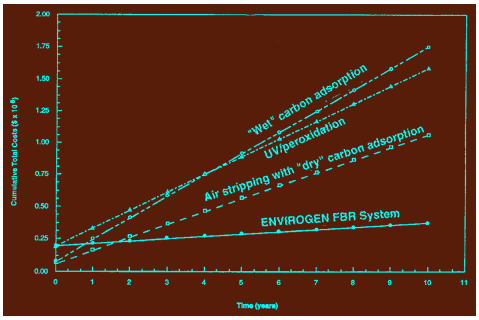



Figure 10. Cost Comparison

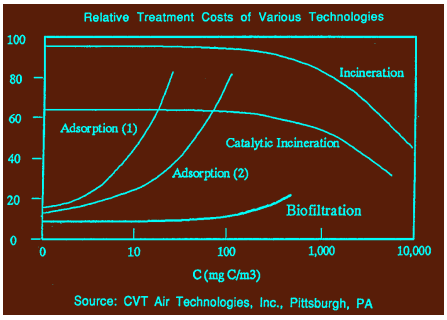



Figure 11. Comparison of Total Capital Investment (TCI) for Biofilters (Three Residence Times) and RTO

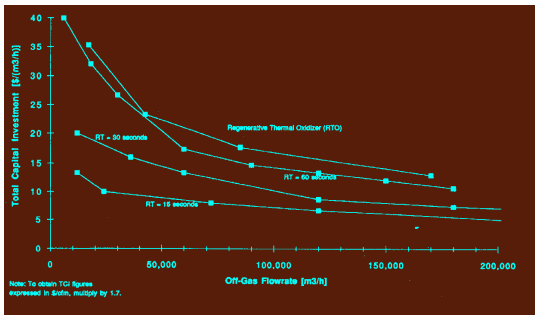



Figure 12. Comparison of Energy Cost for Biofilters and RTO