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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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Bioremediation of Hazardous Waste Sites:
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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% 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); 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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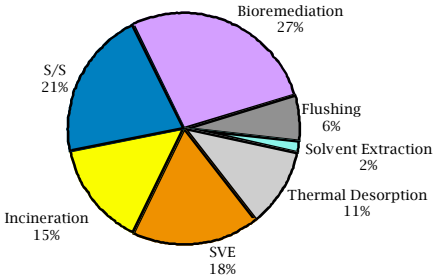
Background Information for Bioremediation Applications

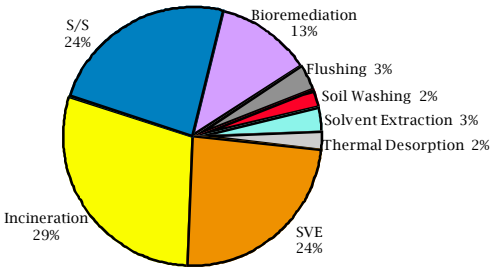
- National Status on Applications
- Biodegradation and Metabolism
- Environmental Factors Affecting Biodegradation
- Site Characterization
- General Concept of Treatability Studies

National Status on Applications

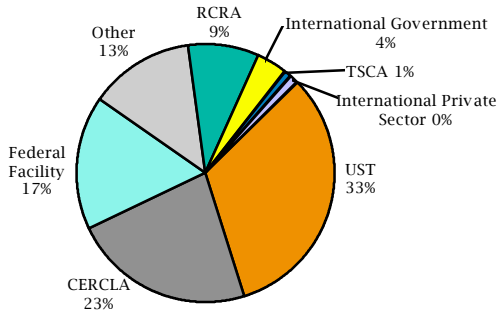
Superfund Remedial Actions Technologies Selected in FY94



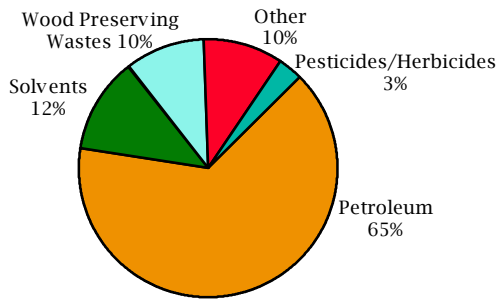
Superfund Remedial Actions Technologies Selected in FY89



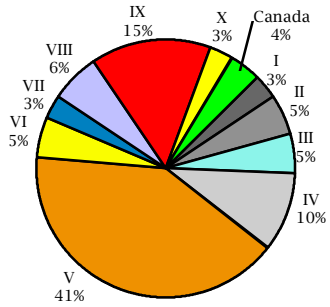
Legislative Authority for Sites Using Bioremediation



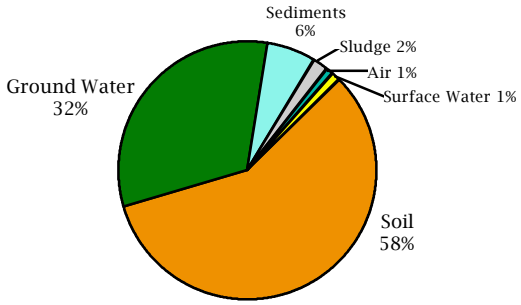
Breakdown of Sites by Type of Contamination



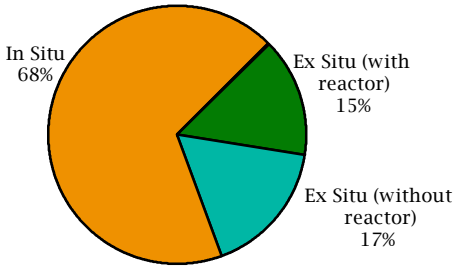
Distribution of Bioremediation Projects by Region



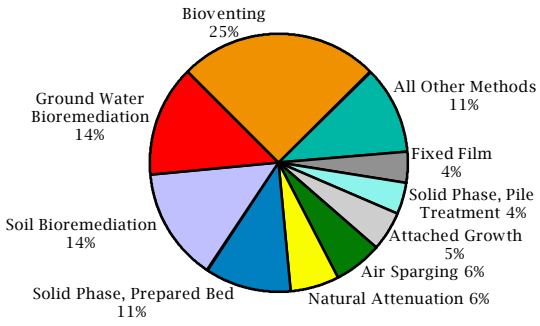
Percentage of Sites Treating Each Medium



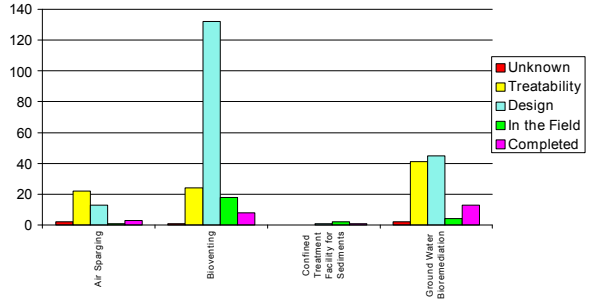
Breakdown of Processes by Treatment Technology
(Includes Laboratory-, Pilot-, and Full-Scale)



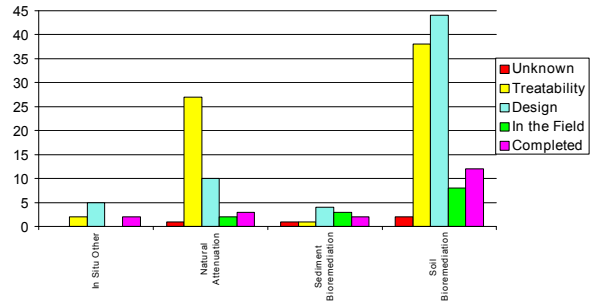
Top 9 Bioremediation Methods



In Situ Biotreatment Processes



In Situ Biotreatment Processes
(continued)



Biodegradation and Metabolism

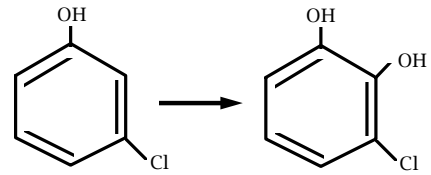
Biodegradation and Metabolism

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

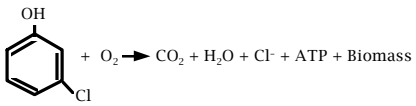


m-chlorophenol
3-chlorophenol

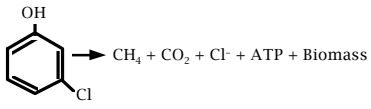
m-chlorocatechol
3-chlorocatechol

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



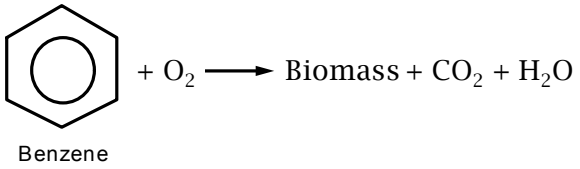
Co-metabolism

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

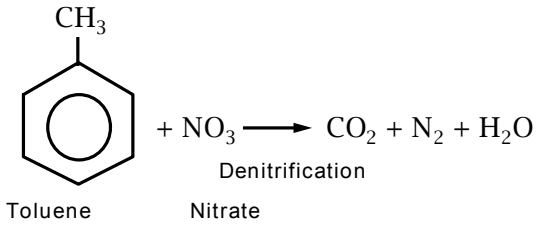
Methane — Methanotrophs — Methanol

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

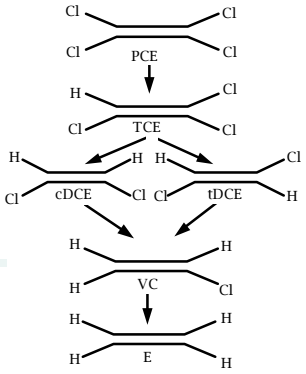
Aerobic Biodegradation



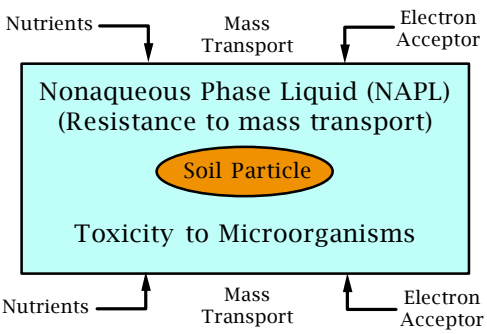
Anaerobic Biodegradation



Anaerobic Biodegradation (Reductive Dechlorination) of Chlorinated Alkenes



Environmental Factors Affecting Biodegradation



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

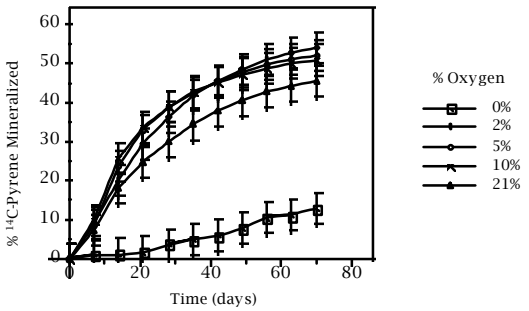
Critical Environmental Factors for Soil Microbial Activity

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

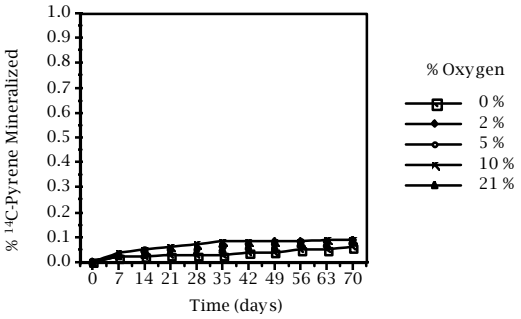
Reference: (9)

Oxygen Supply

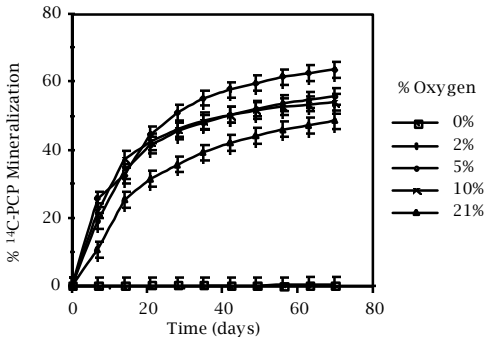
Oxygen diffuses through water at a rate that is 10,000 times less than oxygen diffuses through air



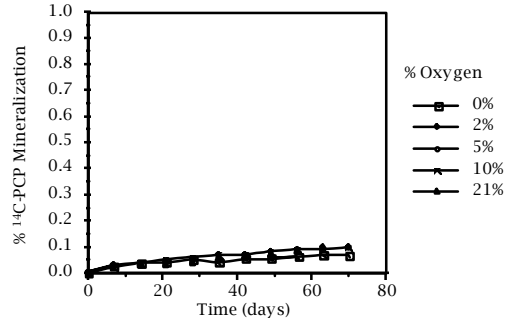
Mineralization of ^{14}C-pyrene in non-poisoned soil microcosms as a function of time and oxygen concentration. Error bars represent the least significant difference of 7.94. Values are the means for triplicate reactors.
Reference: (12)



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%.



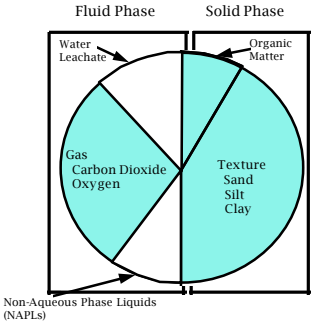
Mineralization of ^{14}C-PCP in poisoned soil microcosms as a function of time and oxygen concentration. Values are the means for triplicate reactors.

Environmental Factors

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

Site Characterization

Physical Phases at a Site To Be Considered for Bioremediation Technologies

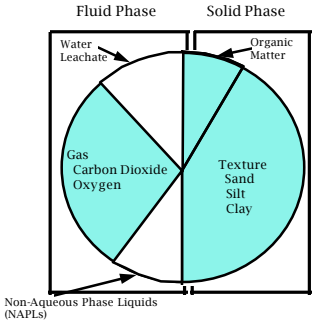


General Concept of Treatability Studies

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

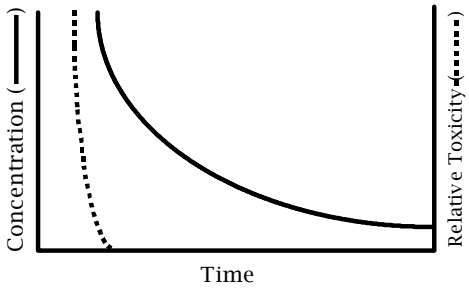
Reference: Ginn, J., W.J. Doucette, and R.C. Sims. 1994. Chemical mass balance approach for estimating fate and transport of polycyclic aromatic metabolites in the subsurface environment. Polycyclic Aromatic Compounds 5:225-234.

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

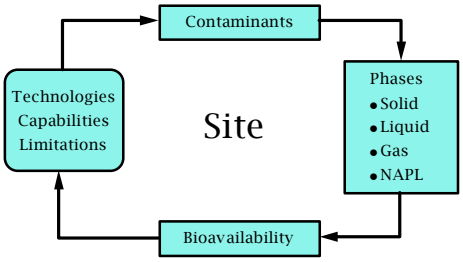
Reference: (12)

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
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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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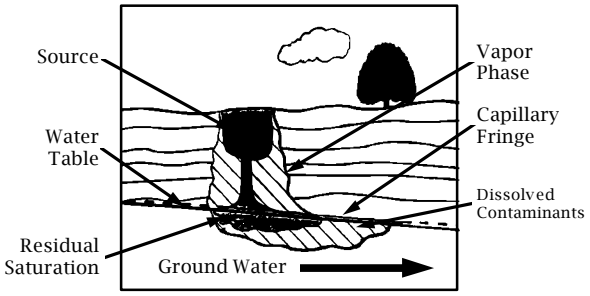
Outline

- 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

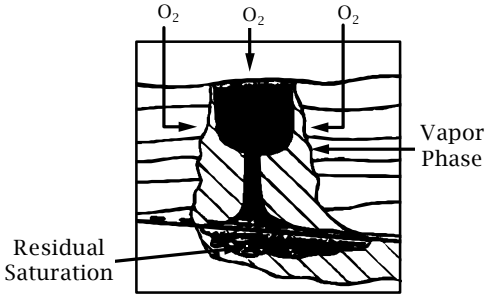


Distribution of a 148,000 kg Spill (200 m^3)

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

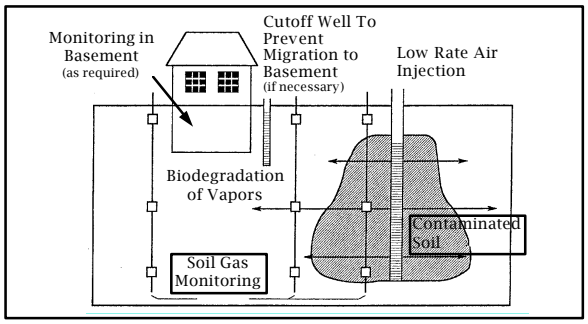
$$C_6H_{14} + 9^1/_2\ O_2 \longrightarrow 6\ CO_2 + 7\ H_2O$$

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

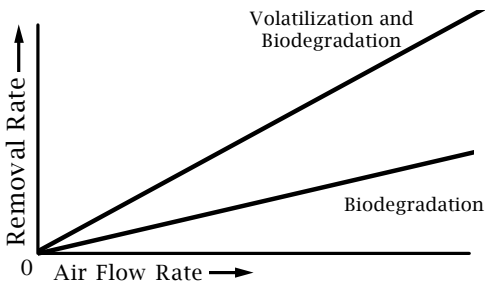


What Is Bioventing?

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

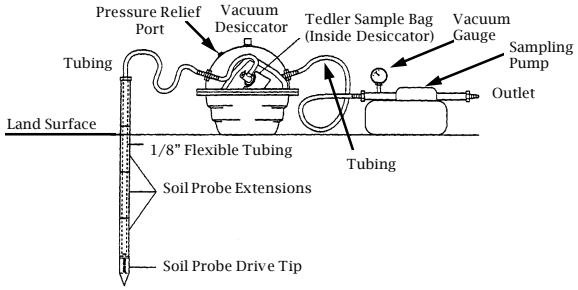
- Known spills, overfills, leaks
- Soil and GW data
- Location and levels

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

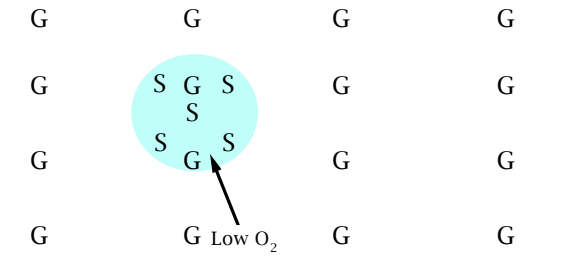
- Low O_2, high CO_2
  - Bioactivity present, but needs O_2
  - Candidate location for bioventing
- High O_2, low CO_2
  - Bioactivity low, something else is retarding biodegradation
  - Not a candidate site for bioventing

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:

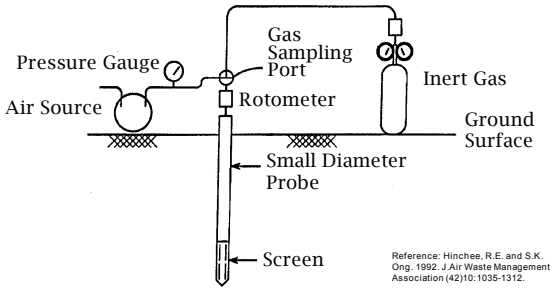
1. Install:
   - air injection tube
   - soil gas monitoring points

into contaminated area and background

In Situ Respiration Test (continued)

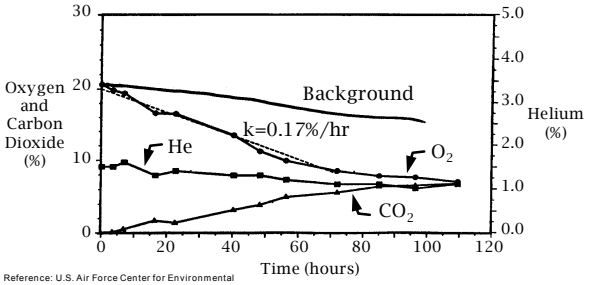
2. Aerate (air + helium) for 1-2 days, until soil gas levels steady
3. Shut off aeration
4. Monitor O_2, CO_2, and He with time

In Situ Respiration Test Apparatus



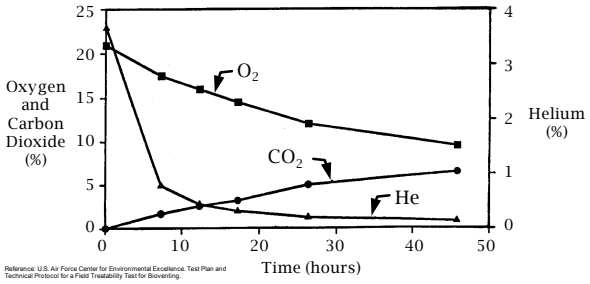
Reference: Hinchee, R.E. and S.K. Ong. 1992. J.Air Waste Management Association (42)10:1035-1312.

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



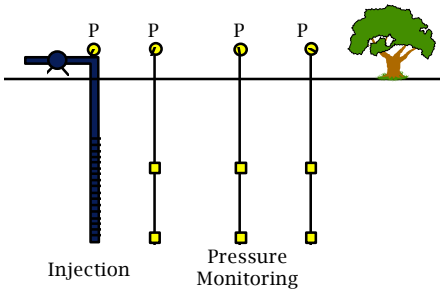
Reference: U.S. Air Force Center for Environmental Excellence. Test Plan and Technical Protocol for a Field Treatability Test for Bioventing.

Soil Gas Permeability Test

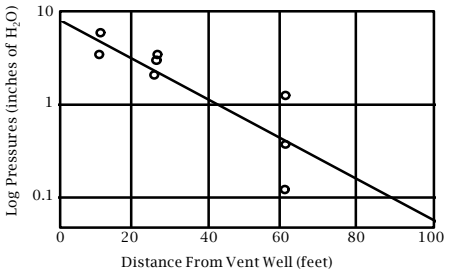
Purpose:

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

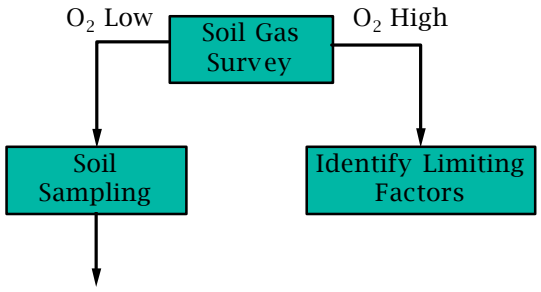
Radius of Influence Test



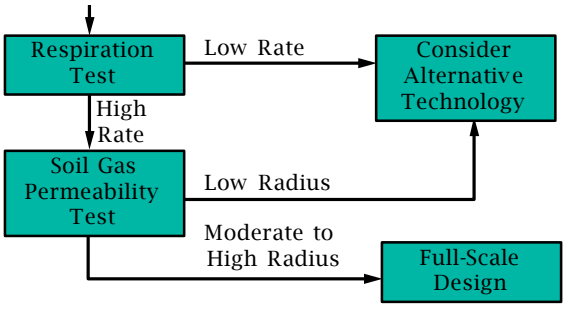
Radius of Influence Data, Saddle Tank Farm, Galena AFS, Alaska



Bioventing Decision Tree



Bioventing Decision Tree (continued)



Full-Scale Design

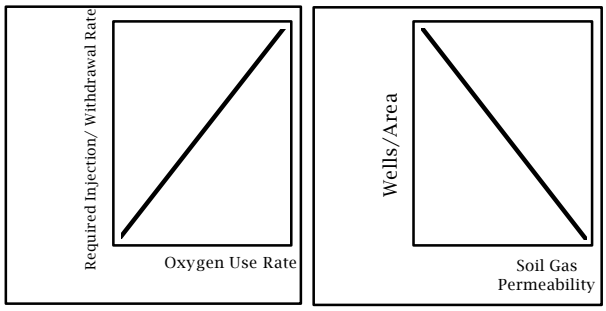
- Air flow rate
- Wells/Area
- Air injection vs. withdrawal
- Other well configurations

Flow Rate and Wells

Using
- O_2 use rate
- Radius of influence

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

Design Approach

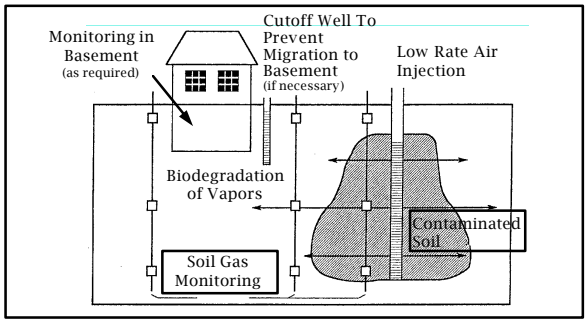


Injection vs. Withdrawal

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

But, be careful of subsurface structures!

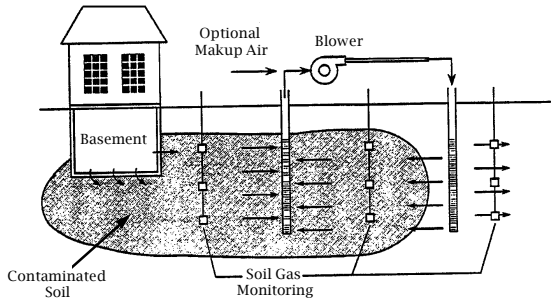
Conceptual Layout for Bioventing Process with Air Injection Only



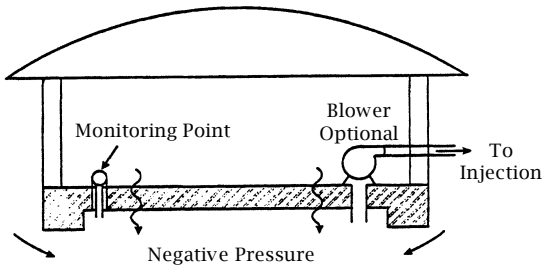
Other Configurations

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)

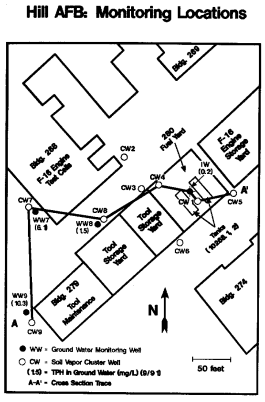
- Respiration tests at least semi-annually
- Operate year round
- t = end determined by rate → 0

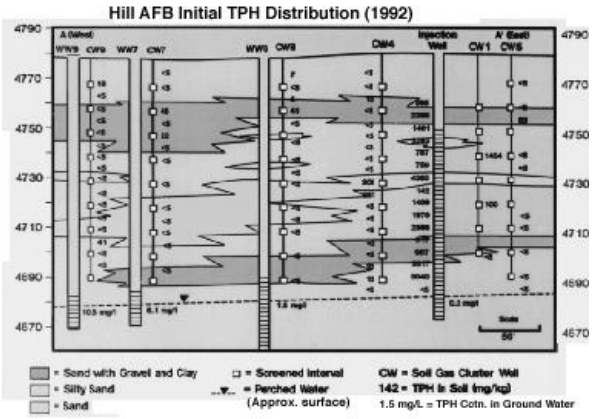
Results From the Field

- 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





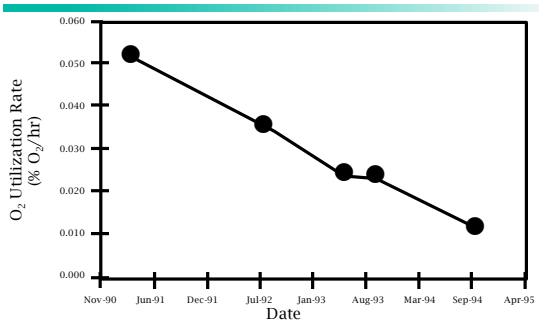
HILL AFB Site 280 - Operations

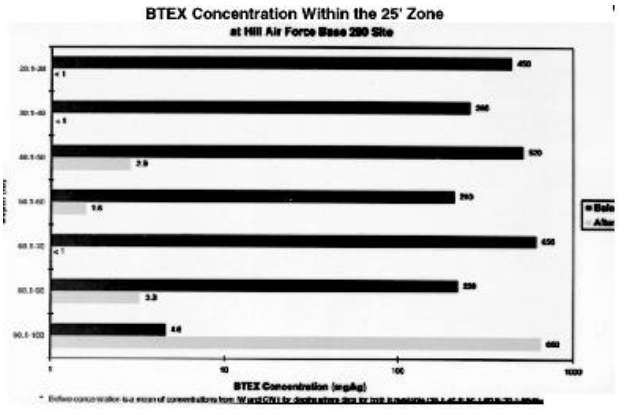
Injection pressure = 0.8 psig

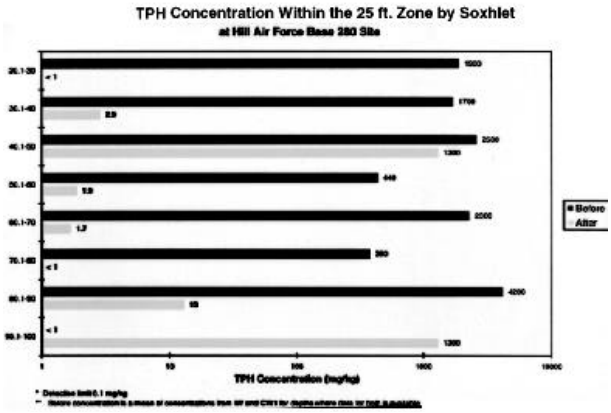
Monthly soil gas monitoring

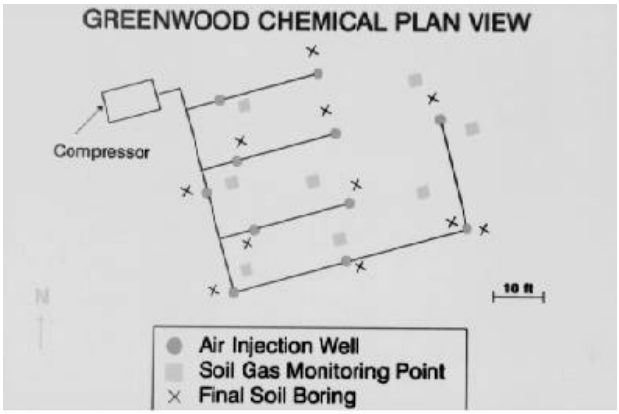
Periodic in-situ respiration tests, surface emissions tests

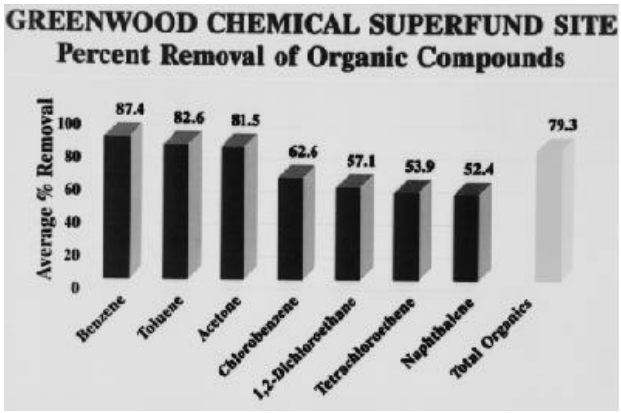
Mean Oxygen Utilization Rate vs. Time Within the IW 25-ft Zone at Hill Air Force Base 280 Site











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

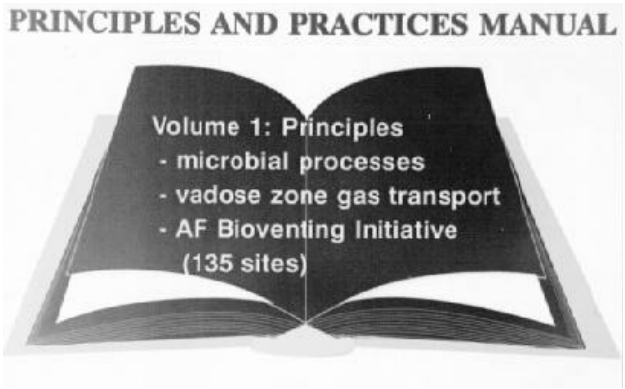
* "Bioventing Performance and Cost Summary," AFCEE, July 1994.

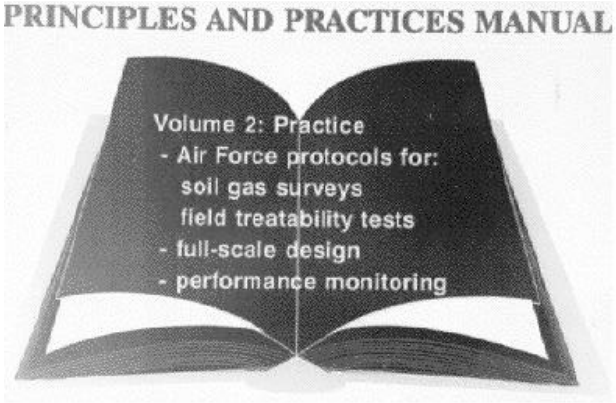
Example (continued)

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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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.

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Bioremediation of Sediments

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F. J. Mondello
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

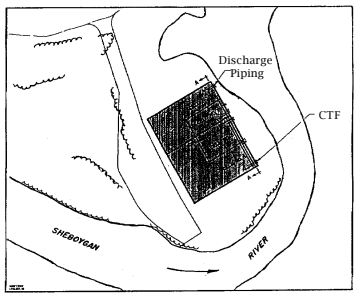


Table 1. CTF Bioreactor Cells

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

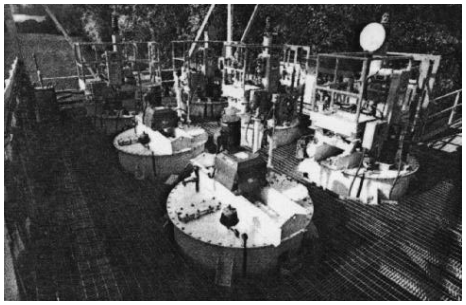


Table 2. In Situ Slurry Reactor Experimental Design

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

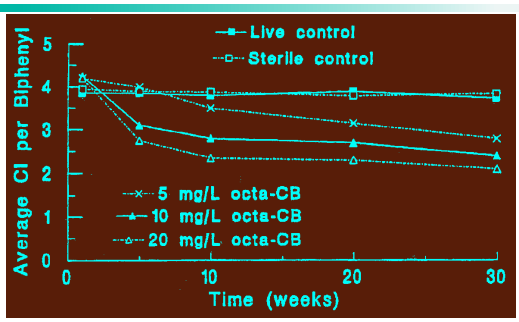


Figure 4. Congener Homologs in Sheboygan River Sediments

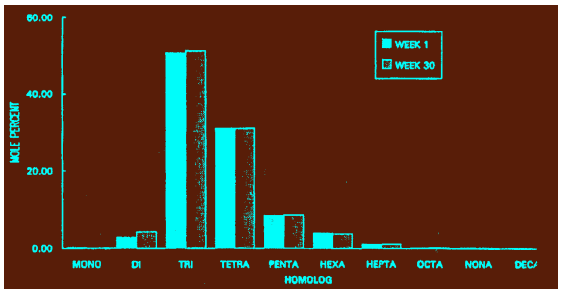


Figure 5. Congener Transformation by Octachlorobiphenyl Amendment

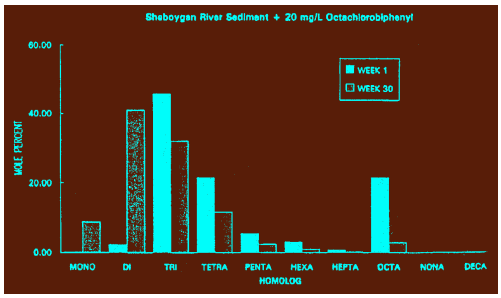
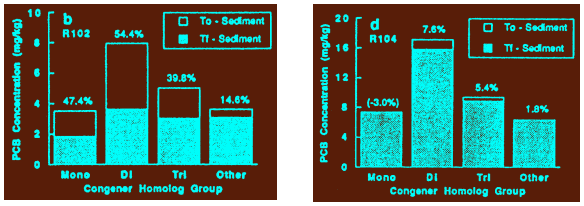


Table 5. PCB Transformations in Hudson River Sediments

	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

Presented by
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Acknowledgements

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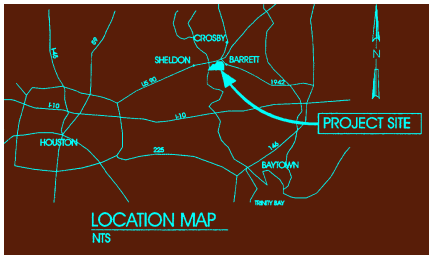
French Limited Waste Disposal Site

- 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

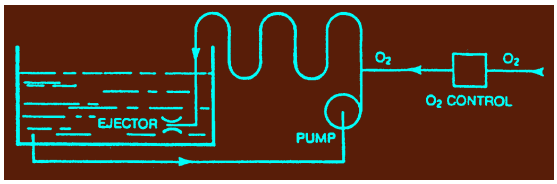


Table 1. Comparison of Mixflow and Fine Bubble Aeration

	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

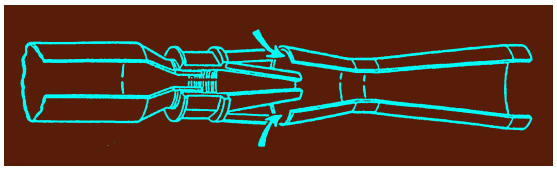


Table 2. Performance of Indicator Compounds

	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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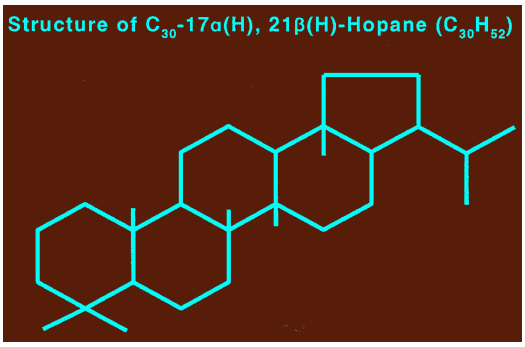
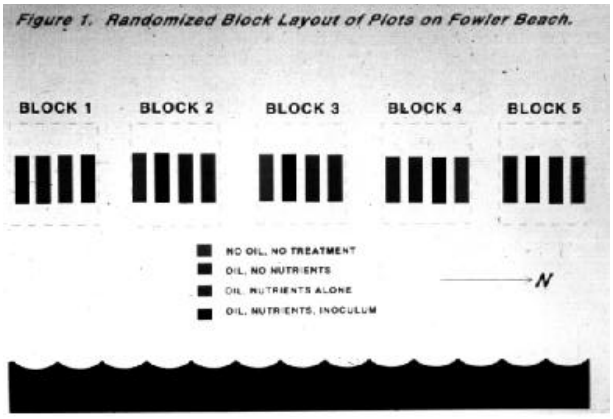
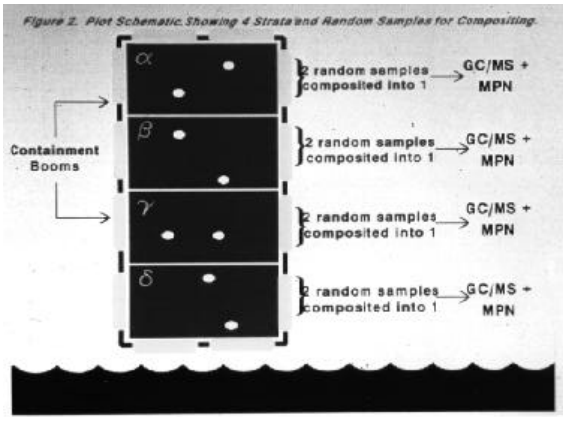
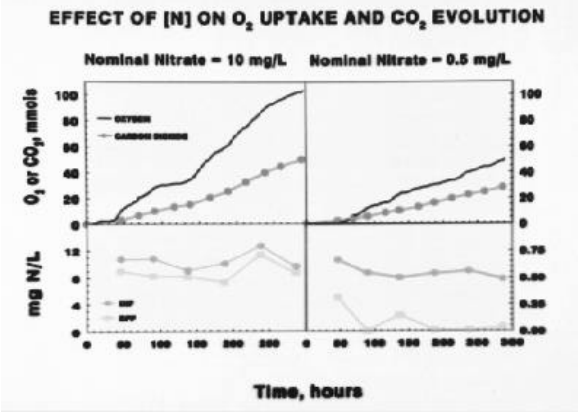
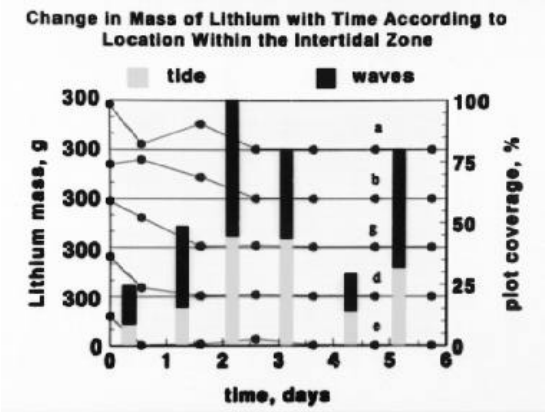
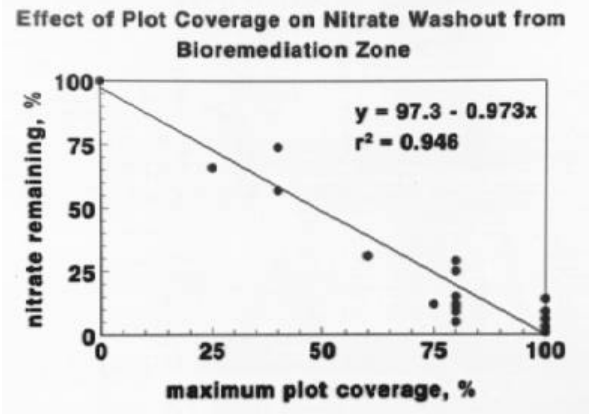






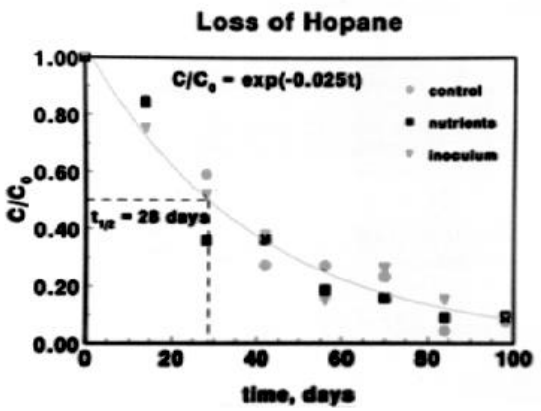


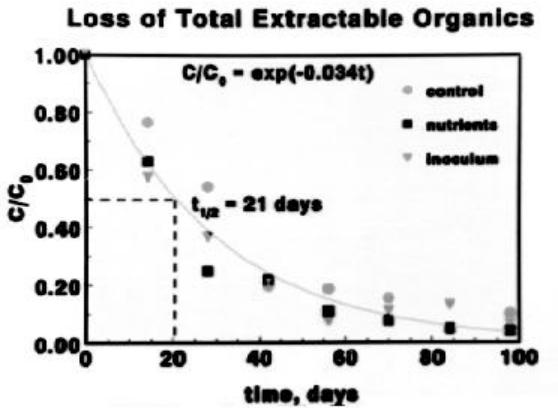


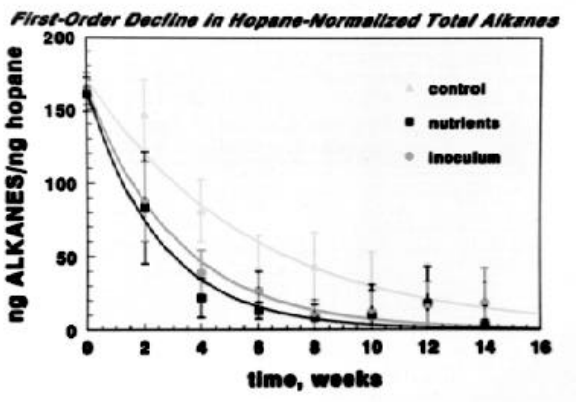


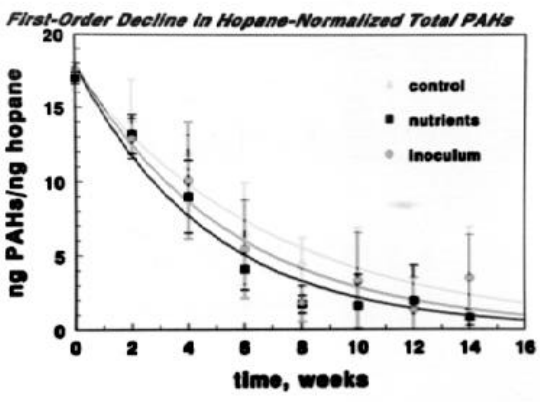
Average and Standard Deviation of Nitrate-N Concentrations for the 3 Treatments

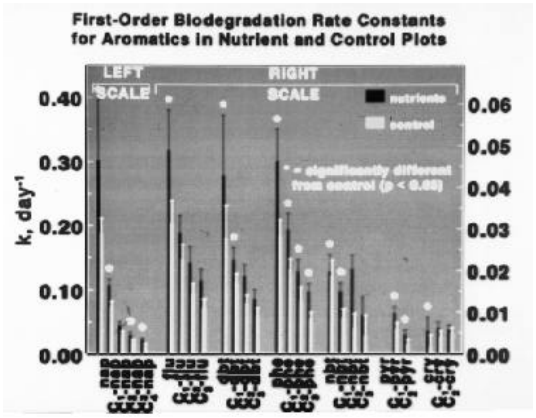
Treatment	Avg., mg/L	SD, mg/L
Control	0.8	0.3
Nutrients	6.4	2.7
Inoculum	3.5	1.7

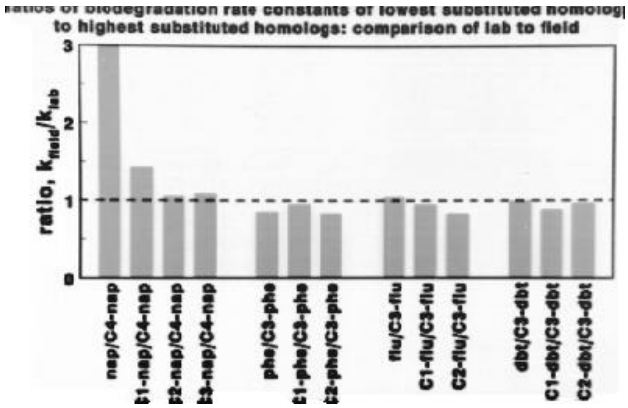









First-Order Biodegradation Rate Constants
for Aromatics in Nutrient and Control Plots
LEFT
SCALE
RIGHT
SCALE
nutrients
control
* = significantly different
from control (p < 0.05)
k, day-1
0.40
0.30
0.20
0.10
0.00
0.06
0.05
0.04
0.03
0.02
0.01
0.00


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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Ada, OK

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
Dynamac Corporation, Ada, OK

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

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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

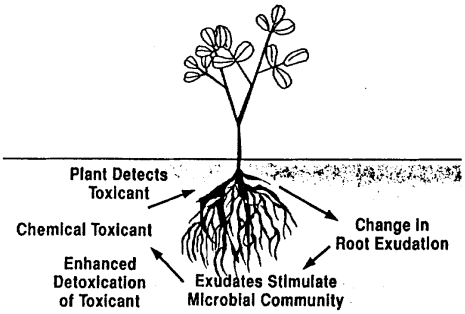


Figure 2. Diagram of Phyto-remediation

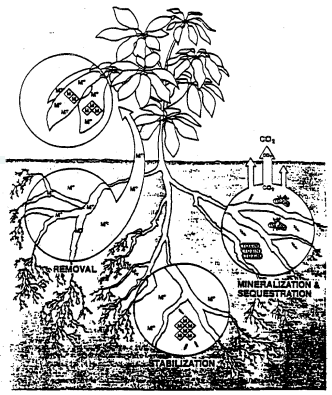


Table 1. Examples of Metal Hyperaccumulators

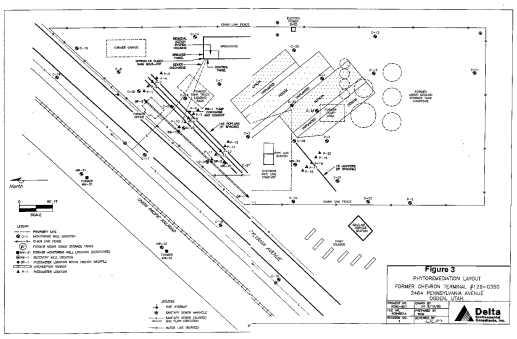
Metal	Plant Species	Metal in Dry Weight of Leaves (%)	Original Location
ZN	Thlaspi calaminare	<3	Germany
	Viola species	1	Europe
Cu	Aeolanthus biformifolius	1	Zaire
Ni	Phyllanthus serpentinus	3.8	New Caledonia
	Alyssum bertoloni and 50 other alyssum species	>3	Southern Europe and Turkey
	Sebertia acuminata	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

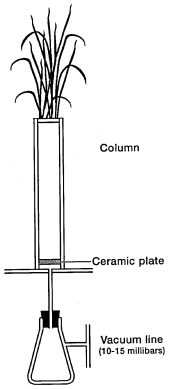
Site Map



Phytoremediation uses slightly modified standard agronomic practices

Treatability study in greenhouse to determine best species for site

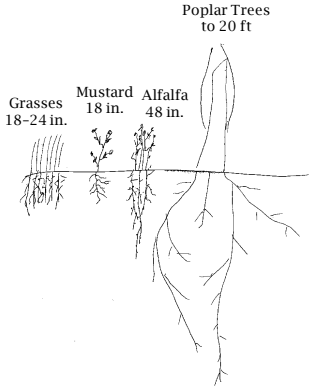
Schematic of Soil Column



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

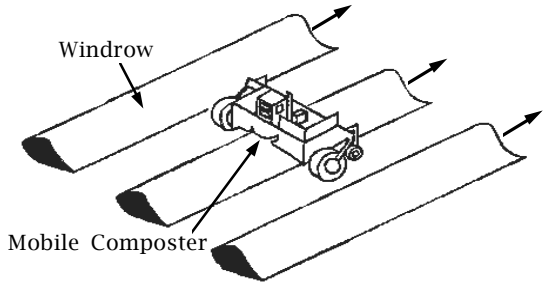
TYPES OF COMPOST OPERATIONS

Static Pile
- Forced air

Windrow (Turned Pile)
- Turn pile periodically to aerate

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

Windrow Compost System



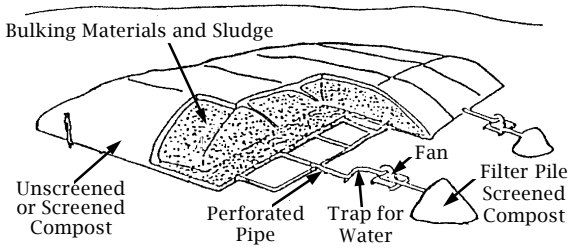
ADVANTAGES Windrow Systems

- 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

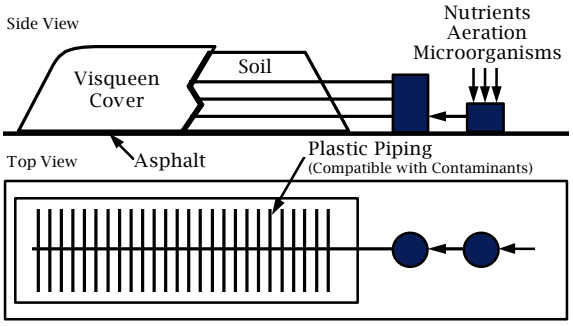
- Not space efficient
- Equipment maintenance cost can be significant
- Aeration is highly dependent on operator skill
- Subject to changing climate conditions unless covered
- Demands significant moisture control
- Requires large volume of bulking agent
- Poor control of pollutant treatment rate in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

Schematic Diagram of Extended Aerated Pile



Composting Extended Piles with Forced Aeration

Static Pile Composter

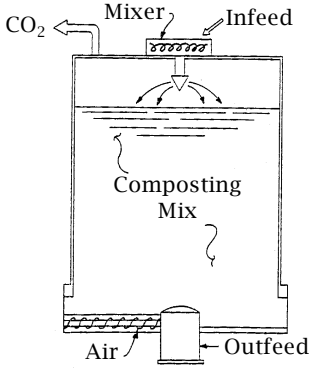


ADVANTAGES
Static Pile Systems

- **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

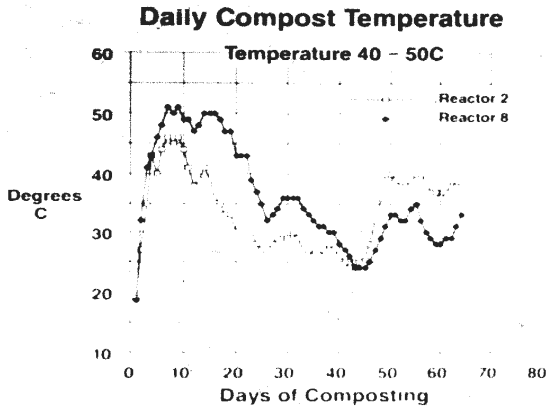
PAH contaminated soil from Reilly Tar Pit Superfund Site, St. Louis Park, MN

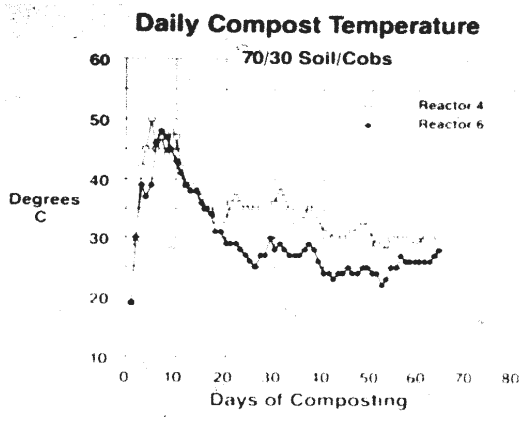
Soil blended with ground corn cobs (bulking)

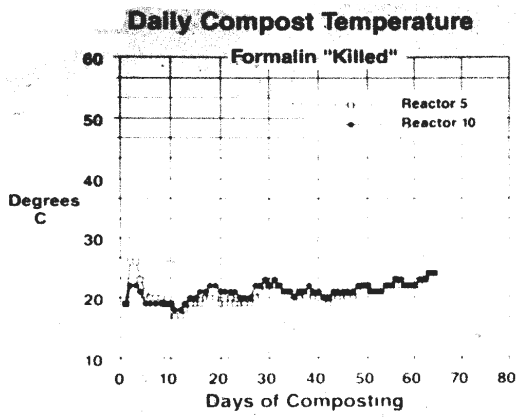
Reactor contents mixed daily

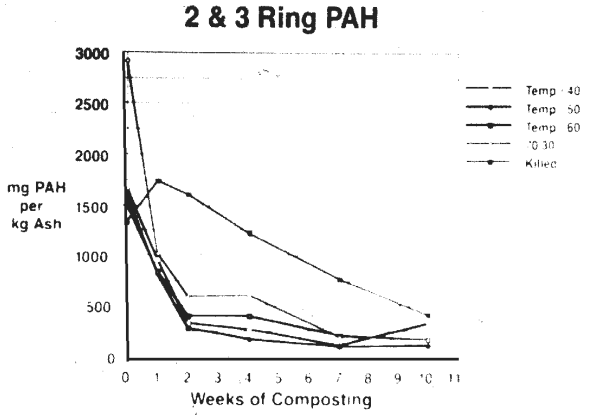
Moisture: 40% – 50%

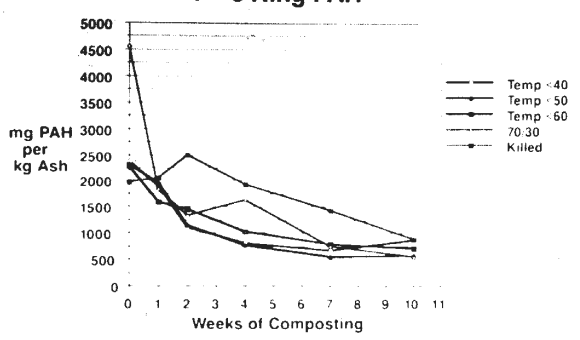
Air flow:
Regular: 5 l/min
High: 50 l/min (for cooling)

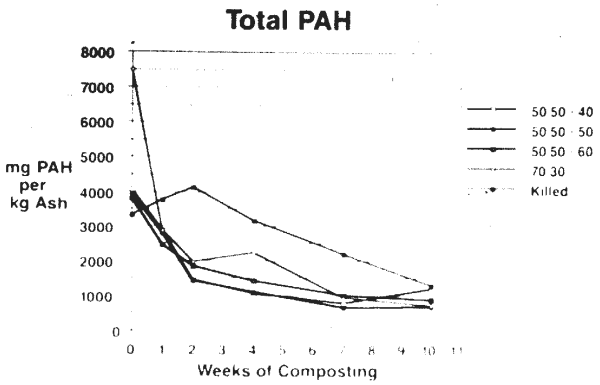












Conclusions

- 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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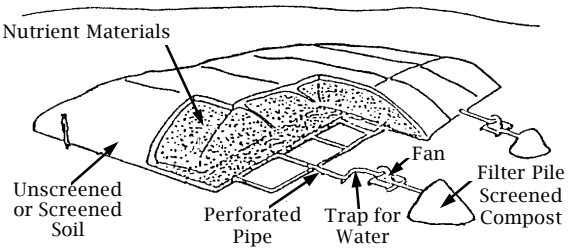
Schematic Diagram of Extended Aerated Pile



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

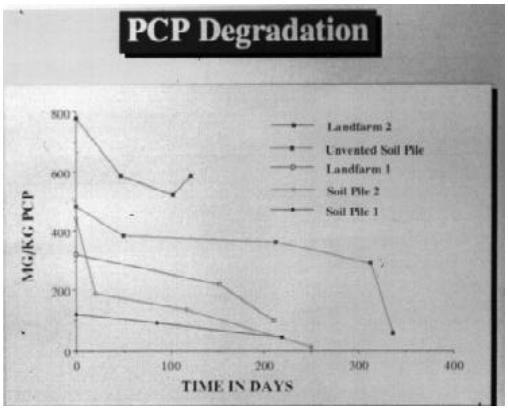
Bioremediation Cost
- Type of contaminants (biodegradability)
- Contaminant concentrations (time required)
- Typically $50 to $100/ton of soil

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

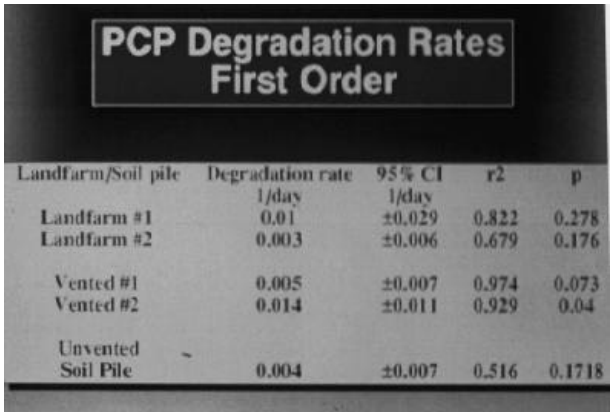
Field Example

- 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 μg/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 μg/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

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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

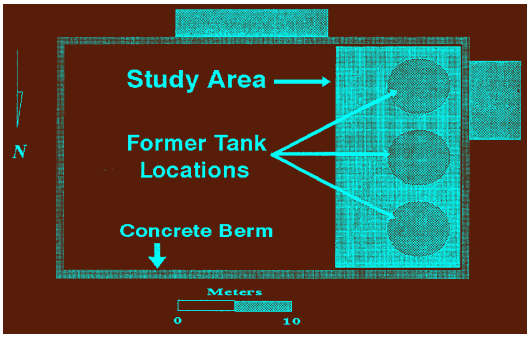
- Lignin peroxidases (LIPS)
- Manganeses-dependent peroxidases (Mn Ps)
- Laccases

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

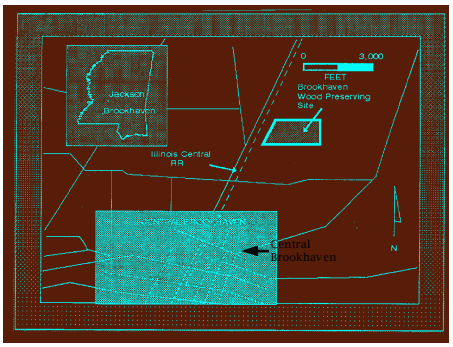


Table 5. Mississippi Soil Characteristics

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

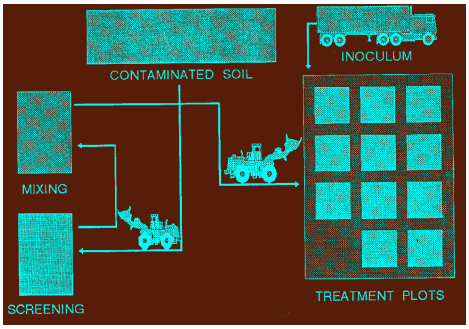


Table 6. Mississippi Experimental Design

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

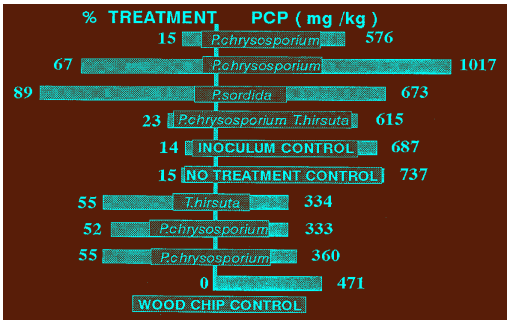


Table 7. Transformation of PAHs

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

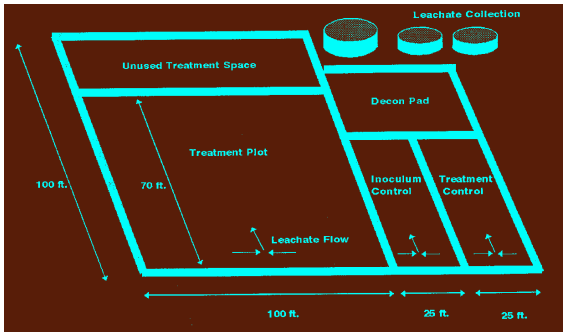
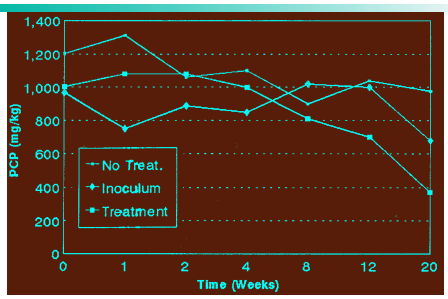


Figure 6. Pentachlorophenol Depletion



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

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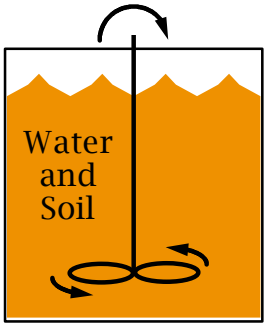
Slurry Bioreactors

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

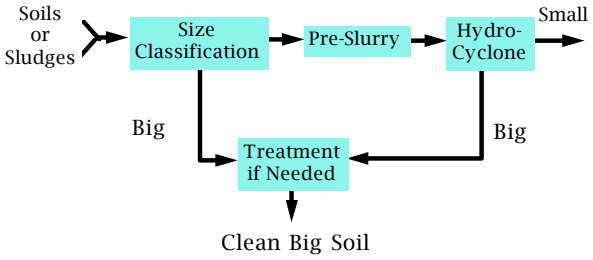
Bioreactor Feed Characteristics

- 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

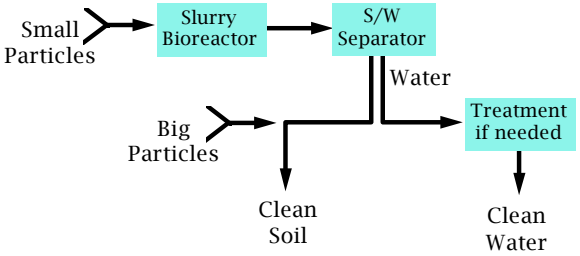
Contaminated Soil Characterization Requirements

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)



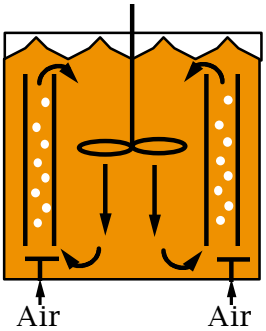
Reactor Configurations

- 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

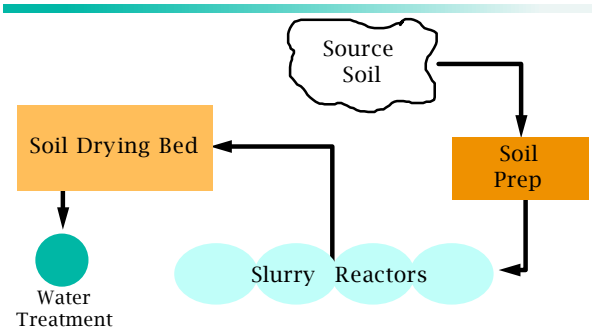
Examples of Slurry Bioreactor Use in the U.S. (continued)

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

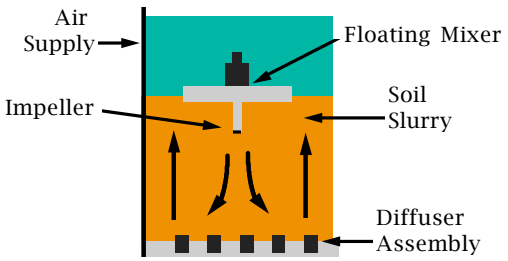
Canton Site Layout



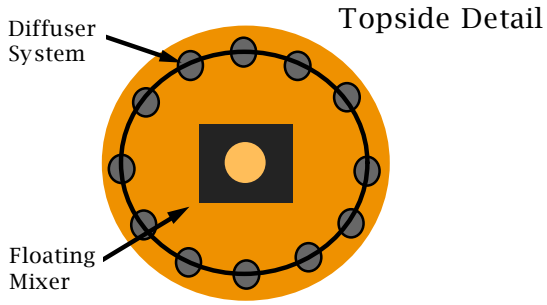
Contaminated Material Size Fractions

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

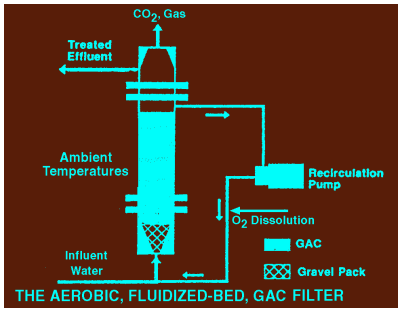
Fixed Film Support Media

- 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

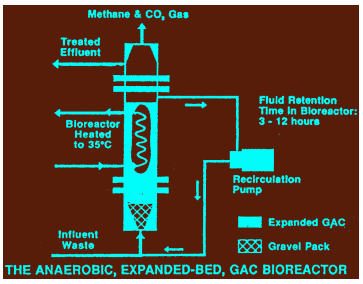


Figure 3. Commercial Biofilters

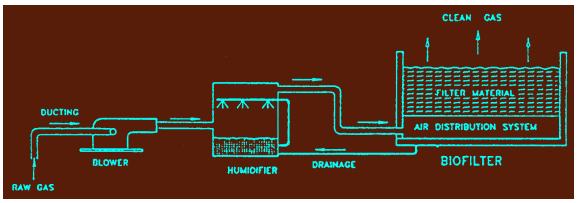
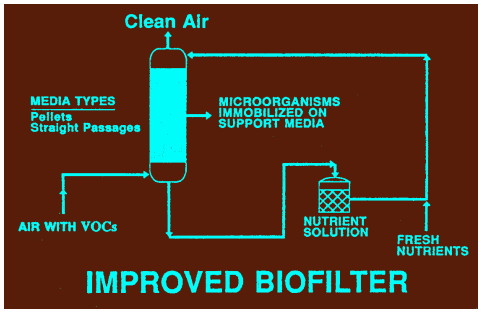


Figure 4. Trickling Biofilters



Commercial Biofilter Characteristics

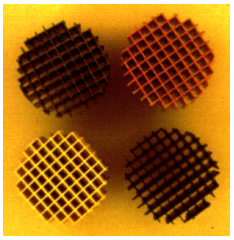
- VOC destruction unlike some control technologies
- Some VOC poorly removed
- Low energy usage
- Efficient moisture control essential
- Plugging at high VOC loading
- Periodic media replacement

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

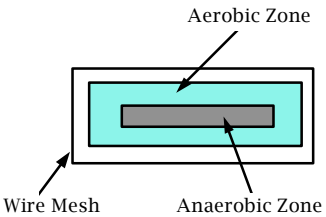


Table 1. BTEX Removal in a Fluidized-Bed GAC Reactor

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

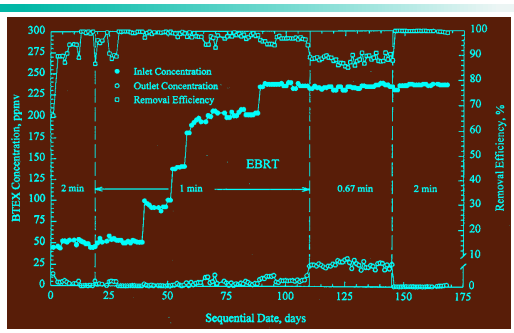


Figure 7. Biofilter Performance on Individual BTEX Components

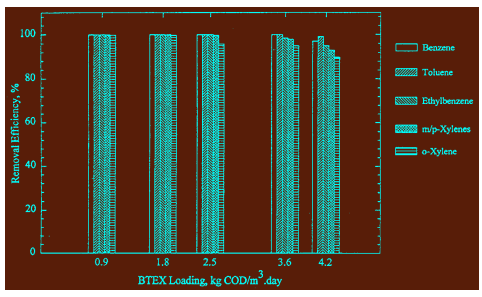


Figure 8. Typical Toluene Removal Recovery Following Biofilter Backwashing Cycle

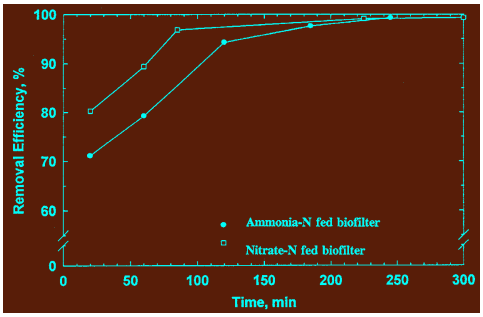


Figure 9. Life Cycle Cost Comparison

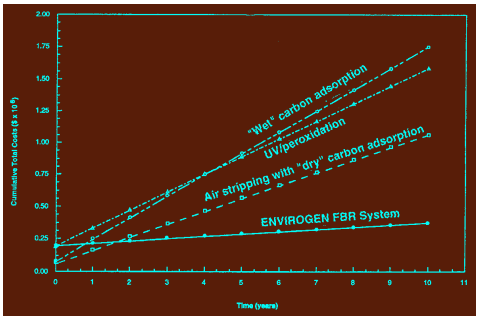


Figure 10. Cost Comparison

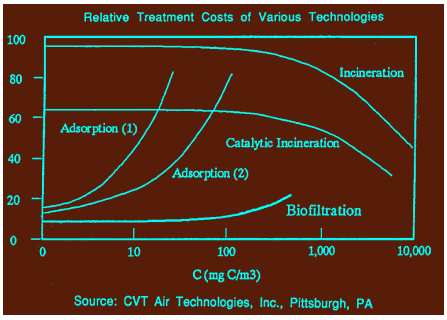


Figure 11. Comparison of Total Capital Investment (TCI) for Biofilters (Three Residence Times) and RTO

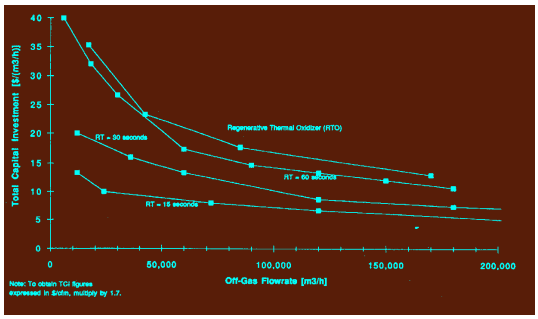
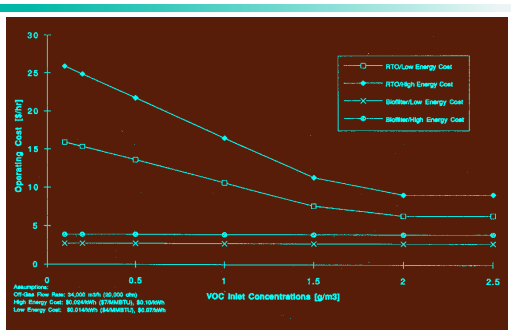


Figure 12. Comparison of Energy Cost for Biofilters and RTO



Suspended Growth Bioreactors

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Introduction

Suspended growth bioreactors are standard technology for treating organic contaminants in aqueous and waste sludge systems. The reactors use microbial metabolism under aerobic, anaerobic, or sequential anaerobic/aerobic conditions to biosorb organic compounds and biodegrade them to innocuous residuals. The microbial activity in the systems produces biomass that is removed by gravity sedimentation, with a portion of the settled biomass recycled to maintain a desired mixed liquor suspended solids concentration in the bioreactor. The excess biomass is wasted to a sludge disposal process. Reactor configurations include sequencing batch reactors (SBRs), completely mixed activated sludge systems, plug flow activated sludge systems, and aerobic and anaerobic digestors.

The reactor systems used to efficiently treat hazardous wastes in aqueous streams or sludges require sufficient amounts of organic carbon in the stream or sludge to support a stable microbial culture in the bioreactor (i.e., at least 5 to 10 pounds influent biochemical oxygen demand [BOD] per day per 1,000 cubic feet of bioreactor volume and at least 100 pounds influent volatile suspended solids [VSS] per day per 1,000 cubic feet of aerobic or high-rate anaerobic digester volume) (1). Conversely, influent concentrations and/or loadings of hazardous wastes high enough to cause inhibitory effects and process performance disruption must be avoided. Typical loading ranges for suspended growth processes (1) are shown in Tables 1 and 2.

The restrictions noted above limit application of suspended growth reactors in hazardous waste biotreatment, although addition of powdered activated carbon to a bioreactor (1) may expand the application area. Thus, ground water or leachates contaminated with low levels of BOD often will not be efficiently treated at the contaminated source by onsite suspended growth bioreactors without the addition of supplemental organic carbon. With this limitation, an alternative approach for treatment of dilute hazardous waste streams in suspended growth bioreactors can be considered. The dilute waste stream can be discharged to a central wastewater treatment plant (with plant management approval) for combined offsite treatment with municipal wastewater.

Representative Reactor Systems

A typical system for onsite treatment (2) of aqueous waste streams (Figure 1) for leachates or highly contaminated ground water includes an equalization tank, a splitter box, and a contact stabilization activated sludge process with a secondary clarifier. Ancillary processes include a waste sludge digester with supernatant return to the equalization tank and a volatile organic compound (VOC) stripper for unproved management of poorly degradable VOCs in the aqueous effluent. This

relatively complex biosystem may also require tertiary treatment processes such as sand filtration and/or carbon adsorption to meet effluent discharge standards. Carbon adsorption may also be applied to VOC stripper air discharges, if required.

The alternative approach of discharging the hazardous waste stream to a central wastewater treatment plant (3), if available, offers more cost-effective biotreatment. U.S. Environmental Protection Agency (EPA) evaluated such an approach in two pilot clarification/activated sludge systems (Table 3) typical of continuous plug flow municipal wastewater treatment plants. One bioreactor was operated at a sludge retention time (SRT) of 4 days, the other at an SRT of 8 days. The municipal wastewater fed to the systems was spiked with up to 28 hazardous organic compounds. The spiked concentrations in the wastewater were less than or equal to 0.25 mg/L and less than or equal to 0.5 mg/L for the 4- and 8-day SRT systems, respectively. Finally, the sludges produced in the municipal pilot system receiving wastewater with 0.5 mg/L of spiked contaminants were treated in pilot anaerobic digesters to evaluate the impact of the hazardous contaminants in the wastewater sludges on the anaerobic digestion process (4). Three completely mixed pilot-scale digesters (Figure 2) maintained at 35.5°C with a 30-day solids retention time were used to simulate typical digester operation. Two of the digesters were fed contaminated primary and secondary sludges from the pilot study. The third digester (used as a control) was fed similar sludges without the hazardous organic contaminants.

Performance and Conclusions

The onsite activated sludge system achieved moderate to high removal efficiencies (Table 4) of benzene, toluene, ethyl benzene, and xylenes (BTEX) and low to high removals (Table 5) of chlorinated solvents (2). The performance of the complex onsite system suggests that tertiary treatment may be necessary if stringent effluent discharge standards are required. Alternative fixed film bioreactors, in general, would provide superior and more cost-effective bioremediation.

The alternative approach, evaluated by EPA, of discharging contaminated ground water or leachates to a central wastewater treatment plant generally resulted in high removals (Tables 6 and 7) of the influent hazardous contaminants (3). Removals were superior to those provided by the onsite activated sludge system. The two treatment systems were not identical, however, and did not treat the same contaminants. The superior performance at the central plant may have been related to more effective biomass generated by the large amount of easily degradable organic substrate in the municipal wastewater. In any event, the complex onsite system will exhibit substantially increased costs per unit of contaminant removed when compared with costs at central treatment plants.

The performance of anaerobic digestion on the contaminated sludges from the pilot study evaluating the central treatment plant alternative was compared with that of a control digester (4). Gas production and solids reduction for digestion of contaminated sludges and control sludges were nearly identical. Degradation of the hazardous contaminants (Table 8) was apparent. Twelve chemicals appeared consistently in the digester treating contaminated sludge, and, at steady state,

contaminant degradation or transformation ranged from 93 to 98 percent. Sorption into the digester solids also was an important removal mechanism, especially for aromatics.

EPA generated an integrated model for predicting the fate of organics in wastewater treatment plants (5), which includes components for stripping or volatilization, sorption on solids, and biodegradation. The biodegradation component (6) includes a structural activity group contribution method for estimating contaminant biodegradation kinetics.

The experimental data generated by the EPA studies described above were used to successfully validate the integrated model.

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2. Nelson, C., et al. 1993. Reactors for treatment of solid, liquid, and gaseous phases. In: Proceedings of Seminars on Bioremediation of Hazardous Waste Sites: Practical Approaches to Implementation. EPA/600/K-93/002. Washington, DC.

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Suspended Growth Reactors

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Suspended Growth Bioreactor Configurations

- Completely mixed activated sludge systems (continuous wastewater feed)
- Plug flow activated sludge systems (continuous wastewater feed)
- Sequencing batch reactors (batch wastewater feed)
- Aerobic digesters (batch or continuous sludge feed)
- Anaerobic digesters (batch or continuous sludge feed)

Table 1. Activated Sludge Loading Ranges

Reactor Configuration	Detention Time (hr)	Volumetric Loading (lb BOD/day/1,000 ft³)
Plug flow (conventional)	4–8	20–40
Completely mixed	3–5	50–120
Step feed	3–5	40–60
Contact stabilization	1.5–3	60–75
Extended aeration	18–36	10–25
SBR	12–50	5 –15

Table 2. Sludge Digester Loading Rates

Sludge Digester Type	Retention Time (day)	Solids Loading (lb SS/day/1,000 ft³)
Aerobic		
Waste activated sludge (WAS)	10–15	100–300
Primary + WAS	15–20	100–300
Standard-rate anaerobic	30–60	40–100
High-rate anaerobic	15–20	100–200

Applications of Suspended Growth Reactors

- Onsite applications limited to moderate or high strength leachates or ground water
- Inhibitory concentrations of hazardous wastes can prevent onsite application
- PAC addition to activated sludge reactors can extend onsite inhibitory waste applications
- Alternatively, ground water and leachates can be routed to and processed at central wastewater treatment plants

Figure 1. Onsite Activated Sludge System

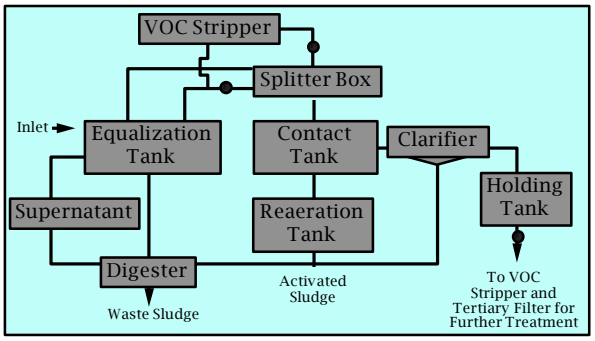

Table 3. Conventional Operating Performance of Pilot Systems*

	% Removals			
	4-day SRT		8-day SRT	
Component	Continuous	Intermittent**	Continous	Intermittent**
TSS	97	97	95	94
COD	82	81	88	87
NH_4-N	76	81	88	98

*Feed to systems was Mill Creek municipal wastewater at the EPA Test and Evaluation Facility in Cincinnati, OH

**Continous or intermittent hazardous contaminant addition

Figure 2. Pilot Digester System

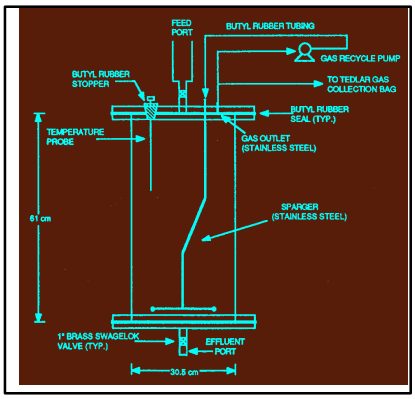

Table 4. Representative Onsite Activated Sludge System Performance for BTEX Compounds

Compound	Influent Conc. (ppb)	% Removal
Benzene	120	78
Toluene	1,000	89
Ethylbenzene	270	94
Xylenes (total)	700	95

Table 5. Representative Onsite Activated Sludge System Performance for Chlorinated Compounds

Compound	Influent Conc. (ppb)	% Removal
Chlorobenzene	180	78
Methylene chloride	31	100
Trichloroethane	250	80
1,2-Dichloroethane	100	56
1,2-Dichloropropane	21	67

Table 6. Representative Removals in Acclimated Pilot System Operating at 4-Day SRT

Compound	Influent Conc. (ppb)	% Removal
Toluene	284	99
Xylenes (total)	175	99
Chlorobenzene	255	99
Trichloroethane	201	97
1,2-Dichloropropane	228	77

Table 7. Representative Removals in Pilot System Operating at 8-Day SRT

Compound	Influent Conc. (ppb)	% Removal
Di-n-bytylphthalate	428	96
1,4-dichlorobenzene	391	95
Lindane	425	56
Naphthalene	431	98
1,2,4-trichlorobenzene	655	85

Table 8. Fate of Representative Organics in Digesters

Compound	Feed mg/kg	Fate Mechanism (% Distribution) Sol.	Vol.	Sorpt.	Biodeg.
Di-n-bytylphthalate	270	1	0	3	96
1,4-dichlorobenzene	275	4	16	68	13
Lindane	490	0	0	2	98
Naphthalene	230	4	4	65	27
1,2,4-trichlorobenzene	750	3	5	66	26

Model for Predicting Fate of Organics in Wastewater Treatment

- Primary sedimentation mass balances
- Mass balances in secondary treatment
  - Biodegradation
  - Sorption
  - Volatilization (diffused aeration)
  - Stripping (surface aeration)
- Group contribution method for estimating biokinetics

Natural Attenuation:
Site Characterization Attenuation of Petroleum Hydrocarbons and Solvents in Ground Water

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Two Basic Questions for Bioremediation

- When to start?
- When to stop?

When to Stop?

- When proactive remediation is no longer doing any good
- When proactive remediation is no faster than intrinsic remediation or natural attenuation

After Proactive Remediation

Is the spread of contamination contained by natural attenuation?

- Yes? Go into long-term monitoring
- No? Implement another approach

Natural Attenuation or Passive Bioremediation

- The preferred description is natural attenuation
- All bioremediation is “natural”
- Neither the microorganisms nor the microbiologists are “passive”

Natural Attenuation

Usually implemented as a component of a comprehensive remedial strategy that includes source control or source removal

- Free product recovery
- Soil vacuum extraction
- Bioremediation

Natural Attenuation

- Determination is site specific
- Requires extensive site characterization
- Requires a risk assessment

Natural Attenuation

- Burden of proof is on the proponent, not the regulator
- Not a default technology or presumptive remedy
- Not complete until goals of the regulatory agency have been reached to their satisfaction

Patterns of Natural Bioremediation

- Limited by supply of a soluble electron acceptor
  - Aerobic respiration
  - Nitrate reduction
  - Sulfate reduction
- Controlled by mixing processes (bioplume)

Patterns of Natural Attenuation

- Limited by biological activity
  - Iron reduction
  - Methanogenesis
  - Sulfate reduction
- First-order kinetics

Patterns of Natural Attenuation

- Limited by supply of electron donor
- Reductive dechlorination
- Controlled by supply of electron donor

Initial Elements of a Quantitative Assessment of Natural Attenuation

1. Thoroughly delineate the extent of contaminated ground water
2. Determine trajectory of ground-water flow
3. Install monitoring wells along plumes

Additional Elements of a Quantitative Assessment of Natural Attenuation

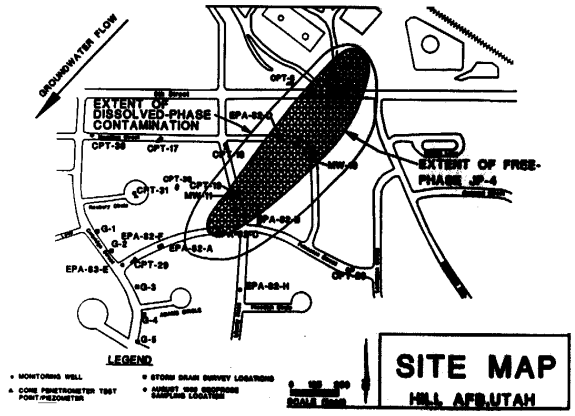
4. Determine apparent attenuation along plumes
5. Correct apparent attenuation for dilution or sorption
6. Assume corrected attenuation is bioattenuation
7. Confirm bioattenuation from stoichiometry of electron acceptors or donors

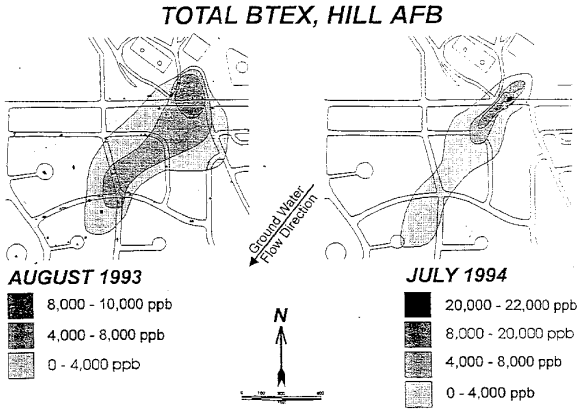
Lines of Evidence

- Documented loss of contaminants at the field scale
- Geochemical indicators
- Laboratory microcosm studies, accumulation of metabolic end-products, volatile fatty acids, FAME

Document Occurrence of Natural Attenuation

- Use geochemical data to support natural attenuation
- Trends during biodegradation (plume interior vs. background concentrations)
  - Dissolved oxygen concentrations below background
  - Nitrate concentrations below background
  - Iron II concentrations above background
  - Sulfate concentrations below background
  - Methane concentrations above background





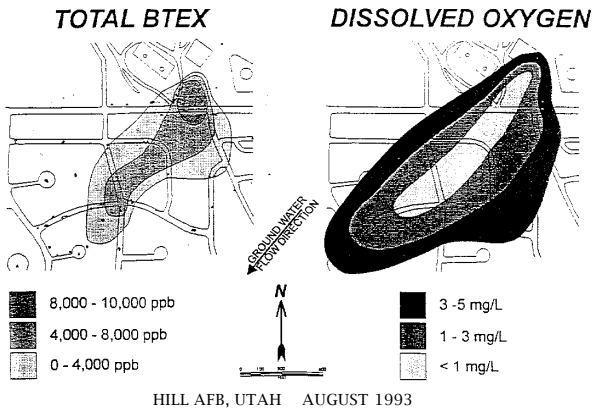
Benzene Oxidation Aerobic Respiration

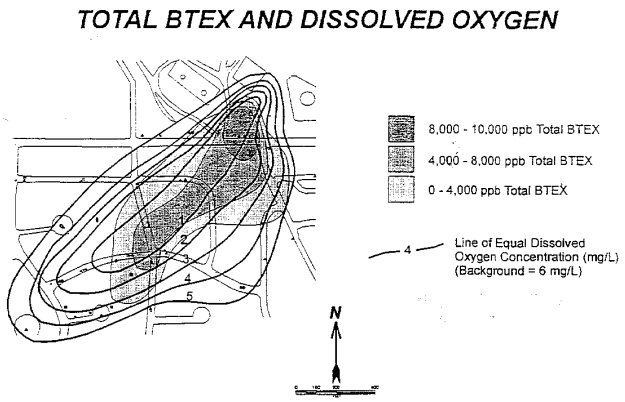
$$7.5\ O_2 + C_6H_6 \longrightarrow 6\ CO_{2(g)} + 3\ H_2O$$

ΔG°_r = - 3566 kJ/mole Benzene

Mass Ratio of O_2 to C_6H_6 = 3.1:1

0.32 mg/L C_6H_6 Degraded per mg/L O_2 Consumed





Aerobic Biodegradation

Background Dissolved
Oxygen Concentration = 6.0 mg/L

$$\frac{0.32 \text{ mg/L BTEX}}{1 \text{ mg/L } O_2} \quad (6.0 \text{ mg/L } O_2)$$

Assimilative Capacity - Aerobic Biodegradation
1.92 mg/L
1920 µg/L

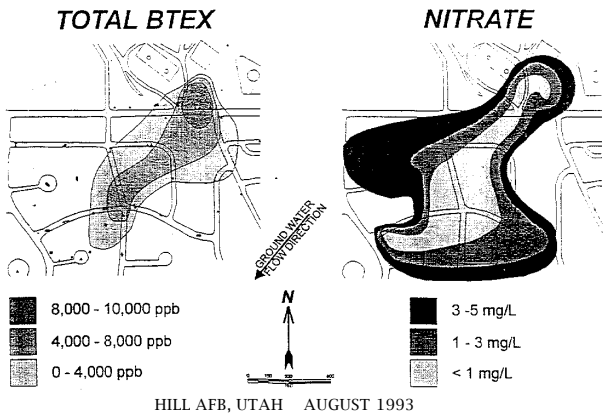
Benzene Oxidation Denitrification

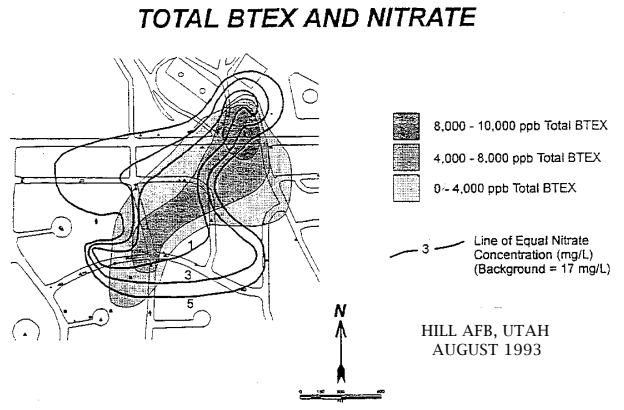
$$6NO_3^- + 6H^+ + C_6H_6 \longrightarrow 6CO_{2(g)} + 6H_2O + 3N_{2(g)}$$

ΔG°_r = - 3245 kJ/mole Benzene

Mass Ratio of NO_3^- to C_6H_6 = 4.8:1

0.2 mg/L C_6H_6 Degraded per mg/L NO_3^- Consumed





Denitrification

Background Nitrate
Concentration = 8.0 mg/L

$$\frac{0.21 \text{ mg/L BTEX}}{1 \text{ mg/L } NO_3^-} \quad (8.0 \text{ mg/L } NO_3^-)$$

Assimilative Capacity - Denitrification
1.68 mg/L
1680 µg/L

Benzene Oxidation
Iron Reduction

$$60H^+ + 30Fe(OH)_{3(a)} + C_6H_6 \longrightarrow 6CO_{2(g)} + 30Fe^{2+} + 78H_2O$$

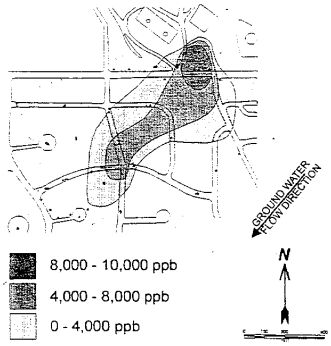
ΔG°_r = - 2343 kJ/mole Benzene

Mass Ratio of $Fe(OH)_3$ to C_6H_6 = 41:1

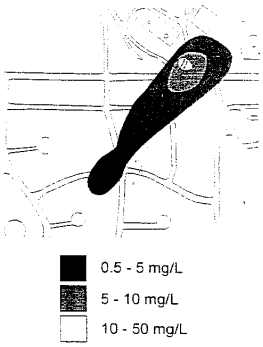
Mass Ratio of Fe^{2+} Produced to C_6H_6 Degraded = 15.7:1

0.06 mg/L C_6H_6 Degraded per mg/L Fe^{2+} Produced

TOTAL BTEX

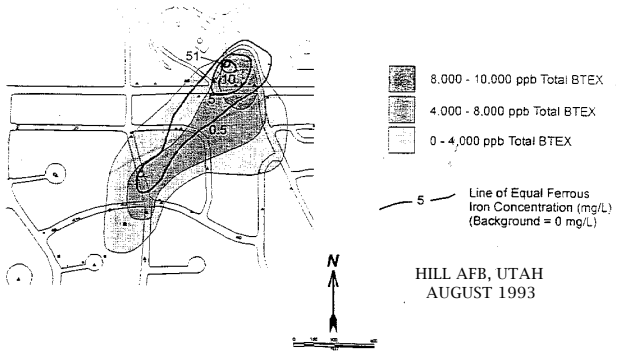


FERROUS IRON



HILL AFB, UTAH AUGUST 1993

TOTAL BTEX AND FERROUS IRON



HILL AFB, UTAH
AUGUST 1993

Iron Reduction

Background Ferrous Iron Concentration = 0 mg/L
Highest Measured Ferrous Iron Concentration = 51 mg/L

$$\frac{0.05 \text{ mg/L BTEX}}{1 \text{ mg/L } Fe^{2+}} \quad (51 \text{ mg/L } Fe^{2+})$$

Assimilative Capacity - Iron
2.55 mg/L
2550 µg/L

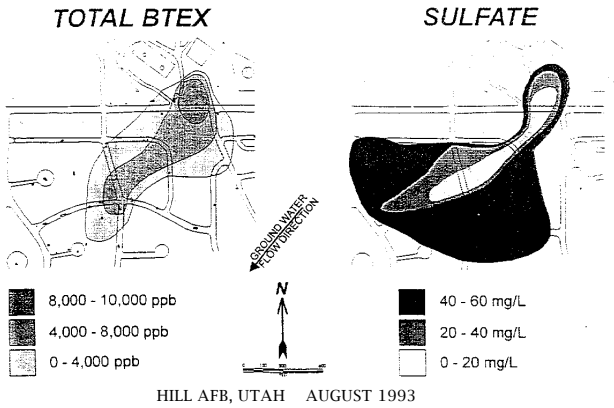
Benzene Oxidation
Sulfate Reduction

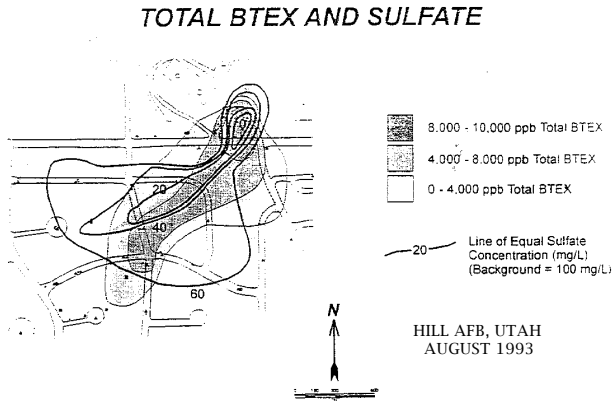
$$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \longrightarrow 6CO_{2(g)} + 3.75H_2S + 3H_2O$$

ΔG°_r = - 340 kJ/mole Benzene

Mass Ratio of SO_4^{2-} to C_6H_6 = 4.6:1

0.22 mg/L C_6H_6 Degraded per mg/L Sulfate Consumed





Sulfate Reduction

Background Sulfate
Concentration = 100 mg/L

$$\frac{0.21 \text{ mg/L BTEX}}{1 \text{ mg/L } SO_4^{2-}} \quad (100 \text{ mg/L } SO_4^{2-})$$

Assimilative Capacity - Sulfate Reduction
21 mg/L
21,000 µg/L

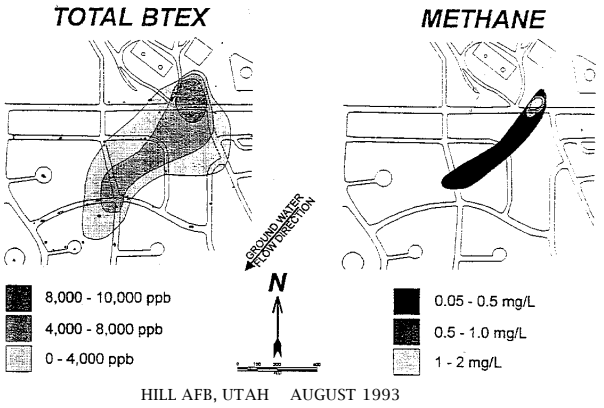
Benzene Oxidation Methanogenesis

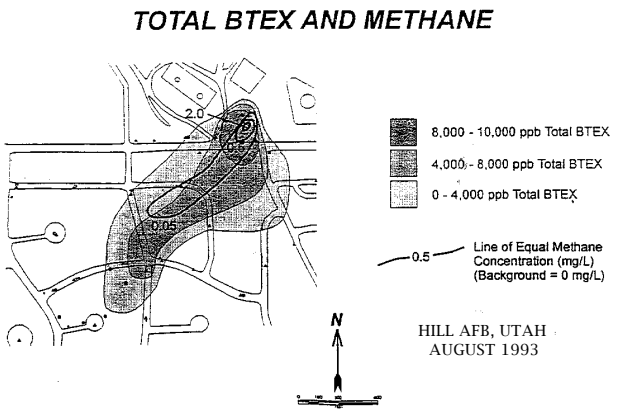
$$4.5\ H_2O + C_6H_6 \longrightarrow 2.25\ CO_{2(g)} + 3.75\ CH_4$$

ΔG^o_r = - 135.6 kJ/mole Benzene

Mass Ratio of CH_4 Produced to C_6H_6 =0.8:1

1.25 mg/L C_6H_6 Degraded per mg/L CH_4 Produced





Methanogenesis

Background Methane Concentration = 0 mg/L

Highest Measured Methane Concentration = 2.0 mg/L

$$\frac{1.28 \text{ mg/L BTEX}}{1 \text{ mg/L } CH_4} \quad (2.0 \text{ mg/L } CH_4)$$

Assimilative Capacity - Methanogenesis

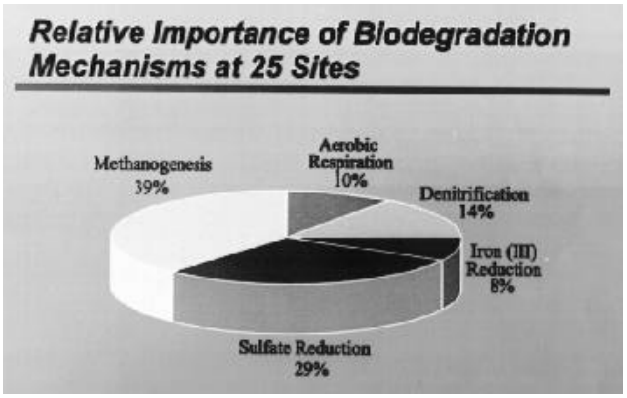
2.56 mg/L

2560 µg/L

Expressed Assimilative Capacity

Hill AFB, Utah

Oxygen	=	1,920	µg/L
Denitrification	=	1,680	µg/L
Iron Reduction	=	2,550	µg/L
Sulfate Reduction	=	21,000	µg/L
Methanogenesis	=	2,560	µg/L
Expressed Assimilative Capacity	=	29,710	µg/L
Highest BTEX Concentration	=	21,475	µg/L



Correcting Attenuation for Dilution or Sorption

Identify a component of the plume that can serve as a tracer

Correcting Attenuation for Dilution or Sorption

To correct apparent attenuation for dilution or sorption, divide the concentration of contaminants by the concentration of a conservative tracer

A Good Tracer

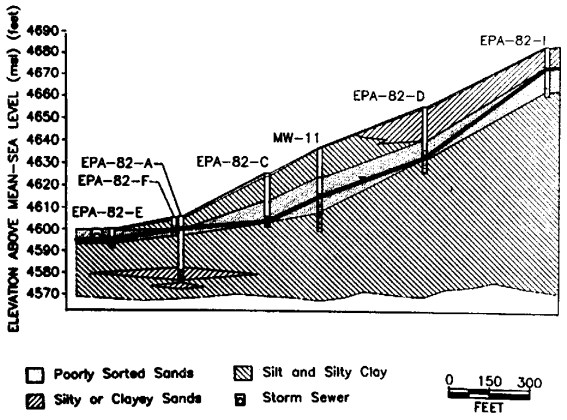
Is not biodegradable in the absence of oxygen

A Good Tracer

Is present in the plume source area at concentrations at least 100 times its detection limit

A Good Tracer

Has the same sorptive properties as the regulated compounds

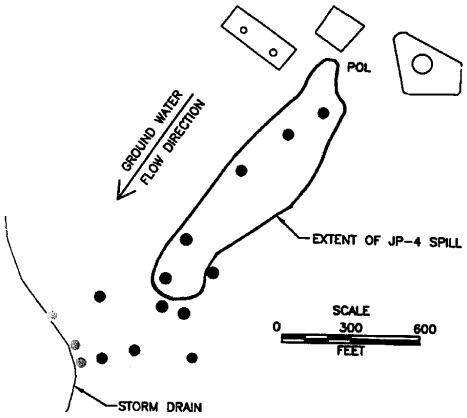


	BTEX & TMB	Oxygen	Nitrate Nitrogen	Sulfate
	(mg/liter)			
82 I	7.7			
MW-11	2.1	0.1	0.4	98
82D	1.3	1.3	0.5	193
82C	2.1	0.5	0.1	50
82F	<0.001	1.1	7.4	64
82E	<0.001	5.6	4.4	40

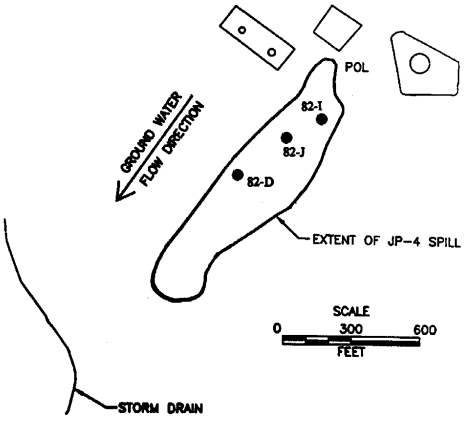
	Benzene	Toluene	Ethyl-benzene	1,2,4-TMB
	(ug/liter)			
82I	2740	327	486	495
MW-11	336	90	139	165
82D	96	10	147	183
82C	4.9	3.1	27	324
82B	<1	4.3	<1	1.4
82F	<1	<1	<1	<1

	p-Xylene	m-Xylene	o-Xylene	1,2,4-TMB
	(ug/liter)			
82I	784	1370	1140	495
MW-11	230	635	204	165
82D	149	383	103	183
82C	43	47	2.6	324
82B	<1	<1	<1	1.4
82F	<1	<1	<1	<1

	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB
	(ug/liter)		
	(percent)		
82I	162	495	240
	100	100	100
MW-11	71	165	69
	44	33	29
82D	129	183	89
	80	37	37
82C	238	324	120
	147	65	50



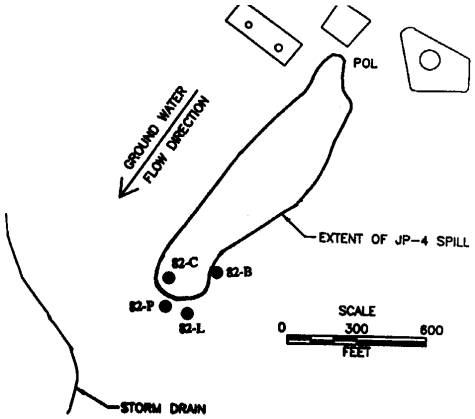
Near Source



	82-I	82-J	82-D
	----- (mg/liter) -----		
Oxygen	0.0		0.2
Nitrate	<0.05	<0.05	<0.05
Sulfate	<0.5	<0.5	<0.5
Iron II	10.3	1.3	7.4
Methane	1.9	0.05	0.002
Alkalinity	491	430	657

	82-I	82-J	82-D
	----- (ug/liter) -----		
Benzene	5600	4260	456
Toluene	5870	3910	10
Ethylbenzene	955	816	454
p-Xylene	1620	1370	272
m-Xylene	5130	4220	442
o-Xylene	2300	1760	51
1,2,4-TMB	1270	1310	176

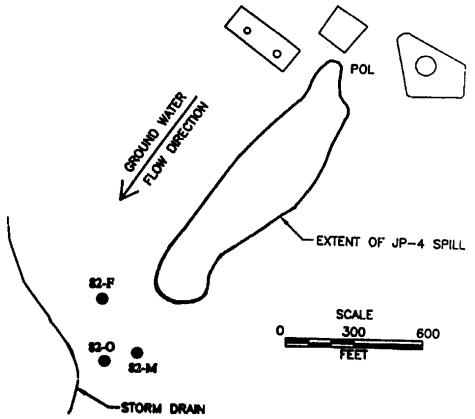
Toe of the Plume



	82-P	82-L	82-B
	----- (mg/liter) -----		
Oxygen	0.1	0.3	0.4
Nitrate	<0.05	<0.05	0.15
Sulfate	<0.5	<0.5	74
Iron II	0.2	2.4	0.1
Methane	0.004	0.018	0.001
Alkalinity	792	730	428

	82-C	82-P	82-L	82-B
	----- (ug/liter) -----			
Benzene	7	<1	6	<1
Toluene	10	<1	18	<1
Ethylbenzene	23	4	103	<1
p-Xylene	26	12	379	<1
m-Xylene	18	17	572	<1
o-Xylene	3	6	604	<1
1,2,4-TMB	143	159	433	<1

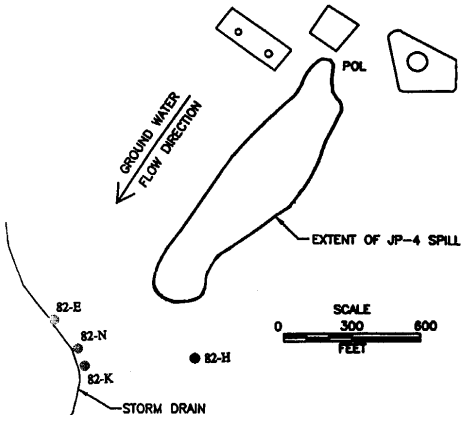
Remediated



	82-F	82-O	82-M
	----- (mg/liter) -----		
Oxygen	0.1	0.2	0.2
Nitrate	1.7	1.6	1.8
Sulfate	52	37	35
Iron II	0.5	<0.05	<0.05
Methane	0.58	0.001	0.12
Alkalinity	490	566	666

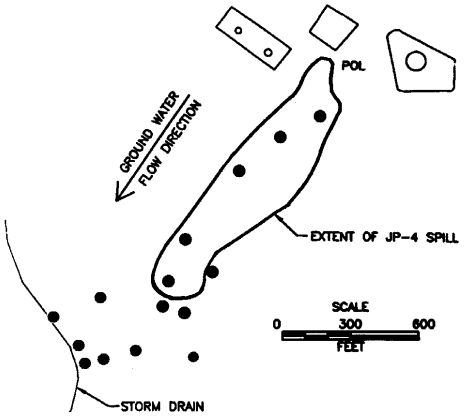
	82-F	82-O	82-M
	----- (ug/liter) -----		
Benzene	<1	<1	<1
Toluene	<1	<1	3
Ethylbenzene	<1	<1	2
p-Xylene	<1	<1	3
m-Xylene	<1	<1	8
o-Xylene	<1	<1	5
1,2,4-TMB	<1	<1	4

Background



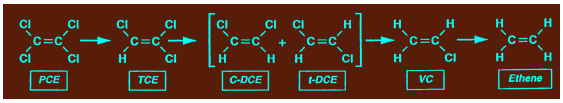
	82-E	82-N	82-K	82-H
	----- (mg/liter) -----			
Oxygen	3.7	2.0	2.0	5.9
Nitrate	4.4	1.1	4.4	1.5
Sulfate	37	43	60	62
Iron	<0.05	<0.05	<0.05	<0.05
Methane	0.001	0.004	0.003	0.001
Alkalinity	375	256	498	492

	82-E	82-N	82-K	82-H
	----- (ug/liter) -----			
Benzene	<1	<1	<1	<1
Toluene	<1	<1	<1	<1
Ethylbenzene	<1	<1	<1	<1
p-Xylene	<1	<1	<1	<1
m-Xylene	<1	<1	<1	<1
o-Xylene	<1	<1	<1	<1
1,2,4-TMB	<1	<1	<1	<1



Natural Attenuation of Chlorinated Solvents

Mechanism of Chloroethene Biotransformation



Reductive dehalogenation:

- Oxidation/reduction reaction where electrons are transferred from donor to chlorinated hydrocarbon acceptor

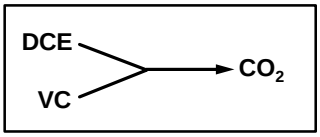
Co-metabolic process:

- Organisms growing on alternate carbon sources

Primary substrates:

- Potential for natural (soil organic matter) and anthropogenic sources

Alternative Pathways for Chloroethene Biotransformation



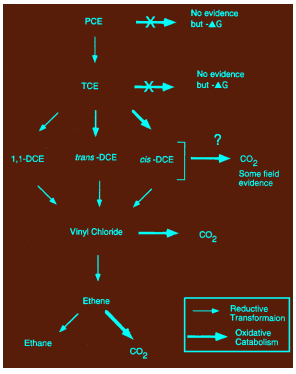
Oxidative biodegradation:

- Vinyl chloride shown to biodegrade under aerobic conditions
- Fe reducers may also oxidize vinyl chloride

Supporting evidence:

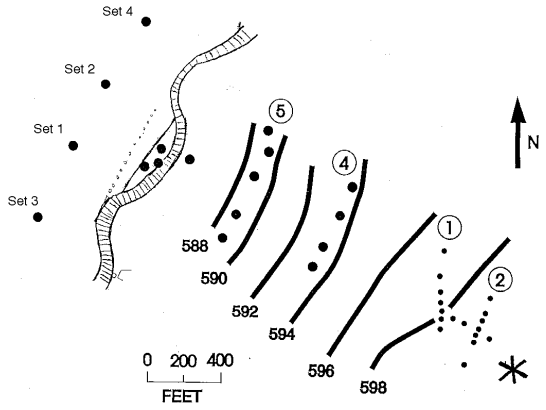
- Transport properties (migration) of DCE and VC relative to TCE
- Aerobic biodegradation of vinyl chloride to CO_2 demonstrated in microcosms

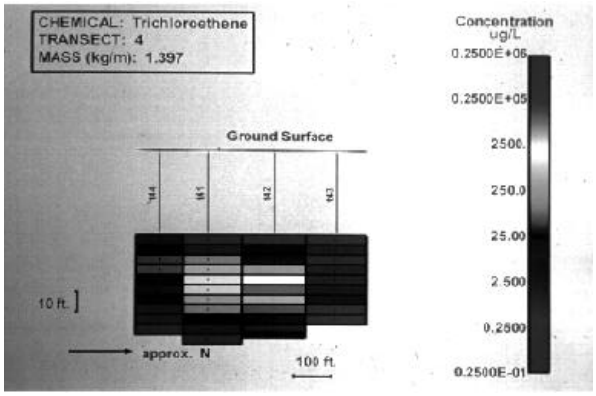
Native Biotrans-formations for Chloroethenes

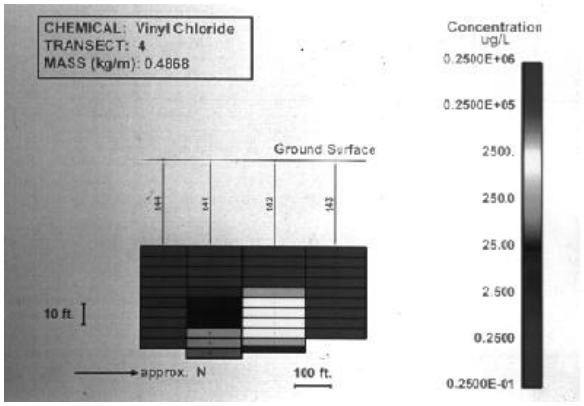


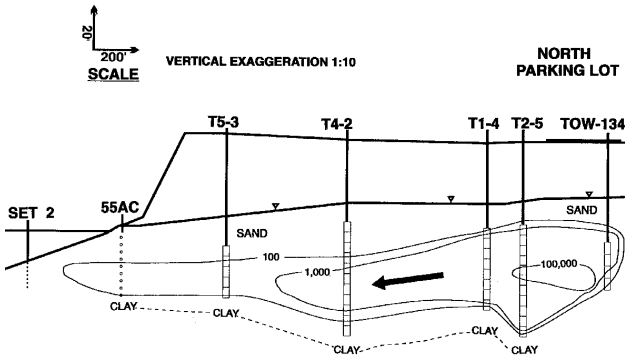
Patterns of Natural Attenuation Sites

Type I	Low background organic matter concentrations, dissolved oxygen and possibly nitrate greater than 1 mg/L
Type II	Anthropogenic carbon sources (e.g., BTEX, landfill leachate) are present
Type III	Native organic carbon drives dechlorination









Methods to Estimate Rate Constants

1) **Change in concentration from well to well along a flow path (must correct for dilution)**

2) **Change in flux (mass per unit time) between one transect and another perpendicular to the flow path**

3) **Laboratory Microcosm Study**

MASS FLUX AND TRAVEL TIMES

Advective mass fluxes estimates from calibrated ground water model (MODFLOW--Tiedeman and Gorelick, 1993) and transect averaged concentrations

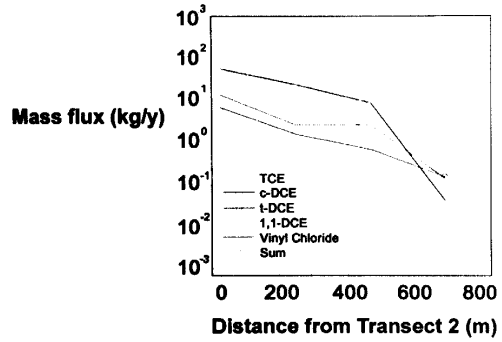
Travel times for each chemical from: transect locations seepage velocities retardation factors

Average hydraulic conductivities with 95% confidence limits give a range of estimates for the travel times

Attenuation in West Plume at St. Joseph, Michigan

Distance	Chloride	Organic Chlorine	TCE	c-DCE	Vinyl Chloride
Meters	-----(mg/liter)-----		----------(µg/liter)----------		
Background	14	0	0	0	0
130	55	151	68,000	128,000	4,400
390	109	15	8,700	9,800	1,660
550	71	0.8	56	870	205
855	57	<0.1	1.4	0.8	0.5

Mass Flux (kg/y) vs Distance from Transect 2 (m)



Chemical Mass Flux for the Sum of the Chlorinated Ethenes

Transect	Low Estimate (k_s = 4.92 m/d) (kg/y)	Average (k_s = 7.51 m/d) (kg/y)	High Estimate (k_s = 10.1 m/d) (kg/y)
2	203	311	418
4	57.1	87.1	117
5	7.99	12.2	16.4
Lake	0.0539	0.0822	0.111

Apparent Loss Coefficients

$$\ln\left[\frac{c_{j+1}}{c_j}\right] = \lambda s\ t$$

c_{j+1} Average concentration in the downgradient transect

c_j Average concentration in the upgradient transect

λ Apparent loss coefficient

$s\ t$ Travel time between the transects

For TCE from transect 2 to 4

$\Delta t = 340$ weeks

$c_{j+1} = 5.04 \times 10^{-4}$ kg/m^3

$c_j = 6.70 \times 10^{-3}$ kg/m^3

$\lambda = -0.0076$ / week

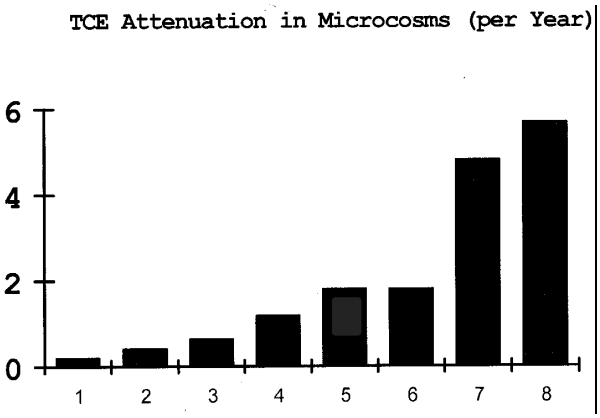
Transect Pair	TCE	c-DCE	Vinyl Chloride
	Apparent Loss Coefficient (1 / week)		
2 to 4	0.0074	0.0097	0.0035
4 to 5	0.025	0.016	0.017
5 to Lake	0.018	0.059	0.043

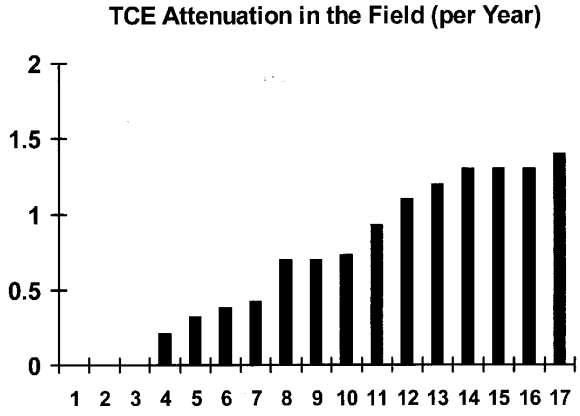
Microcosm Studies for Complex Technical Issues

Resources Required

To conduct ground-water microcosm studies:

- 18–24 months
- $100–$300 K





How is residence time at field scale being determined (Spring 1996)?

Remedial Investigations or Natural Attenuation Treatability Studies usually use Darcy's Law and assume the aquifer is homogeneous.

Information needed:
Hydraulic conductivity from aquifer test.
Hydraulic gradient from water table elevations in monitoring wells.
Effective porosity from Freeze and Cherry.

As an approximation:

After acclimation, the kinetics of natural attenuation of chlorinated solvents can be described as being first-order on residence time in the aquifer (follows a half-life rule).

The range of rate constants is relatively narrow. Most of the uncertainty in estimating the contribution of natural attenuation of chlorinated solvents is in the estimate of residence time in the aquifer.

Proposed preliminary screening approach to determine if further characterization of natural attenuation of chlorinated organic compounds is warranted.

1) Measure geochemical parameters to determine if reductive dechlorination is expected. If so-

2) Assume a first order rate of attenuation of 1.0 per year (half life of eight months).

3) Conduct a rigorous estimate of the residence time to the point of compliance.

4) Calculate the expected concentration at the point of compliance from the assumed rate of attenuation and the residence time.

5) Compare expected concentrations to measured concentrations, if available.

6) If within an order of magnitude, complete the characterization.

What is the problem with this approach?

Aquifers are not homogeneous. They have more permeable regions and less permeable regions.

What is the consequence?

Plumes find their way to the more permeable regions, and move much faster than expected from average conditions. Frequently they move as much as ten times faster.

Current Approach:

1) How much water will a well yield?

Conduct an aquifer test in an existing well that is screened across the aquifer.

2) How permeable is the aquifer around the well?

Divide the transmissivity determined from the aquifer test by the length of the screened interval to estimate hydraulic conductivity.

3) How fast does the water flow?

Darcy's Law says that the flow in a aquifer is proportional to the permeability and to the slope of the water table. Multiply the hydraulic conductivity by the hydraulic gradient to estimate Darcy flow.

4) How fast does the plume move?

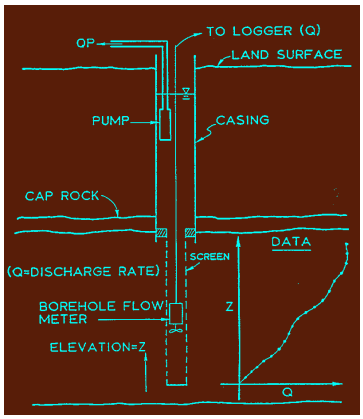
Ground water moves through the pores. Divide Darcy flow by porosity to estimate interstitial seepage velocity.

How can we do a better job of estimating true plume velocity?

Down-hole flow meters can be used to identify the vertical intervals that significantly contribute to flow to a well, and can contribute to flow in an aquifer.

Divide the transmissivity as determined from an aquifer test by the depth of the intervals contributing to flow, instead of the total screened interval of the well.

Apparatus and Geometry Associated with a Borehole Flowmeter Test



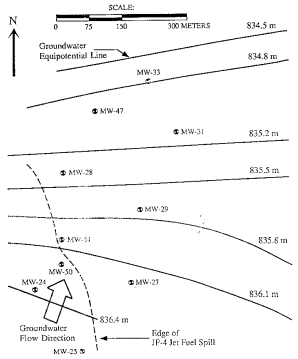
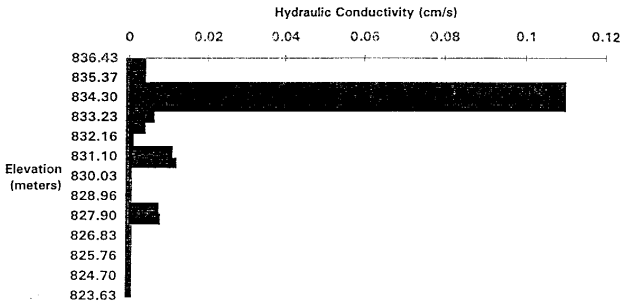
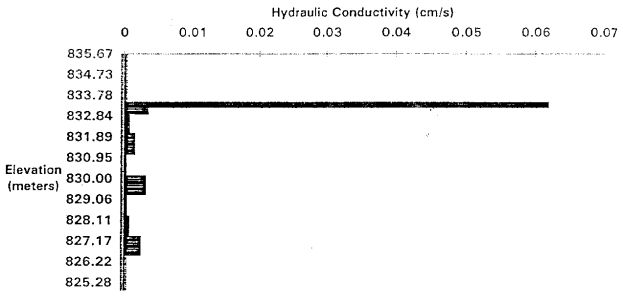


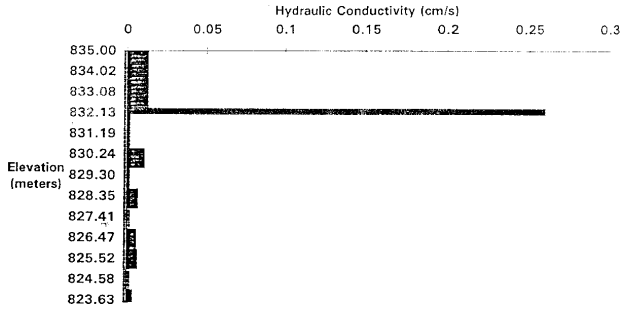
FIGURE 1. Location of monitoring wells near or under the flight line at George AFB, CA. The arrow indicates the direction of groundwater flow. The water table is contoured with an interval of 1 ft (0.305 m).



Vertical distribution of hydraulic conductivity in the aquifer sampled by well MW-27



Vertical distribution of hydraulic conductivity in the aquifer sampled by well MW-29

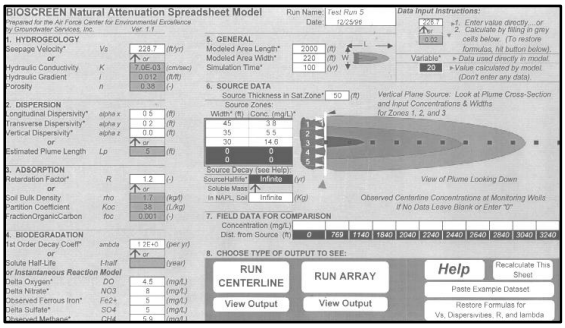


Vertical distribution of hydraulic conductivity in the aquifer sampled by well MW-31

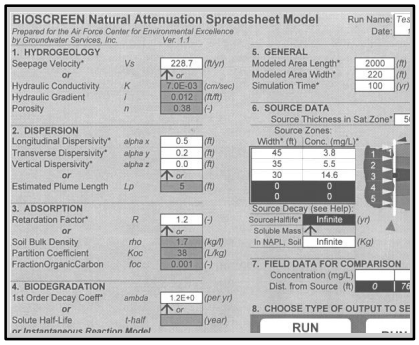
Error produced by using the average hydraulic conductivity as revealed by a conventional aquifer test to estimate the interstitial seepage velocity (and thus residence time) of the JP-4 plume at George AFB

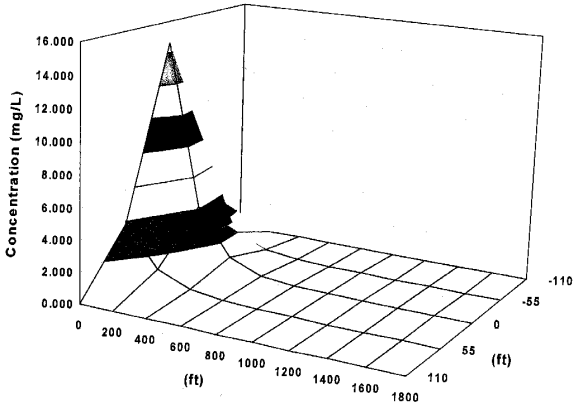
Monitoring Well	Average Hydraulic Conductivity (cm/sec)	Hydraulic Conductivity of Most Transmissive Interval (cm/sec)
MW-27	0.0074	0.11
MW-28	0.0046	0.022
MW-29	0.0028	0.062
MW-31	0.013	0.26
MW-45	0.0032	0.0056
MW-46	0.018	0.40

Bioscreen Input Screen



Bioscreen Input Screen





Bioscreen

Bioscreen will be available on the NRMRL/SPRD Web page:

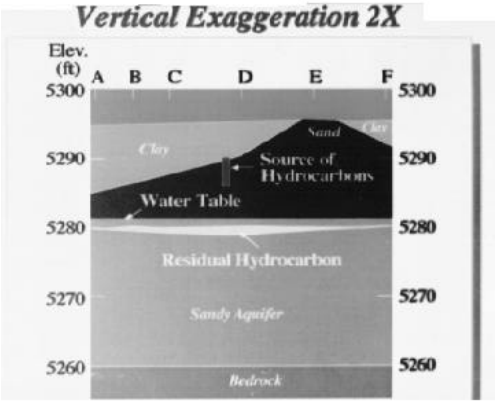
www.epa.gov/ada/kerrlab.html

A Retrospective Evaluation of In Situ Bioremediation

Procedure used to estimate the impact of residual petroleum hydrocarbons on ground-water quality at the Public Services site in Denver, Colorado.

In many floodplain landscapes, the most important transfer of contaminants from LNAPL to ground water is through diffusion from the LNAPL to transmissive layers in the aquifer, rather than through dissolution and direct advection.

This suggests an approach to estimate the impact of spills of petroleum hydrocarbons on ground water.



Will the Plume Return?

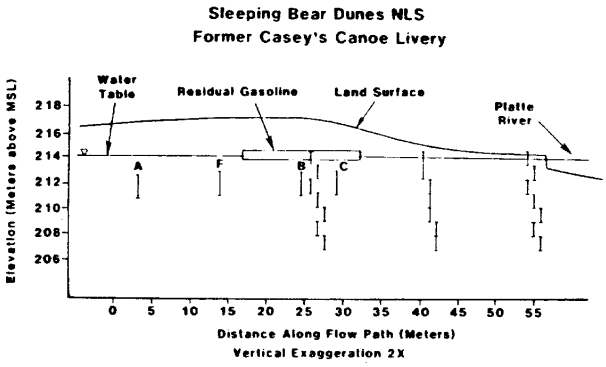
Has active treatment weathered the spill to the point that intrinsic bioremediation prevents development of a plume?

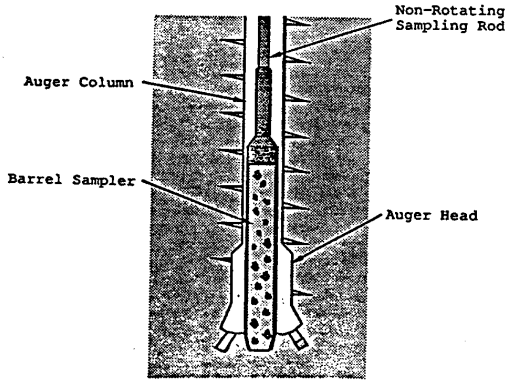
Will a Plume of Contaminated Ground Water Return?

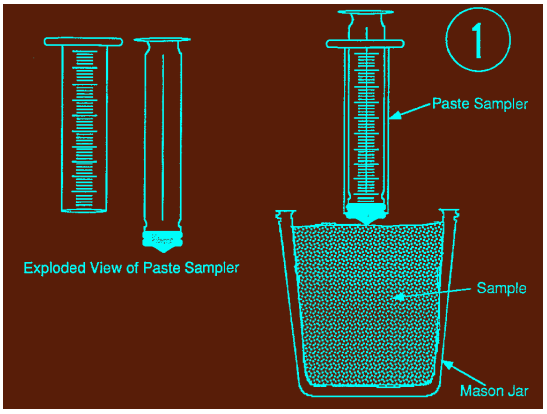
- Is the electron acceptor supply greater than the demand?
- What is mass transfer from residual oily phase to moving ground water?

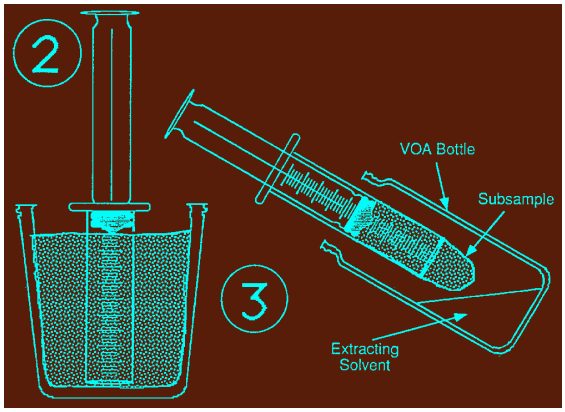
State of Practice for Determining Contaminant Mass

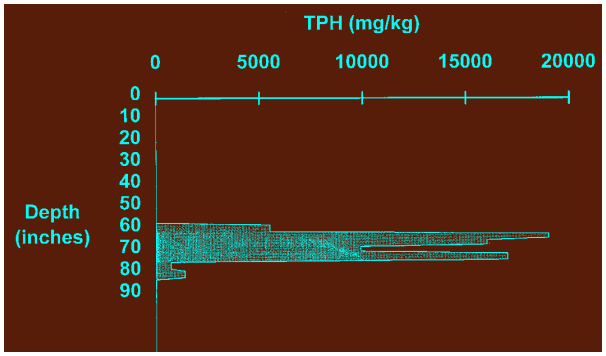
- Subsample cores in the field for extraction and analysis of specific contaminants and total petroleum hydrocarbons.
- Cores can be screened with a hydrocarbon vapor analyzer.

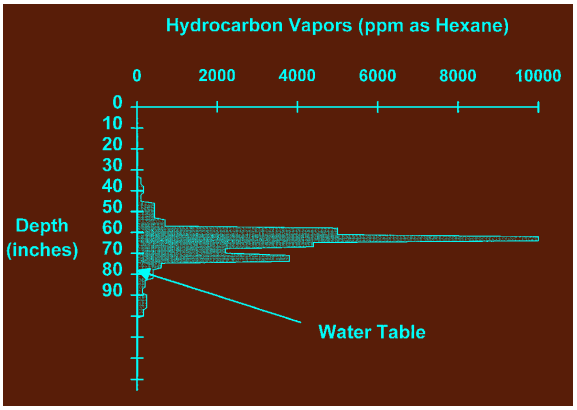

Sleeping Bear Dunes NLS
Former Casey's Canoe Livery
Water Table
Residual Gasoline
Land Surface
Platte River
A
F
B
C
Elevation (Meters above MSL)
218
216
214
212
210
208
206
0 5 10 15 20 25 30 35 40 45 50 55
Distance Along Flow Path (Meters)
Vertical Exaggeration 2X

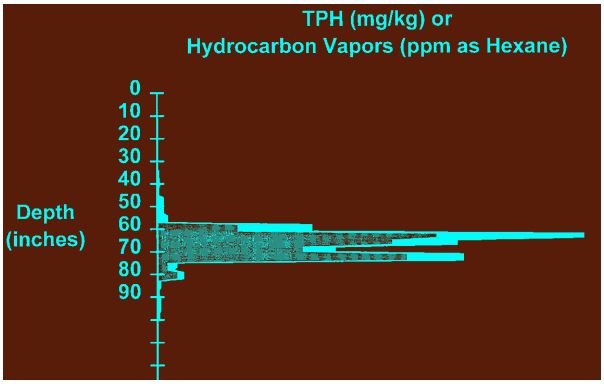

Non-Rotating Sampling Rod
Auger Column
Barrel Sampler
Auger Head

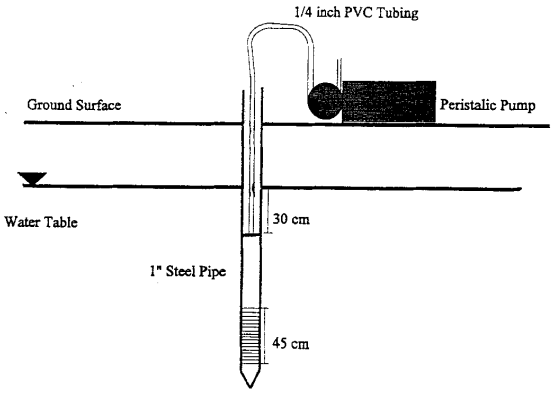

1
Paste Sampler
Exploded View of Paste Sampler
Sample
Mason Jar


2
VOA Bottle
Subsample
3
Extracting Solvent


TPH (mg/kg)
0
5000
10000
15000
20000
Depth (inches)
0
10
20
30
40
50
60
70
80
90


Hydrocarbon Vapors (ppm as Hexane)
0
2000
4000
6000
8000
10000
Depth (inches)
0
10
20
30
40
50
60
70
80
90
Water Table

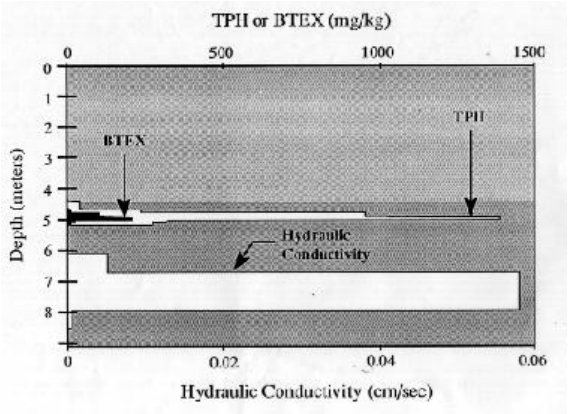




Calibration of Aquifer Test Using a Geoprobe

Location	Hydraulic Conductivity (cm/sec)	Method	Yield (ml/ cm sec)	Factor
Eglin AFB Florida	0.036	Slug Test 2 inch well	0.32	0.11
Eglin AFB Florida	0.015	Permeameter test on core	0.35	0.043
Plattsburgh AFB, NY	0.0089	Permeameter test on core	0.34	0.026
Pontotoc Co.,OK	0.0078	Permeameter test on core	0.40	0.020
Pontotoc Co., OK	0.000018	Permeameter test on core	0.0044	0.004

Calibration Factor for SPRD/NRMRL Geoprobe Hydraulic Conductivity (cm/sec) equals Yield (mL per sec per cm drawdown) multiplied by 0.03



Fuel Derived Organic Compounds at the Public Services Site

Depth	Hydraulic Conductivity	MTBE	Benzene	BTEXTMB
meters below land surface	cm/sec	ug/liter		
5.48 to 6.10	0.00012	10.6	11.3	636
6.10 to 6.71	0.0049	<1	2.8	64.1
6.71 to 7.21	0.058	<1	1.0	25.7
7.21 to 7.92	0.058	<1	<1	22.7
7.92 to 8.53	0.000204	<1	<1	23.9
8.53 to 9.14	<0.000001	<1	<1	92.4

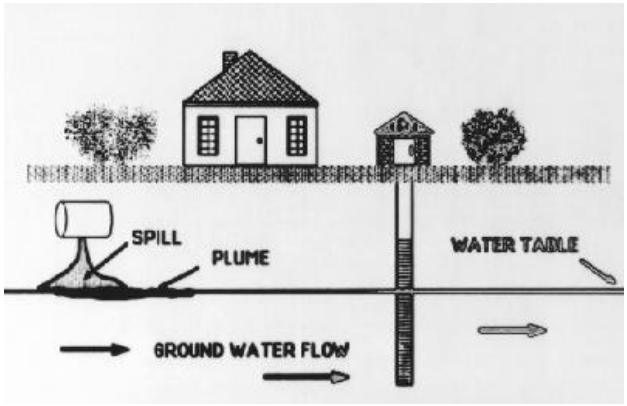
Electron Acceptor Supply at the Public Services Site

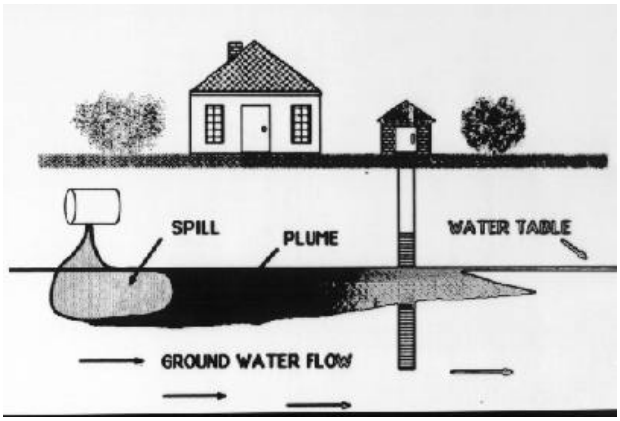
Depth	Hydraulic Conductivity	Dissolved Oxygen	Nitrate Nitrogen	Sulfate
meters below land surface	cm/sec	mg/liter		
5.48 to 6.10	0.00012	no data	no data	no data
6.10 to 6.71	0.0049	0.6	8.9	226
6.71 to 7.21	0.058	0.3	7.1	232
7.21 to 7.92	0.058	0.5	4.9	239
7.92 to 8.53	0.000204	1.4	4.8	215
8.53 to 9.14	<0.000001	no data	no data	no data

1. Determine hydraulic conductivity in the first transmissive interval below the LNAPL.
2. Determine hydraulic gradient in that interval.
3. Assume a porosity, and calculate a seepage velocity under the LNAPL.
4. Determine the length of the LNAPL in the direction of ground-water flow.
5. Calculate residence time of water in the transmissive interval moving under the LNAPL.
6. Determine the highest concentration of contaminant dissolved in ground water in contact with LNAPL (Raoult's Law using core samples or direct measurement on water).
7. Measure the vertical distance between the bottom of the LNAPL and the top of the transmissive part of the aquifer.
8. Calculate the diffusion gradient.
9. Look up the diffusion coefficient of the contaminant in water (Chemical Engineering).
10. Calculate the diffusive flux from the LNAPL to the transmissive part of the aquifer.
11. Use the residence time of ground water under the NAPL to calculate total loading by diffusion to the transmissive part of the aquifer.
12. Determine the volume of water in the transmissive part of the aquifer.
13. Estimate the concentration of contaminant in the transmissive part of the aquifer in the absence of biodegradation.
14. Measure the supply of oxygen, nitrate, and sulfate in the uncontaminated ground water upgradient of the spill.
15. Compare the electron acceptor demand of the contaminants to the electron acceptor supply associated with oxygen, nitrate, and sulfate in ground water upgradient of the spill.
16. If methane concentrations in the ground water in contact with the LNAPL are greater than 0.1 mg/L, include methane in the calculation of electron acceptor demand.

Residence time	235 days
Highest conc. BTEX	175 mg/L
Diffusion path length	1.5 meters
Thickness of transmissive interval	1.2 meters
Loading BTEX mg/liter	0.6
BTEX capacity	51 mg/L

What are the prospects that natural attenuation is preventing the spread of BTEX contamination in ground water? (containment, not remediation)



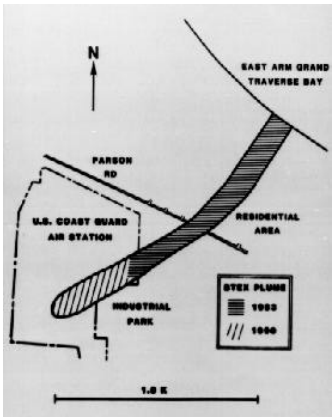


Where Should It Work?

- River valley alluvial deposits
- Unglaciated coastal environments on the Gulf of Mexico and Atlantic Ocean

What To Watch Out For!

- Glacial outwash
- Upland landscapes
- Fractured bedrock aquifers
- Karst landscapes, limestone aquifers



- How far will a plume move if it is subject to Natural Attenuation?
- How far will ground water move in 10 years?
- How fast is water moving through the source of ground-water contamination?

- What is the hydraulic conductivity of the most transmissive material that has LNAPL?
- What is the hydraulic gradient?
- Multiply conductivity by gradient, then divide by porosity (0.3) to predict plume velocity, use velocity; to predict plume length after ten years.

- Hydraulic conductivity >10 feet per day: Might have a huge plume
- Hydraulic conductivity 10 to 0.1 feet per day: Need more information
- Hydraulic condictivity <0.1 foot per day: Natural Attenuation often will take care of it

Appendix: Procedure Used To Estimate the Impact of Residual Petroleum Hydrocarbons on Ground-Water Quality at the Public Services Site in Denver, Colorado

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1. Determine hydraulic conductivity in the first transmissive interval below the light nonaqueous phase liquid (LNAPL).

   This was done using a Geoprobe to conduct a series of aquifer tests.

2. Determine the hydraulic gradient in that interval.

   This was calculated using water elevations in monitoring wells. It also corresponded with the gradient of the Platte River on a topographic map. Flow in the transmissive layers of the floodplain was parallel to the river.

3. Assume a porosity, and calculate a seepage velocity under the LNAPL.

   The assumed porosity was 0.35. Seepage velocity is the product of the hydraulic conductivity (0.058 cm/sec) multiplied by the hydraulic gradient (0.0012 meter/meter) and then divided by the assumed porosity (0.35). In this case, seepage velocity was 0.17 meter per day.

4. Determine the length of the LNAPL in the direction of ground-water flow.

   The length is based on analysis of core samples. It is estimated to be 40 meters.

5. Calculate residence time of water in the transmissive interval moving under the LNAPL.

   Residence time is the length of the LNAPL divided by the seepage velocity of the ground water. In this case, 40 meters divided by 0.17 meters per day or 235 days.

6. Determine the highest concentration of contaminant dissolved in ground water in contact with LNAPL (Raoult's Law using core samples or direct measurement on water).

   Raoult's Law says that the concentration of a particular compound in solution in ground water should equal the water solubility of that compound multiplied by its mole fraction in the NAPL. We will make two important conservative assumptions. Because most fuels are a "boiling cut" at the refinery, we will assume that the molecular weights of the components are approximately the same, and that mass fraction equals mole fraction. We will also assume that the solubility of benzene, toluene, ethylbenzene, and xylenes (BTEX) is the solubility of the most soluble component, benzene. The hot spot contained 206 mg/kg BTEX in 1,176 mg/kg total petroleum hydrocarbon (TPH), predicting a mole fraction of 0.18. Multiplying that mole fraction by the solubility of benzene (1,000 mg/liter) predicts a concentration of BTEX of 180 mg/liter.

   Direct measurements often underestimate the true concentrations estimated from analysis of core samples due to dilution from uncontaminated water.

7. Measure the vertical distance between the bottom of the LNAPL and the top of the transmissive part of the aquifer.

   This was done by "sniffing" core samples and by analysis of TPH in core samples, and by close-interval measurement of hydraulic conductivity using the Geoprobe. In this case, the vertical distance was 1.5 meters.

8. Calculate the diffusion gradient.

   The gradient is the change in concentration divided by the depth interval. The conservative assumption is that the concentration at the bottom of the gradient is zero. Under this assumption, the gradient is estimated as the highest concentration in contact with the NAPL divided by the depth interval to the transmissive layer. In this case, the gradient is 180 mg/liter to zero over 1.5 meters. The gradient is 180 mg/liter per 150 centimeters, or 1.2 E-03 mg/cubic centimeter per centimeter.

9. Look up the diffusion coefficient of the contaminant in water.

   A variety of chemical engineering handbooks are available, such as Chemical Engineering. In general, diffusivity is inversely proportional to the square root of molecular weight. Of the BTEX compounds, benzene is the lightest and diffuses the fastest. The diffusion coefficient of benzene is 0.8 E-05 square centimeters per second.

10. Calculate the diffusive flux from the LNAPL to the transmissive part of the aquifer.

    The flux is estimated by multiplying the diffusion gradient by the diffusion coefficient and then by the porosity. In this case 1.16 mg/cubic centimeter per centimeter multiplied by 0.8

E-05 centimeter squared per second, then by 0.35 cubic centimeters water per cubic centimeter aquifer material equals 3.2 E-09 mg/square centimeter per second, or 2.8 mg/square meter per day.

11. Use the residence time of ground water under the NAPL to calculate total loading by diffusion to the transmissive part of the aquifer.

    The loading is the flux multiplied by the residence time. In this case, 2.8 mg/square meter per day multiplied by the residence time of 235 days is 658 mg per square meter.

12. Determine the volume of water in the transmissive part of the aquifer.

    The volume is the thickness of the transmissive interval multiplied by the porosity. Based on the vertical mapping of hydraulic conductivity using the Geoprobe, the effective thickness is 1.2 meters. Under each square meter there is 1.2 cubic meters of aquifer material in the transmissive zone. The assumed porosity is 0.35, equivalent to 0.42 cubic meters or 420 liters of ground water under each square meter.

13. Estimate the concentration of contaminant in the transmissive part of the aquifer in the absence of biodegradation.

    The estimated concentration is the loading due to diffusion divided by the volume of water in the transmissive interval. In this case, 235 mg per square meter divided by 420 liters under each square meter equals 0.6 mg/liter BTEX.

14. Compare the electron acceptor demand of the contaminants to the electron acceptor supply associated with oxygen, nitrate, and sulfate in ground water upgradient of the spill.

    In this case, the analysis will be done on water samples at the downgradient edge of the LNAPL. Based on the stoichiometry of bacterial metabolism, 0.21 mg/liter of BTEX is consumed for each mg/liter of sulfate, 0.21 mg/liter of BTEX is consumed for each mg/liter of nitrate, and 0.32 mg/liter of BTEX is consumed for each mg/liter of oxygen. Concentrations of 0.5, 4.9, and 239 mg/liter of oxygen, nitrate, and sulfate have the capacity to support microbial metabolism of 0.16, 1.0, and 50 mg/liter of BTEX, respectively. This compares favorably with an estimated loading of only 0.6 mg/liter BTEX.

Natural Attenuation of Soils

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Generally, the following factors must be considered when evaluating contaminated soil for the use of natural attenuation as a remedial alternative:

- The mass/concentration, mobility, and toxicity of contaminants.
- The proximity of receptors, including both human and environmental receptors, with particular emphasis on sensitive human receptors and threatened/endangered species/habitats.
- The current and planned use of the aquifer underlying or adjacent to the site for public and private water supplies.
- The applicability and practicality of using of institutional controls to reduce the risk of exposure of sensitive receptors and ground water to soil contamination.

Site investigation may reveal one of the following scenarios in which natural attenuation of contaminated soil is a viable option:

1. Contamination is found essentially only in the unsaturated zone, and the contamination concentration/mass and mobility are low enough that no significant threat to ground-water quality exists. In this case, natural attenuation may be considered as a primary remedy.
2. Active remediation has reduced soil contamination to the equivalent of Scenario 1.
3. Active remediation is ongoing, but Scenario 1 is applicable in certain areas of the site; natural attenuation can be used for those areas while active measures continue in the areas not suitable for natural attenuation.

Natural attenuation in soils in the unsaturated zone involves a complex interaction among the chemical, physical, and biological properties of the site and contaminants. As in the saturated zone, evaluation of natural attenuation involves assessment of site characteristics, including geology, water flux, and soil chemistry; site microbiology, including microbial populations, microbial ability to degrade contaminants, and degradation rates; and contaminant characteristics, including solubility, toxicity, volatility and degradability.

Contaminants in the unsaturated zone may be dissolved in the soil pore water adsorbed to soil particles, or retained as residual saturation of free-phase liquid in soil pores or as vapor in the soil gas. The applicability of natural attenuation depends on the interrelationship between the contaminant parameters (e.g., mass/concentration, toxicity) and the factors that affect contaminant mobility and degradation. If mobility of the contaminants is low enough that sensitive receptors are

not at risk and other attenuation mechanisms can operate to reduce contaminant concentration or mass to the desired levels, then natural attenuation may be applicable as an alternative remedy.

Mobility of contaminants in each compartment of the unsaturated zone varies according to the contaminant, soil type and chemistry, water flux, and associated factors. Estimates of mobility should be made using one of the models applicable to contaminants in the unsaturated zone. Attenuation mechanisms include those that essentially dilute the contaminant concentration, those that reduce contaminant mobility (adsorption, and for metals a change of oxidation state), and those that change the contaminant to less harmful forms, such as biodegradation of organics and change of oxidation state for metals.

In the unsaturated zone, evaluation of natural attenuation of organic contaminants focuses on biodegradation, because the other significant components of natural attenuation for most contaminants either transfer the contaminants to another location (leaching, volatilization) or merely reduce contaminant mobility and perhaps biodegradability (adsorption). The site characteristics favorable for natural attenuation of soils and sediments are essentially those favorable for aerobic bioremediation, because in unsaturated zone soils, aerobic bioremediation is usually the most important factor in bioremediation. Even in an aerobic zone, however, anaerobic degradation may be occurring. For instance, it has been found that pentachlorophenol (PCP) may degrade better in soils that are "moderately aerobic" than in soils with high oxygen content or very low oxygen content. Anaerobic microsites in the soil may favor removal of chlorine from the aromatic ring of PCP, and then aerobic bioremediation could complete the degradation.

Soil oxygen levels greater than or equal to 2 percent are usually enough to support aerobic remediation. Earlier workers recommended that soil oxygen be above 10 percent, but experience indicates that many sites do not seem to show a significant increase in biodegradation as soil oxygen is raised above 2 percent.

A redox potential (Eh) of 50 millivolts is considered the minimum for oxidizing, aerobic conditions. An Eh below 50 millivolts (mV) indicates reducing, anaerobic conditions. An Eh of 400 to 800 mV indicates highly aerated conditions, while 100 to 400 mV indicates less aerated but still aerobic conditions. Generally, if the redox potential is less than 100 mV, active measures would be considered if aerobic conditions are desired. Soil color can give a qualitative estimate of redox conditions: reds, yellows, or browns indicate oxidizing conditions; gray or blue indicates reducing conditions; and mottled colors indicate spatial variability of redox conditions.

Soil pH strongly influences the microbial activity, availability of nutrients, and chemistry of some contaminants. Usually a pH of 5 to 9 is acceptable for bioremediation, although pH may affect bioremediation of varying contaminants differently, and specific types of degradation may not occur at certain pHs.

Soil moisture is closely associated with soil biological activity. Low soil moisture usually causes low biological activity. Low soil moisture may decrease contaminant mobility, allowing more time for bioremediation to work. Generally, soil moisture is optimum for bioremediation at about 50 to 80 percent of field capacity, where the large pores are filled with air and the small soil pores are filled

with water. At least 10 percent air-filled porosity is recommended for oxygen diffusion.
Soil temperature is closely related to biological activity. Biodegradation essentially stops at 0°C. Most biodegradation rates are determined at about 20 to 25°C. Generally, metabolic activity is halved by a 10°C drop in temperature, all other conditions staying the same. This does not necessarily mean that biodegradation is twice as fast at a site where the mean temperature is twice that of another site. For instance, there is at least some evidence that microbes acclimated to low temperatures can biodegrade petroleum hydrocarbons at low temperatures about as fast as microbes acclimated at 20°C can degrade contaminants at 20°C.

Microorganisms require nutrients such as nitrogen and phosphorus for metabolic activity. Soil nutrient levels are usually considered from a soil concentration perspective or from the perspective of ratios of the nutrients. For instance, a desirable concentration range for nitrogen and phosphorus in the soil solution might be 150 to 200 ppm nitrogen and 25 to 35 ppm phosphate, although firm evidence for recommending particular levels for bioremediation is generally lacking. From a nutrient ratio perspective, a carbon:nitrogen:phosphorus (C:N:P) ratio of 120-300:10:1 is often recommended. This ratio was originally based on the ratio of nutrients in microbial cells, with the assumption that the ratio of nutrients presented to the microorganism in its environment should be the same as the ratio in the cell. There has been little research conducted in the field to determine the best soil nutrient concentrations or ratios for bioremediation. Also, there is little information available on the desirable amount of trace nutrients in soils, although apparently enough trace nutrients are available in most soils and sediments so that increasing their levels has no discernable effect on bioremediation.

For the biological component of natural attenuation to be effective, there must be a suitable microbial community at the site that can degrade the contaminants. Microorganism communities can be evaluated in many ways. Unfortunately, most of the evaluation methods do not give clear answers to the question of most practical importance: Will the indigenous microorganisms degrade the contaminants quickly enough to levels low enough that the contaminants will be prevented from reaching sensitive receptors at toxic levels?

Microbial evaluation techniques include measures of microbial presence and activity such as population counts, community profiles, degradation ability, and metabolic activity. Microbial population counts ordinarily range from 1 to 10 x 10^6 counts/g soil, depending on the soil and the method of counting. The correlation between population counts and biodegradation rates is difficult to determine. Microbial identification techniques include techniques for identification of particular species, as well as community assessment techniques including FAME profiles and sole carbon source profiles. Generally, species identification is of limited usefulness for making decisions in field remediation activities.

Of more interest are techniques to determine microbial ability to degrade the contaminants of interest under laboratory conditions. Indigenous microorganisms can be grown in culture media containing the contaminants of interest, or simply in samples of the site soil. Contaminant degradation rates can be determined from these types of studies, although the laboratory rates may not be representative of the rates that will be found in the field. In cases where microbial ability to degrade the contaminants is in question, however, these tests can be helpful to establish the feasibility of using bioremediation/natural attenuation at the site.

Also useful both in the field and in the laboratory are tests to indicate microbial activity. Respiration measurements to determine O_2 consumption and CO_2 production are most commonly used. Measuring CO_2 production alone can be misleading, since CO_2 sources and sinks other than microbial activity may be significant. O_2 depletion in contaminated zones compared with similar "background" zones is strong evidence for biological degradation of contaminants when O_2 depletion data parallels contaminant disappearance, daughter product appearance, and secondary indicators.

Contaminants vary in their biodegradability. Generally, more water soluble compounds are more degradable. For instance, petroleum hydrocarbons with longer chains or more rings are less water soluble and less easily degraded. Specific examples include n-alkanes, n-alkylaromatics, and aromatics from 5-22 carbons, which usually are biodegradable. Petroleum hydrocarbons with more than 22 carbons tend to have fairly slow biodegradation rates. Fused aromatics and cycloparaffinics with four rings or more may be very slow to biodegrade. The larger compounds tend to be more strongly adsorbed to soil or trapped in soil pores, reducing their bioavailability, mobility, and potential to reach receptors.

Wood preserving contaminants, also often candidates for bioremediation/natural attenuation, vary widely in biodegradability, since wood preservatives by definition are selected for their toxicity to microorganisms. Polynuclear aromatics (PAHs) of three rings or less are generally considered to be readily biodegradable. Chlorinated phenols, such as PCP and tetrachlorophenol, are biodegradable, but their toxicity to microorganisms is a significant factor in their resistance to biodegradation at high concentrations. Dibenzodioxins and dibenzofurans appear to be difficult to biodegrade.

Physical and chemical components of natural attenuation in the unsaturated zone include volatilization and leaching as the most significant factors, although chemical reactions such as hydrolysis can be significant for some contaminants, such as pesticides. Adsorption significantly affects contaminant mobility, availability, and potential biodegradability. Volatilization can be a significant factor for those contaminants with high vapor pressure, such as gasoline and similar petroleum contaminants, naphthalene, methyl naphthalene, and three-ring PAHs, and chlorinated aliphatics. Loss of contaminants by volatilization is more likely in the unsaturated zone than in the saturated zone. Leaching of contaminants must be monitored and controlled, since leaching to ground water is one of the most important potential impacts of soil contaminants. Lysimeters can be used so that excessive leaching can be detected before the contaminants enter ground water. Both the potential for leaching and volatilization can be modeled to estimate the part these play in attenuation of the contaminants.

Natural Attenuation of Soils

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What Are the Requirements for NA To Be Used as the Primary Remedy for Soils?

- Further impairment to GW quality not a serious threat
- Receptors not impacted
- Site is controllable through institutional controls

What Are the Requirements for NA To Be Used as a Secondary Remedy for Soils?

- Along with ongoing active remediation alleviating serious threats
- After active remediation alleviated serious threats

Natural Attenuation as a Remedial Alternative for Soils

Contaminant Releases

- Migrate from source area
- Area of contamination expand until equilibrium reached
- Natural attenuation equals source output

When/Where Is Equilibrium Reached?

- Site factors – Soil type, precipitation influx . . .
- Contaminant factors – Solubility, concentration, carrier . . .

Equilibrium

- Eventually, natural attenuation exceeds rate of source output, and concentration of contaminant(s) stabilizes or decreases
- Importance of source control as the primary remedial alternative

Advantages of Natural Attenuation

- Actual contaminant degradation in many cases, rather than just phase transfer or sequestration
- Nonintrusive – allows continued use of site
- Less potential for releases due to site disruption, lack of control of remedial process

Advantages of Natural Attenuation

- Works in conjunction with other technologies
- Generally less costly than alternatives
- Can be evaluated by site characterization and monitoring

Advantages of Natural Attenuation

- Data necessary for proving applicability of natural attenuation are readily applicable to other technologies
- Site accessibility, equipment limitations are not a problem
- Common contaminants of regulatory concern (BTEX) are susceptible to NA

Disadvantages of Natural Attenuation

Upfront costs may be greater than other technologies, though long-term costs will probably be lower

Evaluating the Potential for Natural Attenuation in Soils

Site Characterization

- What site characteristics are favorable or unfavorable for NA?
- Favorable for aerobic bioremediation of vadose zone

Soil Oxygen Levels

- Soil oxygen levels >2%?
- May be enough for aerobic remediation

Redox Potential

- Eh >50 millivolts = oxidizing, aerobic conditions
- Eh <50 millivolts = reducing, anaerobic conditions

Redox Potential

- 400–800 mV highly aerated conditions
- 100–400 mV less aerated, but still aerobic

Soil Color

- Reds, yellows, browns indicate oxidizing conditions
- Gray or blue indicates reducing conditions
- Mottled colors indicate spatial variability

Soil pH

- Usually 5–9 is acceptable
- High pH may not inhibit bioremediation

Soil Moisture

- Low moisture, low biological activity
- But mobility may be low, so may have a long time available for bio

Soil Moisture

- 50–80% of field capacity
- Large pores filled with air, small pores filled with water
- Air/Water in soil inversely related

Soil Moisture

- Sandy Soils ~–0.1 – 0.15 Bar
- Loams ~–0.3 – 0.5 Bar

Air-Filled Porosity

>10% recommended for oxygen diffusion

Soil Permeability

Saturated hydraulic conductivity $>10^{-5}$ cm/sec

Soil Temperature

- Biodegradation stops at 0°C
- Most rates determined around 20–25°C
- Metabolic activity halved by 10°C drop

Soil Nutrient Levels

- Soil concentration
- Concentration ratio

Nutrient Concentrations

TON >1.5%

Nutrient Ratios

- C:N:P 120–300:10:1 often recommended
- Largely based on ratios in cell mass
- Little research conducted in field

Trace Nutrients

- Little specific information for bioremediation in soils
- Apparently enough available in most soils

Measures of Microbial Presence and Activity

- Population counts
- Community profiles
- Degradation ability
- Metabolic activity

Microbial Population Counts

- From 1 to 10 x 10 exp6 counts/g soil
- Relationship to transformation rates is minimal

Microbial Identification

- Isolation of specific degraders
- FAME profiles
- Community profiles by exposure to range of carbon sources

Microbial Ability To Degrade Contaminants

- Culture tests
- Microcosm tests

Microbial Activity

- Respiration O_2/CO_2
- ATP

Biodegradability of Petroleum Compounds

- More water soluble, more degradable, usually
- Longer chains, more rings less water soluble

Biodegradability of Specific Petroleum Compounds

- n-alkanes, n-alkylaromatics, aromatics from C5–C22 usually fairly biodegradable
- above C22 usually are fairly slow biodegradation rates
- Fused aromatics, cycloparaffinics >4 rings may be very slow

Biodegradability of Wood Preserving Contaminants

- Polynuclear aromatics (PAHs)
- Chlorinated phenols
- Dibenzo – dioxins and furans

Biodegradability of Chlorinated Solvents

- Methylene chloride
- 1,2-DCA
- Chloroethane

Monitoring Plan

- Soil and possibly GW
- Soil gas, soil borings, pore water

Case Study

Site History

- Waste oil recycling facility
- Oil blended with benzene, toluene, or xylene
- Two tank farms, with sludge/water in bermed area

Site History (continued)

- Victoria clay soil: low permeability, high water-holding capacity, high to very high shrink-swell potential, poor drainage
- Caliche fill in driveway
- Apparently no GW contamination

Remedial Plan

- Removal of tanks, barrels, buried piping, debris and sludges
- 2,200 yd of soil remaining (TPH up to 50,000 ppm)

Treatment Goals for Soil

- <1% oil and grease (O&G)
- 10,000 mg/kg TPH
- Land treatment chosen as remedial technology

Evaluation for Natural Attenuation

- Contaminant characteristics
- Site characteristics
- Ecological and health receptors

Contaminant Characteristics

- Are the contaminants of concern readily biodegradable?
- Suppose they are not readily biodegradable, but mobility is low?

Contaminant Distribution

- Contaminants in sludge not readily biodegradable in situ
- Contaminants in soil or dissolved probably degradable

Site Characteristics

- Are site conditions favorable?
- Can they be made favorable with minimum input?
- Will they be favorable after active remediation is done?
- Receptors

Time Required for Natural Attenuation

Once contaminants are identified as biodegradable, time/mobility are the main factors

Time Required for Natural Attenuation

Is the timeframe necessary for NA reasonable, considering site-specific circumstances?

What Is a Reasonable Timeframe?

- Depends on amount of contaminant, toxicity, and mobility
- Proximity of receptors – humans, environmental
  - Especially sensitive humans, threatened/endangered species
  - Public/private water supplies
- Potential use of aquifer
- Reliability/enforceability of institutional controls

Contaminated Soil

- Free phase residual
- Adsorbed material
- Dissolved contaminant

Contaminated Soil

- Evaluate mobility of contaminants
- Evaluate means to reduce mobility

Natural Attenuation of Landfills

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Introduction

Evidence is emerging that indicates natural attenuation may play a valuable role in addressing certain types of landfills. Landfills are usually closed municipal fills that may have received mixed wastes, including municipal solid wastes as well as a variety of industrial and hazardous wastes. Some of these landfills may pose a low risk to human health and the environment and, therefore, be candidates for consideration for use of natural attenuation. This decision must be made on a site-by-site basis. It does not indicate a preference over the Agency's current policy to manage landfill content, leachate, and gases by use of containment systems including covers and bottom liners.

The complex mixtures (1) of organic and inorganic nonhazardous and hazardous materials in landfills are slowly being degraded or transformed through natural attenuation (natural abiotic and microbial processes). The contaminants are also being leached (2-4), by rainfall or by ground-water intrusion, from the fill into the ground-water aquifers below. Volatile organic compounds (1) may also volatilize with the principal landfill gases of methane and carbon dioxide. What needs to be defined are the types of hazardous waste landfills and the appropriate conditions where natural attenuation would be considered.

Based on mass balance approaches, municipal landfills also are recognized as globally significant sources (5) of atmospheric methane, but methane field emission measurements are limited and extremely variable. There has been no attempt to reconcile national or global estimates of projected mass balance yields of methane generation with the limited field data on methane emissions (6). Recent research (7), however, has surprisingly revealed that landfills in the active methanogenic stage with aerobic soil covers and with gas recovery systems actually act as methane sinks, removing methane from the atmosphere rather than emitting landfill methane. The effect is attributed to high capacities for methane oxidation to carbon dioxide by indigenous methanotrophs in aerobic soil covers.

With aerobic permeable soil covers, uncapped landfills with substantially stabilized organic fill and limited gas emissions and sites with gas recovery and flaring systems also should develop indigenous methanotrophic and heterotrophic aerobic bioprocesses in aerobic, permeable soil cover. These aerobic processes should degrade both methane emissions and most volatile organic chemicals in the landfill gases. In addition, evidence is evolving that indicates that natural attenuation (intrinsic bioremediation) can stabilize and even shrink contaminated ground-water plumes below landfills.

Landfill Lysimeter Studies

EPA's National Risk Management Research Laboratory conducted a lysimeter study (1) on the West KL Landfill in Kalamazoo, Michigan, to assess bioactivity and the fate of the hazardous contaminants in the fill material under capped and rainfall simulations. The wastes were obtained from an area of the West KL Landfill with industrial wastes and were transported under nitrogen to EPA's Test and Evaluation Facility in Cincinnati. The materials were hand mixed, also under nitrogen, to reduce fill heterogeneity, then placed in lysimeters operated at 35°C. The anaerobic lysimeters, pertinent to assessment of natural attenuation, included three replicate microcosms of capped systems with two abiotic controls and three replicate microcosms simulating rainfall with two abiotic controls. The abiotic controls used sodium azide to minimize anaerobic activity.

The bioactivity in the lysimeters was monitored by measurement of gas production and by assessing the fate of specific contaminants in the fill. The cumulative gas productions (Figures 1 and 2) of the capped and rainfall simulators in the 400-day study revealed a long period of approximately 150 days before redevelopment of bioactivity in the disturbed fill in the rainfall simulator and only marginal bioactivity in the capped simulators. Fill gas analysis on carbon dioxide and methane also confirmed substantial bioactivity in the rainfall simulators compared with the marginal activity in the capped simulators.

Analyses of the fate of specific contaminants in the fill was difficult, unfortunately, with significant variability in the mass balances caused by heterogeneity in the fill and analytical variability associated with fill material. Trends on dehalogenation of highly chlorinated solvents (Figures 3 and 4) for example, also suggested improved bioactivity in the rainfall lysimeters compared with the capped lysimeters. Unfortunately, the poor mass balance results and variability from lysimeter to lysimeter prevented statistically valid assessments of the fate of specific contaminants.

Research Approach

Clearly, with bioactivity in permeable soil covers and with intrinsic bioremediation in ground water, responsible risk/benefit management requires assessing the applicability of natural attenuation processes as cost-effective approaches for managing risk in contaminated high-volume landfills, both as control options when active remediation can be discontinued and as the principal remediation approach in contaminated areas when risk is acceptably low. These natural attenuation processes, however, will require appropriate monitoring to ensure acceptable risk management of the variety of contaminants in landfills. Monitoring methods will include standard individual contaminant analyses in soils, leachates, and gases, as well as ecological and health effects assays.

The rate of natural attenuation of contaminants in landfills is the sum of the rates of several biotic and abiotic processes. These processes include intrinsic biodegradation of the contaminants, the chemical transformation of the contaminant (humification) into the organic matter associated with landfills, and the rates of mass transport of contaminants to the locations of these reactions. The development of a protocol for assessing the use of natural attenuation in landfills on a site-specific basis requires the compilation of a database on rates of pertinent biotic and abiotic processes for various contaminants and environmental settings, and the development or improvement of fate and transport models that employ the rates to describe the activity of these processes.

The tasks in the development of the protocol are to:

- Review and summarize pertinent biotic and abiotic degradation and stabilization (containment) science and engineering in the surface and subsurface of landfills including bioavailability and alternative endpoints. Develop critical supplemental attenuation rate data to support protocol development.

- Develop supplemental attenuation rate data using laboratory and field studies.

- Review, evaluate, improve, and summarize existing fate and transport models for hazardous compounds in landfills.

- Review and summarize available monitoring and sampling tools for landfill characterization.

- Prepare a draft protocol and validate with lab, pilot, and field studies.

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Natural Attenuation of Landfills

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Characteristics of Typical Hazardous Waste Landfills

- Usually closed municipal landfills with permeable soil cover
- No impermeable liners to minimize leachate transport
- Partial anaerobic stabilization of organic materials
- Gas production often highly variable
- Municipal solid wastes and a variety of industrial and hazardous wastes

Landfill Emissions

- Leachate with a variety of contaminants entering ground-water aquifer
- Carbon dioxide and methane gas emissions
- Variety of VOCs at low concentrations in gas emission

Natural Attenuation at Landfills

- Anaerobic bioprocesses degrade municipal solid wastes and many hazardous contaminants in fill
- Intrinsic bioremediation (anaerobic and aerobic processes) occurs in ground water at varying rates
- Aerobic methanotrophs bioxidize methane in permeable aerobic soil cover
- Aerobic bioxidation of VOC can occur in aerobic soil cover
- With aerobic soil cover and gas recovery systems, landfill can remove methane from atmosphere rather than emit methane

Landfill Lysimeter Study

- Superfund West KL Landfill in Kalamazoo, Michigan
- Selected waste from industrial area of the fill
- Hand mixed under nitrogen to reduce heterogeneity
- Lysimeters operation with 3 replicates and 2 abiotic controls simulating capped and rainfall conditions at 35°C
- Bioactivity confirmed by measuring gas production and assessing specific contaminant fate

Figure 1. Cumulative Gas Production for Capped Columns

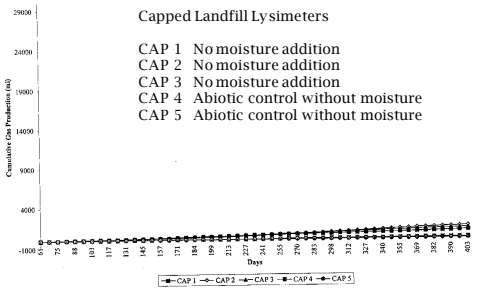


Figure 2. Cumulative Gas Production for Uncapped Columns

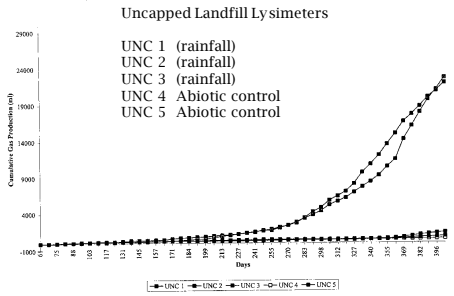


Figure 3. Distribution of Tetrachloroethylene for CAP 3

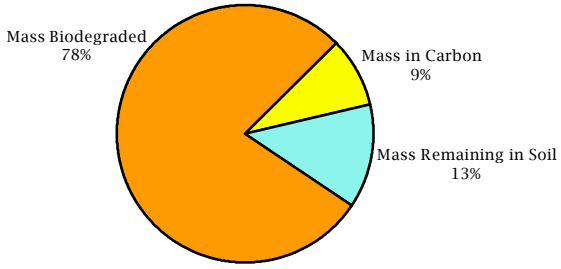
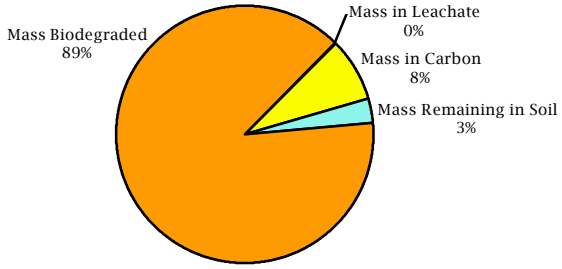


Figure 4. Distribution of Tetrachloroethylene for UNC 3



Natural Attenuation Research Approach

- Review and extend current science in natural attenuation of contaminated landfills
- Review and summarize available natural attenuation rates at sites
- Develop supplemental attenuation rate data
- Review and improve fate and transport models

Natural Attenuation Research Approach (continued)

- Review available monitoring tools
- Evaluate biological and health assays to assess cleanup objectives
- Prepare a draft protocol with information summaries
- Validate and improve protocol with laboratory, pilot and field studies

Natural Attenuation of Sediments

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Introduction

Contaminants in sediments (1) include a wide variety of organic compounds and metals. Metals cannot be destroyed but often can be transformed by bioprocesses to less toxic forms. As representative organic contaminants, high molecular weight polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), from widely used multicomponent Arochlors and creosotes, partition strongly to and persist in sediments (2). They bioaccumulate up the food chain and thus produce potential human health and environmental risks (3).

Intrinsic bioremediation (natural attenuation), even of these persistent compounds, occurs naturally but slowly in sediments, using indigenous microorganism and enzymatic pathways of both aerobic and anaerobic processes (2, 5, 6). In general, increasing the molecular weight of the organic contaminants (Figures 1 and 2) increases partitioning and reduces the bioavailability of the organic compounds, thus reducing the biodegradation rate and extent of degradation.

PAHs biodegrade most rapidly through aerobic processes, with the degradation rates usually decreasing as aromatic ring structure increases from two to six rings (5-7). In PCB biodegradation, anaerobic processes (8-10) slowly dechlorinate the highly chlorinated PCB congeners to lightly chlorinated congeners. Aerobic processes (11, 12) then biodegrade the lightly chlorinated congeners.

Quiescent sediments with substantial contamination are anaerobic (1) except in the upper layer adjacent to water. Dissolved oxygen of approximately 8.0 mg/L in water, slow oxygen diffusion into sediments, and slow diffusion of contaminants to the sites of microbial activity limit the kinetically more rapid aerobic degradation processes. The mass transport limitations reduce bioavailability and increase the persistence of PAHs, lightly chlorinated biphenyls, and other aerobically degradable organic contaminants in sediments. Natural turbulent mixing of sediments with the water column and slow oxygenation at the surface of quiescent sediments do produce limited and slow biodegradation of aerobically degradable contaminants (11).

In contrast, highly chlorinated congeners of PCBs and other chlorinated contaminants are gradually dechlorinated naturally in contaminated sediments, the PCBs (2) to mono-, di-, and trihomologs. The products of anaerobic dechlorination accumulate, increasing concentrations of lightly chlorinated PCBs and other partially dechlorinated contaminants in sediments (11-13). Lightly chlorinated PCBs and other partially dechlorinated organic contaminants, in general, bioaccumulate less strongly. These PCBs have less potential human toxicity (14, 15) than the highly chlorinated congeners.

Natural Attenuation Evaluation

With a pattern of slow natural dechlorination of highly chlorinated contaminants and slow aerobic biodegradation of the less chlorinated residuals and other aerobically biodegradable contaminants (such as PAHs), the U.S. Environmental Protection Agency's (EPA's) Bioremediation Program plans to examine natural attenuation as a possible approach for management of contaminated sediments and will prepare a protocol for assessing the use of natural attenuation as a best management practice for managing risk at specific sites with contaminated sediments.

These natural attenuation processes will require appropriate monitoring to ensure acceptable risk management. The initial priority contaminants are PAHs and metals, found at petroleum, wood preserving, and town gas wastes sites, and PCBs. Monitoring methods will include standard individual contaminant analyses and ecological and health effects assays (alternative endpoints).

The rates of natural attenuation of contaminants in sediments are the sum of the rates of several biotic and abiotic processes. These processes include intrinsic biodegradation of the contaminants, the chemical transformation of the contaminant into organic matter associated sediments (humification), and the rates of mass transport of electron donors or acceptors, amendments, or contaminants to locations where the microbial reactions occur. The development of a protocol for assessing natural attenuation at specific sites requires the compilation of databases on the rates of the biotic and abiotic processes for various contaminants and environmental conditions, as well as the improvement and validation of fate and transport models that employ the rates to describe the integrated action of these processes. Research and development includes:

- Review and summarize pertinent biotic and abiotic degradation and stabilization (containment) science and engineering in sediments, including contaminant bioavailability and alternative endpoints. Extend through experimental and field research.

- Review, evaluate, and improve existing fate and transport models for hazardous compounds in sediments.

- Review and summarize available monitoring and sampling tools for sediment site characterization.

- Prepare a draft protocol, including information summaries.

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Natural Attenuation of Sediments

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Contaminants in Sediments

- Wide variety of organic compounds and metals
- Persistent high molecular weight organic compounds
- Widely distributed contaminants: PCBs and PAHs
- Bioaccumulation in food chain may cause health and environmental risk
- Natural attenuation occurring slowly using aerobic and anaerobic processes

PAH and PCB Natural Attenuation

- PAHs biodegrade most rapidly through aerobic processes
- Rates decrease as aromatic ring structure increases from 2 to 6 rings
- PCBs biodegrade usually through sequential anaerobic/aerobic processes
- High chlorinated PCBs dechlorinate anaerobically to lightly chlorinated congeners
- Lightly chlorinated PCB congeners biodegrade aerobically

Figure 1. Representative PAH Ring Structures

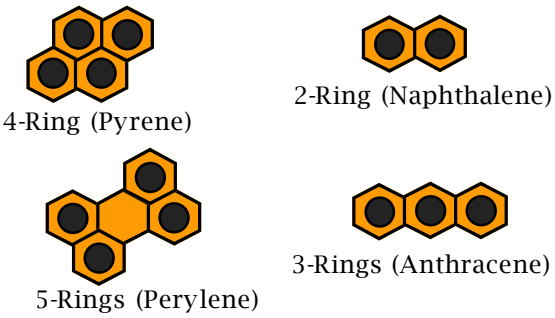
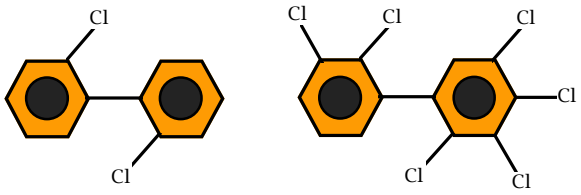


Figure 2. Representative PCB Congeners



Sediment Conditions

- Contaminated sediments are anaerobic below surface layer
- Surface layer adjacent to water is aerobic
- Slow mass transport in sediments limit bioavailability and degradation
- Quiescent sediments favor slow accumulation of lightly chlorinated compounds, especially mon, di, and tri PCB homologs
- Natural turbulent mixing of sediment and water increases aerobic degradation of PAHs and lightly chlorinated PCBs

Natural Attenuation Evaluation

- Pattern of slow natural dechlorination and slow biodegradation of aerobically degradable contaminants
- Assessing use of natural attenuation for managing risks
- Priority contaminants—PAHs, metals, and PCBs
- Monitoring to ensure acceptable risk management
- Monitoring methods—individual contaminant analyses, and ecological and health effect assays

Rates of Natural Attenuation Processes

- Anaerobic vs. aerobic
- Chemical transformation with sediment organic matter (humification)
- Mass transport of electron donors and acceptors, amendments, and contaminants

Protocol Development

- Compilation of databases on rates of attenuation for various contaminants and environmental conditions
- Improvement and validation of fate and transport models describing integrated activity of the attenuation processes

Research and Development Approach

- Review and extend and summarize current science in natural attenuation
- Review and summarize available natural attenuation rates of sites
- Develop supplemental attenuation rate data
- Review and improve fate and transport models

Research and Development Approach (continued)

- Review and summarize available monitoring tools
- Draft protocol including information summaries
- Validate protocol in laboratory, pilot and field studies
- Provide technology transfer

Source Control: Free Product Recovery and Hydraulic Containment

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Nonaqueous Phase Liquids—NAPLS, LNAPLS, DNAPLS

- The NAPLs define the source area of the ground-water plume
- To the extent feasible, these materials should be removed before bioremediation proceeds

Site Characterization Requirements Specific to the Subsurface

Goals:

- Map the contaminant mass in three dimensions
- Determine the co-distribution of contaminant and hydraulic or pneumatic conductivity

Problems With Monitoring Wells

- They cannot estimate contaminant mass in NAPLs
- They cannot estimate contaminant mass adsorbed to solids
- They do not sample contaminant mass above the water table

Comparison of Contaminant Mass in Ground Water to Total Contaminant Mass

At a pipeline spill in Kansas:

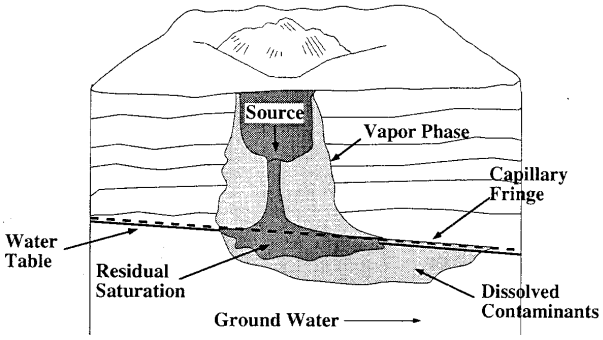
	Mass in Ground Water	Mass in Subsurface
Benzene	22 kg	320 kg
BTEX	82 kg	8,800 kg
TPH	115 kg	390,000 kg

When Total Contaminant Mass Is Unknown

- Cannot estimate requirements for electron acceptors
- Cannot estimate requirements for nutrients
- Cannot determine time required for cleanup

Relationship Between Free Product in Monitoring Wells and Contaminant Mass in Aquifer

- Position and quantity in wells does not relate to position and quantity in aquifer
- Amount of free product related to location of water table



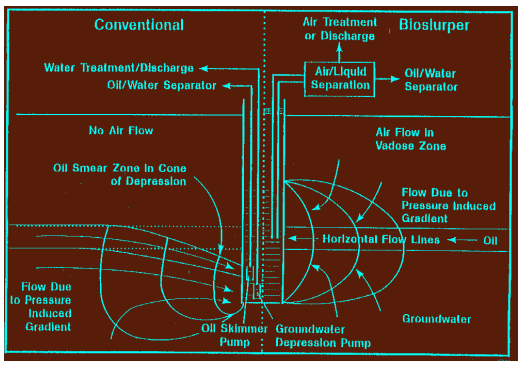
Relationship Between Free Product in Monitoring Wells and Contaminant Mass in Aquifer

- Free product is greatest when water table is low
- Free product can disappear when water table is high

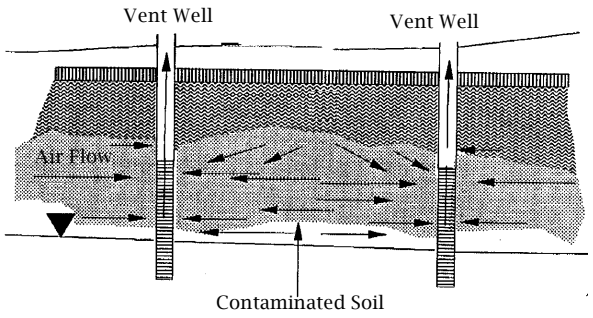
Methods To Remove Nonaqueous Phase Liquids

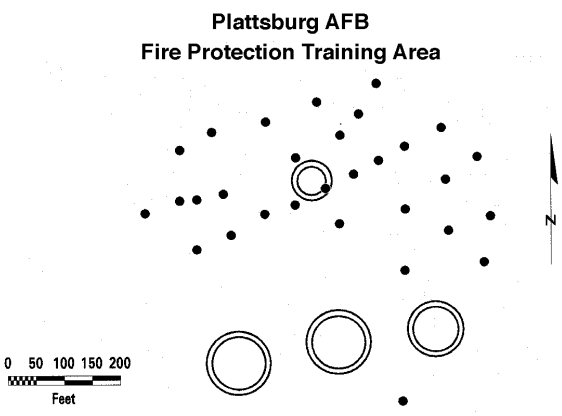
- Free product recovery
- Bioslurping
- Soil vacuum extraction

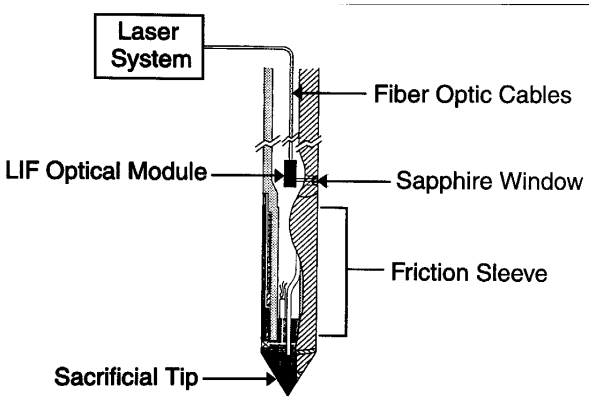
LNAPL Remediation

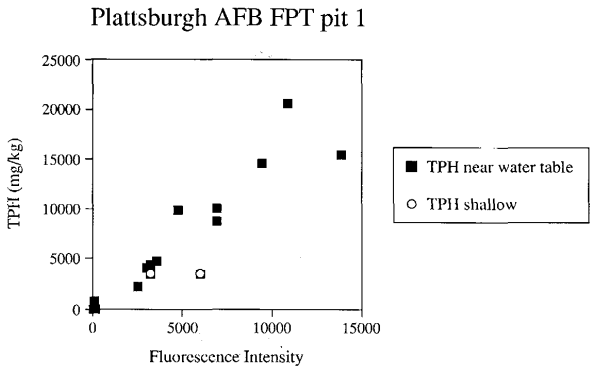


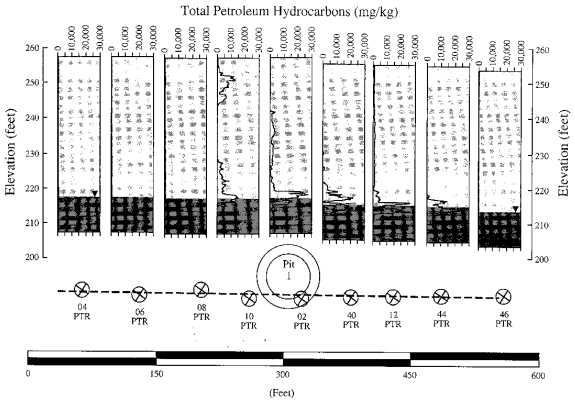
Soil Vent System

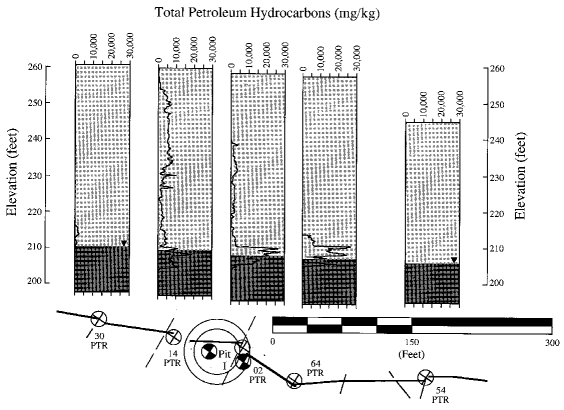


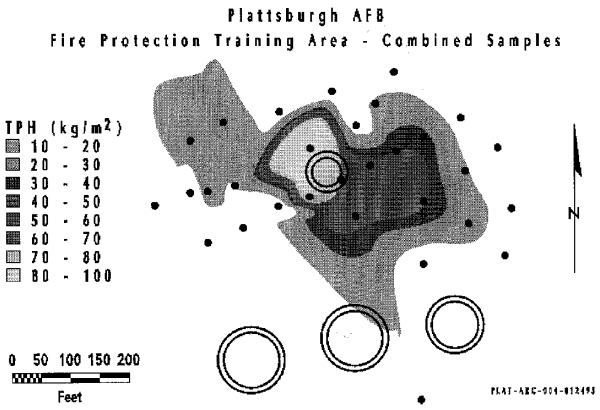

Plattsburg AFB
Fire Protection Training Area
N
0 50 100 150 200
Feet


Laser System
Fiber Optic Cables
LIF Optical Module
Sapphire Window
Friction Sleeve
Sacrificial Tip


Plattsburgh AFB FPT pit 1
TPH (mg/kg)
Fluorescence Intensity
TPH near water table
TPH shallow


Total Petroleum Hydrocarbons (mg/kg)
Elevation (feet)
Pit 1
(Feet)


Total Petroleum Hydrocarbons (mg/kg)
Elevation (feet)
Pit 1
(Feet)


Plattsburgh AFB
Fire Protection Training Area - Combined Samples
TPH (kg/m2)
10 - 20
20 - 30
30 - 40
40 - 50
50 - 60
60 - 70
70 - 80
80 - 100
N
0 50 100 150 200
Feet

Bottom Line

- 12,000 gallons of LNAPL removed
- 122,000 gallons of LNAPL remain

Air Sparging/ Air Injection

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National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Ada, OK

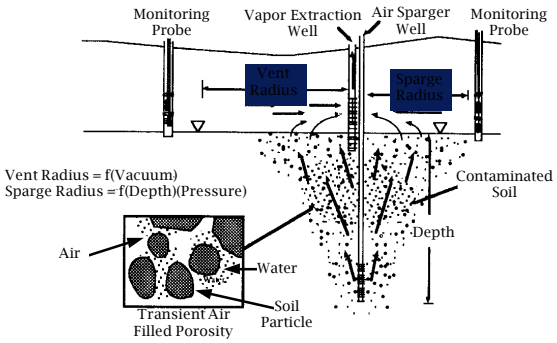
Need for Efficient, Inexpensive Delivery of Oxygen to Saturated Zone

*** Air Sparging ***

Air Sparging

- Injection of air under pressure below the water table
- Creates transient air filled porosity

Air Sparging System



Effects of Air Sparging

- Enhanced oxygenation
- Enhanced dissolution
- Volatilization
- GW stripping
- Physical displacement of GW

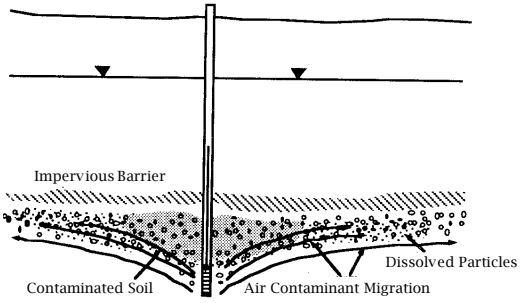
Enhanced Oxygenation

- Replenishes oxygen depleted by chemical/biological processes
- Normal replenishment relies on diffusion from water table surface
- Sparged air, distributed throughout aquifer, has short diffusion path
- Enhanced oxygenation stimulates biodegradation

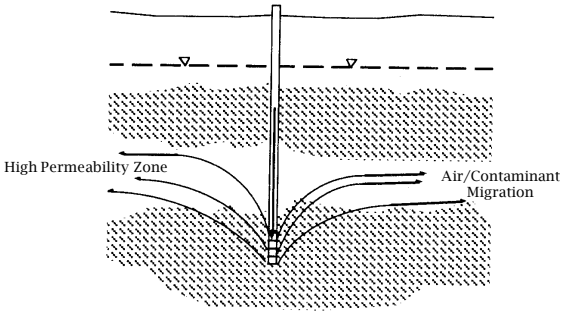
Air Flow Paths

- Injected air travels horizontally, vertically
- Flow impedance by lithological barriers blocking vertical air flow
- Channelization—horizontal air flow captured by high permeability channels
- Small permeability differences can change flow paths

Inhibited Vertical Air Flow Due to Impervious Barrier

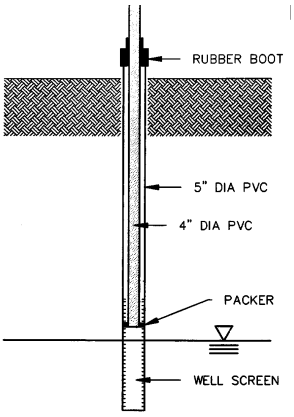


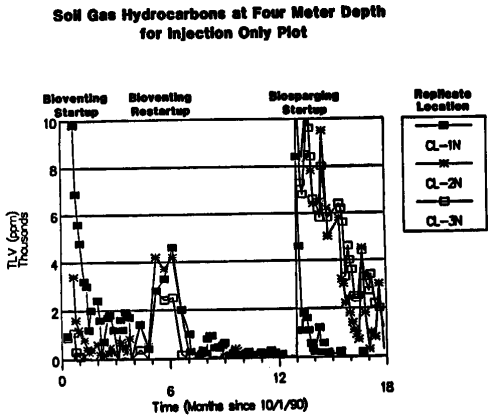
Channeled Air Flow Through Highly Permeable Zone

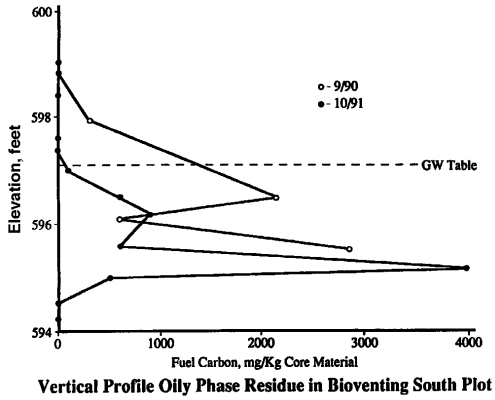


Case Studies on Air Sparging or Air Injection

- Worked well: Traverse City, Michigan
- Worked well enough: Elizabeth City, North Carolina
- Didn't work: Plattsburgh, New York







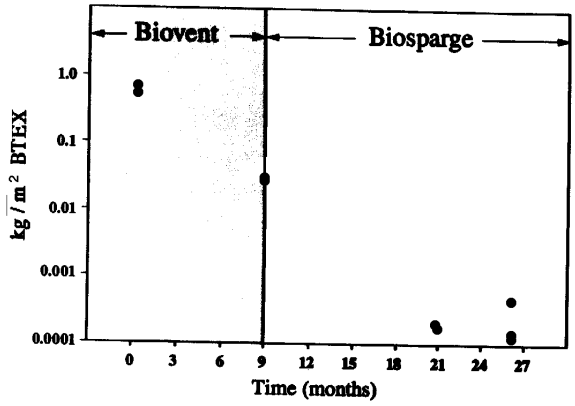
Vertical Profile Oily Phase Residue in Bioventing South Plot

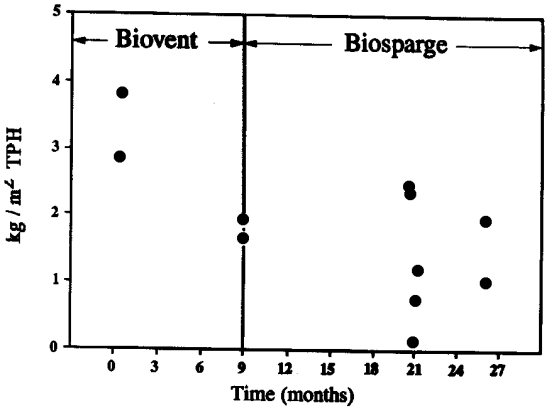
CHANGE IN TPH IN NORTH PLOT DURING PROJECT

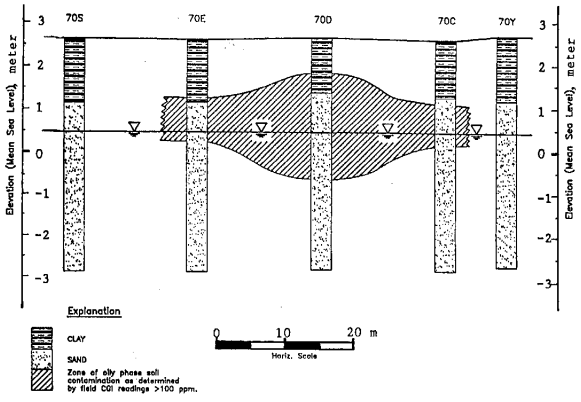
	Sept. 1990	Oct. 1991
	– – mg / sq. ft. area – –	
Above Water Table	48800	302
Below Water Table	227000	178000

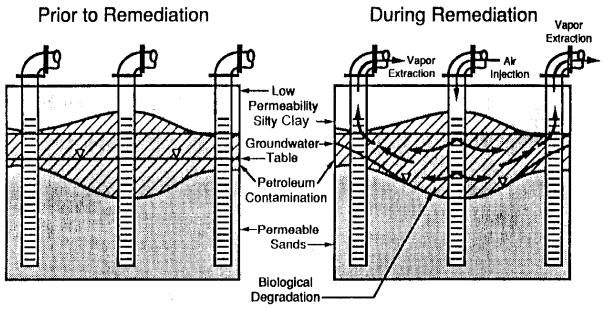
Ground Water Quality after Biosparging

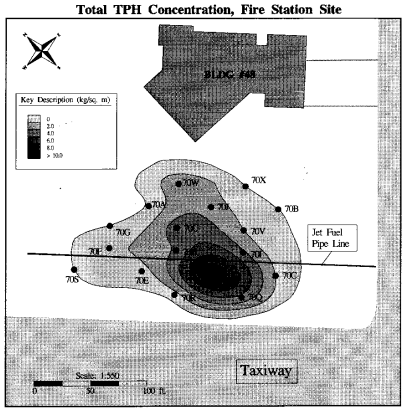
Well	Benzene	Toluene	Ethylbenzene	m+p Xylene	o-Xylene
	----------ug/liter----------				
3 feet	<1	<1	<1	<1	<1
6 feet	<1	<1	<1	<1	<1



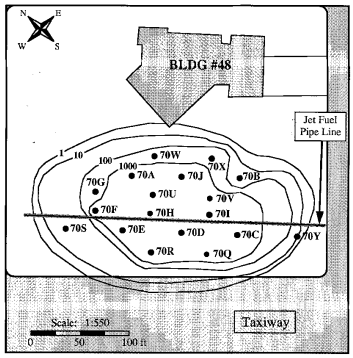




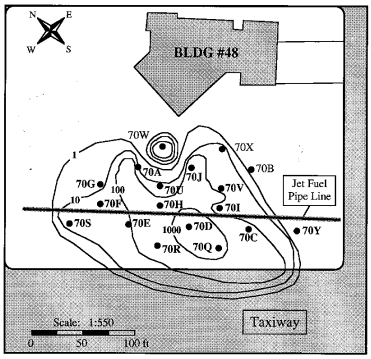


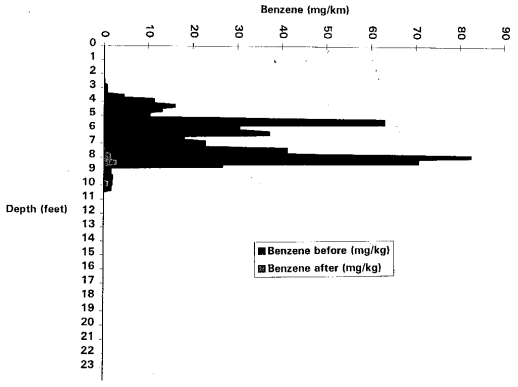


Baseline Total BTEX,
Fire Station Site



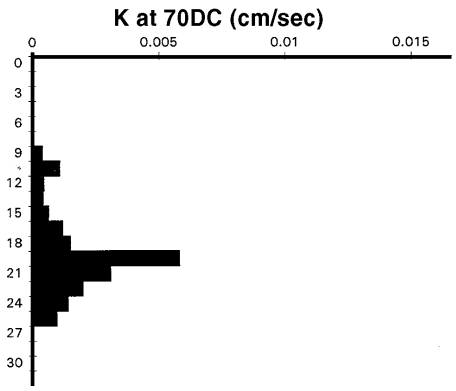
6th Period BTEX,
Fire Station Site

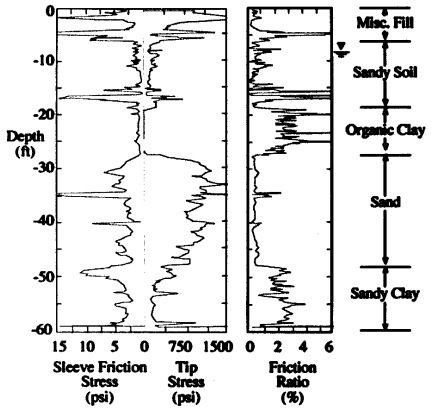


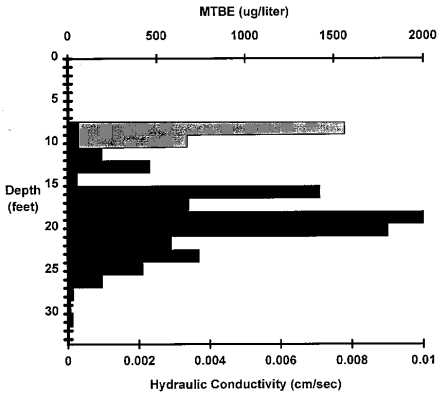


Monitoring wells screened from 7 to 10 meters below grade, 15 and 30 meters down gradient of the NAPL

	Monitoring Well 4		Monitoring Well 6	
	Predicted	Actual	Predicted	Actual
	--------(ug/liter)-----			
Benzene	40	1.9	40	1.3
MTBE	184	325	184	442

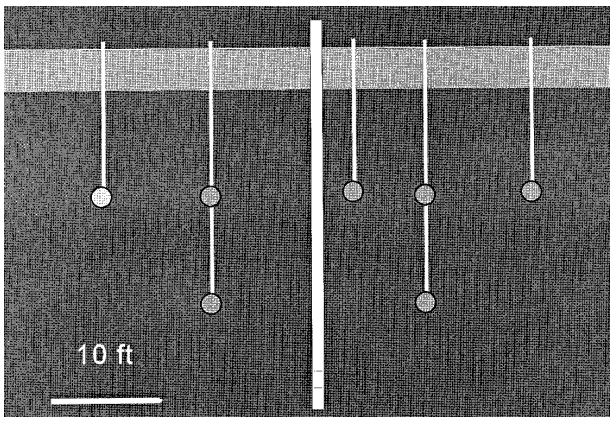


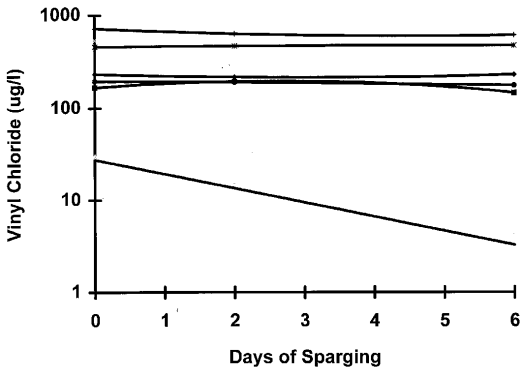


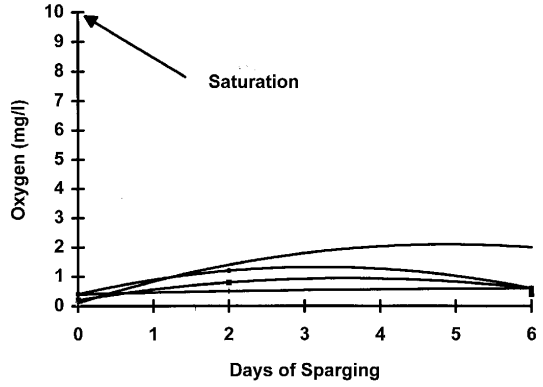


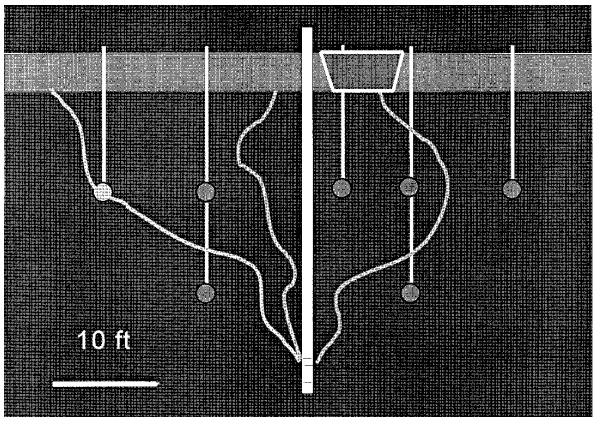
Conditions of Sparge Efficiency Test

- Injected air at 3 cubic feet per minute at 18 psi
- Injected air for four days over a six day interval
- Total air injected: 17,300 cubic feet
- Total porosity to 3 feet from sparge well: 250 cubic feet
- Total porosity to 10 feet from sparge well: 2,800 cubic feet









Why didn't air sparging strip Vinyl Chloride and increase the concentration of Oxygen?

The air moved in Ribbons, fixed channels of preferential flow.

- Air sparging worked well when the contaminant was near the water table and the sand grains were all the same size
- Air sparging did not work well when the contaminants were deep, and there were a mixture of particle sizes

State Review: Natural Attenuation of Ground Water and Soils

Daniel Pope
Dynamac Corporation, Ada, OK

The U.S. Environmental Protection Agency (EPA) recently conducted a survey to determine how different states are proceeding with natural attenuation efforts. States were asked whether they

- Encourage or discourage the use of natural attenuation (NA)
- Have any formal or informal policies or guidelines that address NA
- Use any particular model when deciding on NA
- Consider any compounds other than petroleum hydrocarbons for NA

The table below summarizes the information obtained from this survey.

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Alabama	Encourage case-by-case	No guidelines. Considers NA for petroleum on a case-by-case basis.		Discourage case-by-case
Alaska	Encourage case-by-case	Developing RBCA/ASTM (draft). Working with Wisconsin to develop soil guidance using NA.	AT123D, SESOIL	Discourage case-by-case
Arizona	Neither	Drafting interagency policy for ground-water contaminated sites. Developing RBCA and SSL. Considers NA mostly at UST sites.	Developing BAN Model	Discourage case-by-case
Arkansas	Neither case-by-case	Informal guidelines. Looks at property boundaries. Determines NA on a case-by-case basis.		Neither case-by-case
California	Discourage	Revising Resolution 92-49 to include "containment zones."		Discourage
Colorado	Neither case-by-case	Meets water-quality standards at "point of compliance" (property boundary). However, water-quality standards may be used as "guidelines" by oil inspectors based on technical and economic feasibility.	Half-lives of contaminants (non-UST)	Discourage case-by-case
Connecticut	Neither	Remedial standards allow NA. Uses a ground-water classification system for remedial decision-making.		Neither case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Delaware	Encourage	Informal guidelines for petroleum does not use RBCA. Guidance uses "passive action;" after 2 years need permission to continue. Looks at property boundaries. Non-UST use ground-water management zones. Assesses for "no further action" and deed restriction. Have voluntary action program and Brownfields.		Neither case-by-case
Florida	Encourage	Incorporates RBCA in statutes; is developing NA guidelines. NA now allowed if low concentrations. Expanding to allow higher concentrations, and more widespread contamination and to broaden types of sites. Hazardous waste section considers NA for soils only.		Discourage case-by-case
Georgia	Neither case-by-case	No formal policy. Remediation site specific. Threshold representative standards. Looks at media and risk.		Discourage case-by-case
Hawaii	Encourage	Guidance no policy. Revising manual on risk-based guidance. Source and free product removal.	SESOIL	Neither case-by-case
Idaho	Encourage case-by-case	Developing new ground-water rule. Brownfields beginning. Use beneficial-use criteria.		Neither case-by-case
Illinois	Neither case-by-case	Informal guidelines. Drafting RBCA and SSL approach in developing guidance. RBCA for UST and non-UST. Looks at property boundaries. Brownfields in development.	RBCA & SSL	Neither case-by-case
Indiana	Neither case-by-case	No formal protocol. Developing RBCA.		Neither case-by-case
Iowa	Encourage case-by-case	Uses RBCA. Plans policy changes. Hazardous waste section considers "passive remediation" if exposure risk is low along with source removal and monitoring.		Neither case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Kansas	Neither case-by-case	Considers NA for petroleum. Evaluates aquifer beneficial uses, property boundaries, and receptors. Has dry cleaning state trust fund for solvent waste.	AT123D, SESOIL, VLEACH	Discourage case-by-case
Kentucky	Encourage	Informal guidance for UST. Generally only considers NA for UST. Monitors until plume dissipates. Non-UST use deed restrictions to risk factor of 10^{-6}.		Discourage case-by-case
Louisiana	Neither case-by-case	No guidance or protocol. Requires site characterization, source removal, and monitoring before using NA.	Performance model	Discourage case-by-case
Maine	Encourage	Developing in-house guidance on NA of petroleum (end of May). Considers NA when exposure is low. Gathering information on non-UST for consideration.	May use Bioplume III in future	Neither case-by-case
Maryland	Encourage	No official documents on NA. Uses RBCA approach. NA allowed in areas not environmentally sensitive. Risk is primary factor. CERCLA does not promote NA.		Discourage case-by-case
Massachusetts	Encourage	No NA guidelines. State statutes use RBCA with NA implied in less stringent cleanup standards versus water-quality standards.		Discourage case-by-case
Michigan	Encourage	Drafting bioremediation guidance document with NA (within year). Considers other wastes (e.g., solvents). Requires monitoring and proof that NA occurs before reaching receptors. RBCA uses "Guidance Document for RBCA at LUSTs."	Bioplume II, Modflow	Encourage case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Minnesota	Encourage	UST has own RBCA rules addressing NA. Draft policy statement for non-UST in early development: "Site Response Risk Based Guidance for Cleanup of Site Other Than Petroleum Waste in Ground Water." Uses risk and cost. Remedial action levels in drinking water aquifers, remedial goals for potential drinking water aquifers, and multiple levels for other aquifers.		Neither case-by-case 1 site allows NA of chlorinated solvents & metals
Mississippi	Encourage	Encourages use of NA for petroleum only. UST section adopted RBCA 6 months ago and uses that to address NA. Hazardous waste section beginning to look at NA.		Discourage case-by-case
Missouri	Neither	No policy. Expanding state RBCA system on NA. Source removal not required if economically unfeasible or near cleanup levels. Uses property boundaries. Superfund uses deed restrictions.		Discourage case-by-case
Montana	Encourage	Have informal policy in UST section. No degradation policy in ground-water section. Superfund considers deed restrictions. Will consider NA if best or only technology.		Discourage case-by-case
Nebraska	Encourage	Risk-based guidance incorporates NA. Combining EPA, ASTM, and state guidance. Regulations based on cleanup levels. Superfund allows NA if concentrations low and no receptors. Determines beneficial uses; if drinking water aquifer no NA, if no potential for drinking water consider NA.	Risk-based model being developed to assess NA	Discourage case-by-case
Nevada	Neither case-by-case	No formal NA policy. Adhere to federal UST program. Soil contamination level 100 ppm. Cleanup required if over level.		Discourage case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
New Hampshire	Encourage	Guidance but no policy on NA. Developing ground-water management zones. Other sections are looking at NA. About to pass the Brownfields and have a voluntary action program.		Neither case-by-case
New Jersey	Encourage	Written policy on NA; involves characterization, source removal, and monitoring. Must identify ground water uses based on 25-year plan. Requires at least eight quarters of monitoring. Sentinel well 3 years time of travel upgradient of receptor.		Neither case-by-case
New Mexico	Encourage	No formal guidance. Incorporating NA into regulations as part of RBCA. Looks at property boundaries, cost/benefit, and risk. Source removal and low concentrations use NA. Loosely subscribes to Chevron indices to determine extent of bioremediation. Not as many non-UST sites but has two using NA. Contaminants include carbon tetrachloride and perchloroethylene.	RBCA	Neither case-by-case 2 cases
North Carolina	Encourage	Developed NA Rules in 1993. Over 150 sites approved. Must monitor until reaching cleanup levels. Expanding rules to allow some sources to remain if no further leaching occurs and to consider more compounds for NA.	Accepted USGS models	Neither case-by-case
North Dakota	Encourage case-by-case	No state policy. Believes NA works in significant number of cases. NA approved at over 200 petroleum and 20 solvent sites. Monitoring minimum of 2 years to verify that concentrations are decreasing.		Encourage case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Ohio	Encourage	LUST follows RBCA guidelines. New Voluntary Action Program, Brownfields. Working on draft rule for hazardous waste and petroleum. Various models used. One PRP used POLLUT to demonstrate NA.	Include SESOIL, VLEACH	Neither case-by-case
Oklahoma	Encourage case-by-case	No formal policy on NA. Evaluates on a case-by-case basis. Property boundaries used as point of compliance.		Neither case-by-case
Oregon	Encourage	No state guidance. Revising the ASTM, and NA issue may arise when adopting rules on USTs.	SESOIL, AT123D	Case-by-case
Pennsylvania	Neither case-by-case	No NA policy. Not using RBCA. Developed "Act 2," which drives state programs. Site-specific standards based on risk assessment. "No action" may be designated to sites.		Neither case-by-case
Rhode Island	Neither case-by-case	No guidelines. NA reviewed on a case-by-case basis.		Discourage case-by-case
South Carolina	Encourage	Intrinsic remediation written into RBCA in evaluating LUST sites. Working with USGS on field studies addressing NA. Flexibility in modeling for NA.		Discourage case-by-case
South Dakota	Neither case-by-case	Uses ASTM RBCA system. No formal NA procedures. NA factors include contaminant type/extent and beneficial uses of aquifer. Looks at property boundaries. Soil cleanup required. Consult handbook, soil cleanup regulations, and ground-water quality standards used. Must meet water-quality standards for 1 year before closure.	RBCA	Neither case-by-case
Tennessee	Discourage case-by-case	NA not encouraged, but considers on a case-by-case basis. Encourages an accelerated bioremediation approach.		Discourage case-by-case

State	Encourage/ Discourage NA of Petroleum	Guidelines or Rules	Specific Models to Determine NA	Encourage/ Discourage NA of Nonpetroleum
Texas	Encourage	Developing risk-based rules addressing NA for UST; ready by end of year. Volunteer cleanup program started. Has guidance on NA of soils and is developing guidance for ground water.		Neither case-by-case
Utah	Encourage	Risk-based approach. Approves NA for petroleum but not for other compounds. Non-UST has two levels of industrial risk, 10^{-4} and 10^{-6}. Uses deed restrictions.		Discourage case-by-case
Virginia	Neither case-by-case	No guidance. Recognizes NA occurs with petroleum. Non-UST uses risk-based standards. NA depends on aquifer beneficial use. Have voluntary action program.	REAMS (SESOIL, AT123D)	Discourage case-by-case
Washington	Encourage	Actively looking at NA, particularly soil to ground water. Using SSL after EPA.		Neither case-by-case
West Virginia	Encourage	No definitive rule. Developing state policy for NA incorporating soil cleanup levels. Plans interagency risk-based approach. Brownfields just passed.		Neither case-by-case
Wisconsin	Neither	Developing preliminary guidance for a range of contaminants to be ready by end of year for ground water. Aquifer characteristics, risk, beneficial uses, and aquifer type will be considerations. Has guidance on NA of soils.		Neither case-by-case
Wyoming	Neither	NA considers risk, beneficial uses, aquifer characteristics. Considers NA in industrial areas and no potential receptors. Developing guidance (end of year) looking at a range of contaminants.		Neither case-by-case

North Carolina and New Jersey are the only states with *formal* guidance or rules addressing NA as a remediation option in both ground water and soils. Texas and Wisconsin have written formal guidance with regard to NA in soils and are currently working on ground-water guidance. States with *informal* policies or guidelines include Arkansas, Delaware, Illinois, Kentucky, Montana, North

Dakota, South Dakota, and Vermont. In the North Carolina Implementation Guidance, "the Corrective Action Plan (CAP) must document that conditions at the subject site are conducive to natural remediation processes and should present any evidence that natural attenuation is occurring at the site." NA is generally used as part of a treatment which may include source removal or other types of active remediation. Monitoring data are generally used to demonstrate decreases in volume and concentration over time. For sites where the plume is still expanding, NA could also be demonstrated if it can be shown that the rate of contaminant transport is significantly less than the estimated rate of linear ground-water velocity. Degradation products must also be evaluated since they can sometimes be more toxic the original contaminant of concern.

State agencies widely accept that NA does occur in petroleum-contaminated sites. EPA's Office of Underground Storage Tanks (OUST) found that remediation at leaking underground storage tanks has shifted to using NA across the United States. In 1993, landfilling was the predominant remediation for soils and pump-and-treat the most common in ground-water treatment. As of 1995, NA of soils (28 percent) was a close second to landfilling (34 percent), while NA (47 percent) is the most common form of remediation at ground-water sites. The policy is, however, that NA is not to be regarded as a "default" remediation technology, and free product removal is a prerequisite.

Leaks from underground storage tanks (USTs) are one of the most common causes of ground-water contamination. Many states are using or developing a risk-based corrective action approach when addressing these sites. The *Emergency Standard Guide for Risk-Based Corrective Action* applied at petroleum release sites, issued by the American Society for Testing and Materials (ASTM), looks at "demonstrated and predicted attenuation of hydrocarbon compounds with distance." Corrective action goals are determined based on a tiered approach, the most conservative being at Tier 1, where risk to human health or the environment is high. The other two tiers may allow for site-specific goals to be developed where risk is not imminent. Revisions to RBCA are under way to incorporate the premise that the further a receptor is from a contaminated area, the less likely it is to be affected, consequently allowing for greater amounts of contaminants to be left in place the farther they are from a receptor. Natural attenuation is "assumed" to occur between the source and the receptor.

In risk-based decision-making, proof of NA may not always be as important as the potential impact on a given receptor, the classification or use of the ground-water aquifer, or simply the approaches that are technologically feasible or cost-effective. Some states are assigning different levels of cleanup based on these other factors. Alternate protection levels may be assigned based on the beneficial-use designation of the aquifer. Even in highly populated areas, if the ground water is already contaminated and is not being used as a water supply, then cleanup may not be required. These decisions, although they may be in part based on assumed NA, may not be the main consideration. Many states view remediation with regard to property boundaries. As long as the contamination remains within the property boundaries, then no action may be taken. If a plume migrates off the property, however, NA may be used to address contamination at that point. Some states using "monitoring only" may not necessarily be basing these decisions on the basis of site-specific NA, but on risk. Other states are claiming NA by default, simply due to the length of time required for active cleanup. Also, not all states are requiring source removal before using NA.

Summary

New Jersey and North Carolina have developed policies addressing NA as a stand-alone option for both ground water and soils, primarily for petroleum compounds. North Carolina developed its rule on NA in 1993 and has approved approximately 150 sites for the process. NA is only appropriate after site conditions have been fully evaluated and it has been concluded that natural remediation is a viable option for ground water. This involves an evaluation of all potential impacts in the vicinity of the site, including impacts on ground water used for potable purposes, surface water bodies, and wetlands, to ensure that receptors will not be affected as the contaminant concentrations degrade. Source removal is generally required. Most of these are petroleum sites, but a couple of sites in North Carolina have also included solvents and even lead. Although some of these compounds are not readily biodegradable, North Carolina also looks at sorption and removal of the source. Source removal may not even always be required if it can be proven that no further leaching will occur.

Texas and Wisconsin have written formal guidance regarding NA of soils. They are in the process of developing guidance pertaiing to NA of ground water as well. Wisconsin is currently working with Alaska in developing guidance for soils in that state.

Other states have developed informal guidance for ground-water and soil contamiantion focusing on petroleum waste. Delaware has informal guidelines concerning petroleum waste that allows for a "passive corrective action" plan. Passive action is remediation through natural degradation. Assurance that contaminants will not pose a threat to human health or the environment is required. One year of monitoring must show that the remediation is sufficient for site closure. After 2 years, written permission is required to continue using passive action. Florida recognizes NA and expects this to be a big part of remediation in the future. The state intends to expand NA activities during the next year and broaden the types of sites that will be considered. Monitoring for NA will be allowed at sites with higher contaminant concentrations and more widespread contamination. Michigan is developing a draft bioremediation guidance document to determine criteria considered for bioremediation, including NA. A final version, expected within the year, will not only consider petroleum waste but other wastes, including solvents. Texas is beginning to look at chemicals other than petroleum to be considered for NA as well. A document was recently prepared entitled *Present Remedies Guidance Document for Soils at Texas Superfund Sites*. A similar document on ground water will soon be written and will address NA. Nebraska's Superfund section may also look at NA by allowing it at sites with low levels and simply monitoring. New Mexico has allowed a few sites to use NA of more refractory chlorinated compounds. For example, at one site it was found that carbon tetrachloride was degrading fairly well to methylene chloride, another with NA of PCE contamination. Wisconsin and Wyoming are developing some very preliminary guidance or protocols looking at a range of contaminants; these should be ready by the end of the year. Considerations for use of NA will be based not only on the risk and beneficial uses but other characteristics of the aquifer as well.

Most of the states are either using RBCA or are incorporating it into state guidelines regarding NA of petroleum hydrocarbons at UST sites. California, Iowa, Mississippi, Montana, North Carolina, Washington, and West Virginia are the only states that were not using and did not plan to use the RBCA at petroleum sites. Interested parties in West Virginia, however, recently met to develop a state policy for NA incorporating soil cleanup levels. The state is in the process of accumulating information from other states. A risk-based approach is in review for eventual incorporation into the

overall statewide policy. The state plans to have an interagency approach including UST, RCRA and CERCLA. Idaho is developing a new ground-water rule. Maine is developing a guidance document (draft by the end of May) for in-house staff to determine when intrinsic remediation of petroleum hydrocarbons is appropriate. States have also indicated that NA may be incorporated in other programs as well. In the survey, Illinois, Idaho, West Virginia, Texas, and Ohio are only a few of the states that indicated they have a voluntary action program and have passed state legislation concerning the "Brownfields" Act.

Natural attenuation can play a role in the cleanup of Brownfields sites. Brownfields are abandoned, idled, or underused industrial and commercial sites where expansion or redevelopment is complicated by real or perceived environmental contamination that can add cost, time, or uncertainty to a redevelopment project. In recent years, states have developed voluntary cleanup programs designed to provide liability protection to private parties that clean up Brownfields sites. EPA supports these state cleanup programs and pledges that the successful cleanup of a site under a state program will also satisfy EPA regulations. Eighteen Brownfields National Pilots are currently under way in Alabama, California, Connecticut, Indiana, Kentucky, Louisiana, Maryland, Massachusetts, Michigan, New Jersey New York, Ohio, Oregon, Pennsylvania, Rhode Island, Texas, Virginia, and Washington.

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State Review

Natural Attenuation of Ground Water and Soils

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Natural Attenuation of Petroleum Hydrocarbons

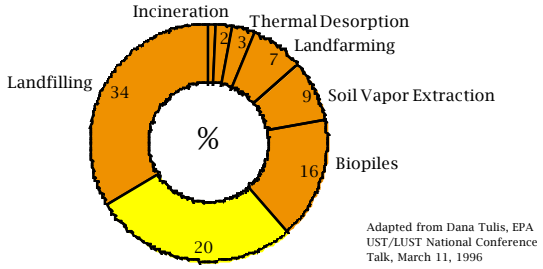
- Leaks from USTs are the most common cause of ground-water contamination
- As of June 1995, there have been over 295,000 confirmed releases

Remediation at LUST Has Shifted to Using Natural Attenuation

- In 1993, landfilling was the predominant remediation for soils, and pump-and-treat the most common in ground-water treatment.
- As of 1995, NA of soils (28%) only second to landfilling (34%), while NA of ground water (47%)

(information obtained from EPA's Office of Underground Storage Tanks [OUST])

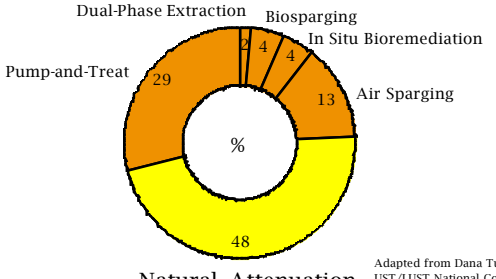
Use of Soil Cleanup Technologies at UST Sites



Natural Attenuation

Adapted from Dana Tulis, EPA UST/LUST National Conference Talk, March 11, 1996

Use of Groundwater Cleanup Technologies at UST Sites



Natural Attenuation

Adapted from Dana Tulis, EPA UST/LUST National Conference Talk, March 11, 1996

Programs That May Look at Natural Attenuation in Cleanup

- UST
- CERCLA
- RCRA
- State Voluntary Cleanup Program
- Brownfields Sites

Risk-Based Corrective Action (RBCA) and NA at UST Sites

- Emergency Standard Guide for RBCA by ASTM
- Most states using/incorporating RBCA into guidelines
- Demonstrated and predicted attenuation of hydrocarbons with distance
- Corrective action goals based on a tiered approach
  - Tier 1 most conservative; high risk
  - Two lower tiers allow site-specific goals; risk not imminent

ASTM Revisions

Currently assembling NA document

- Limited petroleum compounds
- May consider other compounds (e.g., solvents) in future

Document purpose

- Remove stigma that NA is equivalent to "no further action"
- Serve as a conceptual framework in NA decision-making and information needs

EPA's Policy on Natural Attenuation

Office of Underground Storage Tanks (OUST)

- NA is not a "default" remediation technology for LUST sites
- Supports use of the most appropriate technology
- Technology selection should be risk-based on a site-by-site basis
- NA is an active choice, includes site characterization, risk assessment, and monitoring
- Free product removal is a prerequisite to using NA
- Cleanup not complete until reaching state or local cleanup levels

Brownfields

- Abandoned industrial/commercial sites
- Redevelopment complicated by real or perceived contamination
- Successful cleanups under State programs would satisfy EPA regulations
- 18 States currently with Brownfields National Pilot Studies

U.S. EPA Survey Asked States:

(1) Whether they encourage or discourage the use of natural attenuation (NA)

(2) If there are any formal or informal policies or guidelines for NA

(3) If they use any particular model when deciding on NA

(4) If compounds other than petroleum hydrocarbons would be considered for NA

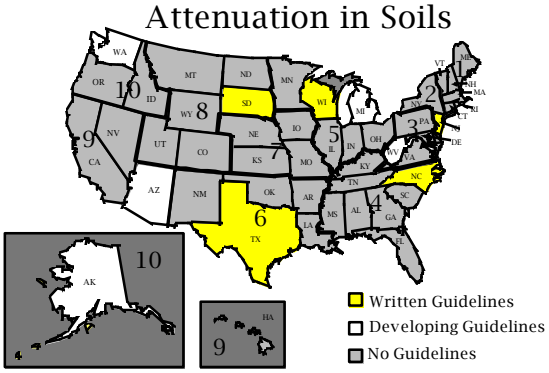
States With Formal Guidance on Soils Using NA

- Texas
- Wisconsin

States Developing Soils Guidance With NA

- Alaska
- Arizona
- Florida
- Michigan
- South Dakota
- West Virginia
- Vermont

State Guidelines on Natural Attenuation in Soils



States With Natural Attenuation Policy on Ground Water

- North Carolina
- New Jersey

Each State Requires:

- Full plume definition and receptor analyses
- Appropriate modeling to predict plume degradation
- Source removal or control
- Monitoring program to demonstrate NA

North Carolina

- Developed rule on natural attenuation in 1993
- Approved approximately 150 sites for NA
- Most are petroleum sites, but some included solvents and even lead
- Looks at sorption and source removal as part of NA, hence NA for Pb possible
- Assesses potential for toxic byproducts
- Source removal may not be required if no further leaching to ground water is proven
- Future land use in the vicinity of the site required

New Jersey Natural Attenuation Rules

- Assess potential impacts, ensure no impact to receptors, and remove/remediate sources
- NA may be used at sites deemed technically impractical for active remediation
- Identify current and potential ground-water uses based on a 25-year plan
- Costs of remedy includes long-term monitoring
- Historical data determine the duration and frequency of sampling

Monitoring Requirements

- New Jersey—at least eight quarters of monitoring
- North Carolina—monitor until appropriate ground-water quality standards achieved
- Both require sentinel wells downgradient of plume if receptor involved

  Minimum time of travel upgradient of receptor:
  - 3 years - New Jersey
  - 1 year - North Carolina
- Monitoring assesses past predictions, plume behavior, and modification needs

Other States Addressing Natural Attenuation

Delaware UST Section's Technical Guidance Manual

- "Passive corrective action" allows NA if no threat to receptors
- Source and free product removal a goal
- Monitor 1 year to demonstrate sufficient remediation for site closure
- Passive action not allowed beyond 2 years without written approval

States Developing Natural Attenuation Guidance on Ground Water

TEXAS	Ground-water guidance similar to "Present Remedies Guidance Document for Soils at Texas Superfund Sites"
MICHIGAN	Draft bioremediation guidance to determine criteria considered for bioremediation including NA. Not only petroleum waste will be considered.
MAINE	In-house guidance document to determine intrinsic remediation of petroleum

States Developing Natural Attenuation Guidance on Ground Water (continued)

WISCONSIN	Preliminary guidance based on risk, beneficial uses, and aquifer characteristics
FLORIDA	Petroleum cleanup rules/ mandating RBCA in State Legislative statutes
SOUTH CAROLINA	Performing field studies with USGS that address intrinsic remediation
WYOMING	Preliminary guidance considering a range of contaminants

Other States Approaches

CALIFORNIA	Does not use NA. Revisions to Resolution 92-49 refer to "containment zones" out of which the contaminant is not allowed to migrate.
TENNESSEE	Does not encourage use of NA. Does encourage more accelerated forms of bioremediation.
CONNECTICUT	Use ground-water classification to establish cleanup standards. Aquifers with lower designation more likely to be considered for NA as a remedial option.

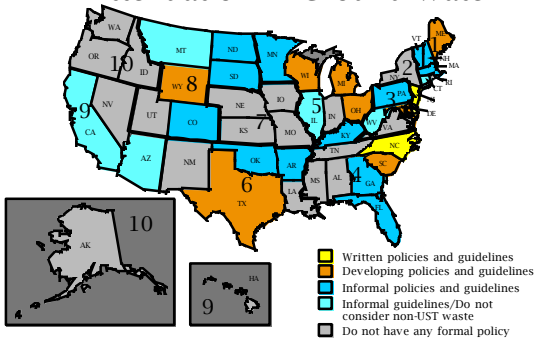
Natural Attenuation Models

- Most states allow PRP to use any peer reviewed model
- Some states have indicated they use mostly SESOIL, VLEACH, and AT123D
- One State indicated interest in Bioplume III when available

Survey Summary

- There are 2 states that have developed official policy
- There are about 7 states developing guidance
- There are about 13 states with unofficial guidance

State Policies Regarding Natural Attenuation in Ground Water



Conclusion

- Interest in NA is increasing and being incorporated into more state environmental regulations and programs.
- Although NA is gaining acceptance, it should be remembered that complete site characterization is an essential part in deciding if this remediation option is appropriate.
- NA is a remedial approach that should be based on the likelihood of success and is not a "no action" alternative.

Monitoring

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Monitoring of bioremediation and natural attenuation can be considered from several viewpoints. First are the contaminant-oriented questions: Are the contaminants disappearing, and, if so, how? The mechanism of disappearance is of interest: Are contaminants being biodegraded, or to what degree are volatilization, leaching, adsorption, or other mechanisms involved?

Next, if the contaminants are being biodegraded, are the contaminants being broken down to intermediate products (which may be innocuous or toxic), mineralized to carbon dioxide and water, or polymerized/humified? Toxicity changes may be monitored to determine whether toxicity is decreasing or whether degradation products may be of higher toxicity than the original contaminants. Finally, the rate of contaminant loss helps to estimate remediation times and to assess degradation relative to contaminant mobility to sensitive receptors.

Geochemical factors associated with contaminant degradation may be monitored. Degradation may cause changes in pH, redox potential, electron acceptors, and alkalinity; these changes may be monitored to help prove remediation is taking place, to establish areas on the site where different kinds of remediation are taking place, and to estimate remediation rates. In addition to the geochemical factors already mentioned, temperature and salinity may affect microbial processes and therefore degradation rates. Operational parameters require monitoring to determine whether appropriate levels of nutrients, electron acceptors, and water necessary for bioremediation are present.

Monitoring of microbial parameters may be required. The various estimates of contaminant degradation, electron acceptor change, and other geochemical changes indirectly measure microbial activity, but there may be a need to measure certain aspects of the microbial population directly. Microbial populations may be estimated by plate counts, most probable number techniques (MPN), or direct microscopic examination. In addition to respiration measurements, ATP activity measurements can estimate microbial metabolic activity. FAME profiles and sole carbon source profiles measurements may provide information about microbial community structure. Several types of culture tests can indicate the ability of the microbial population to degrade contaminants of interest. Generally, microcosm tests using soil or water samples from the site under conditions as similar as possible to site conditions are most likely to yield information about microbial activity and contaminant degradation that can be readily used for making decisions about site activities.

Monitoring may be required to establish the success (or failure) of bioremediation/natural attenuation, give timely warning of the impending impact on sensitive receptors, and determine the potential for site closure. Generally, monitoring is required for a number of years to develop sufficient data to establish that risk to sensitive receptors is not significant, and that the site is ready for closure.

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Monitoring

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Monitoring Bioremediation/Natural Attenuation

- Much information available on monitoring technologies
- This presentation mainly a checklist: what should be monitored, and why?
- References for specific techniques in handout

Monitoring To Determine Remediation Rates (contaminant disappearance)

- Are contaminants disappearing?
- Rate of disappearance

Monitoring To Determine Daughter Products

- Estimate remediation rates
- Determine toxic products (e.g., vinyl chloride from TCE)

Monitoring for Operational Purposes

- Addition of electron acceptors
- Nutrients
- Water

Monitoring To Warn of Potential Impact on Sensitive Receptors

- At or before point of compliance
- Must allow time for remedial measures

Monitoring Mass Balance Approach

- Contaminants "disappear" from analytical view without actually being remediated
- Monitor each phase (soil solids, gas, water, and nonaqueous phase liquid) to determine how much of each waste component is in each phase
- Determine whether remediation is actually taking place or whether contaminants are merely being moved to different phases

Monitoring Breakdown Products

- Many breakdown products known
- Monitoring is not common, except for breakdown products of known high toxicity, such as vinyl chloride, or those that are easy to measure, such as carbon dioxide

Monitoring Toxicity – Microtox Microbial Bioassay

- Cultures of phosphorescent (light-emitting) marine bacteria are exposed to contaminated media or extracts, and decline in light output over time is measured
- Microtox assay measures general metabolic inhibition

Monitoring Toxicity – Microtox Microbial Bioassay

- Major advantages: quick, easy, repeatable, inexpensive, and has a large amount of published literature about its uses and results
- Major disadvantage (as for most acute bioassays): results of the assay have no direct relationship to toxicity of the contaminants to humans or ecology

Monitoring Toxicity – Ames Assay

- A measure of mutagenic potential of a sample
- High correlation between mutagenicity (as measured in the Ames test) and carcinogenicity
- Several days to complete, more expensive than Microtox

Monitoring Toxicity – Other Assays

- Many other species have been used for assessing toxicity of environmental samples
- EPA conducting R&D on ecological and health assays to develop alternative endpoints

Monitoring Microbial Activity

- Plate counts
- Most Probable Number (MPN) counts
- Direct microscopic counts
- Respiration measurements
- ATP activity measurements

Monitoring Microbial Activity

- Oxygen, carbon dioxide levels—general index of microbial activity
- Monitoring oxygen or carbon dioxide alone can be deceiving since abiotic processes can affect oxygen or especially carbon dioxide
- Because the respiration estimated may not result only from transformation of the compounds of interest, respiration cannot be used as a direct measure of transformation of these compounds

Monitoring Microbial Activity

- Soil gas concentrations of CO_2, O_2 fluctuate daily due to microbial activity
- Measure CO_2 and O_2 at the same time of day for each sampling event

Monitoring Microbial Activity

- Soil microorganisms can be cultured on specific media to determine counts of "specific degraders"
- If PAHs are added to a media with no other carbon sources present, any microorganisms that grow in the media can be assumed to have the capability of using PAHs as a sole source of carbon

Monitoring Soil Moisture

- "Visual" methods—require experience
- Gravimetric methods—accurate, but time consuming
- Neutron probes—accurate, expensive, use radioactive material
- Porous cup tensiometers
- Capacitance—not very accurate

Nutrients

- Several standard tests
- Carbon to nitrogen to phosphorus (C:N:P) ratios of 100–300:10:1

Volatilization

- Usually volatiles released from the soil surface
- Canopy placed over defined area of contaminated soil
- Vapors collected under canopy swept into adsorbent for later extraction and analysis
- Sampling pump at site perimeters

Leaching

- Porous cup and pan lysimeters
- Porous cup lysimeters work even when soil is relatively dry
- Pan lysimeters collect only water that is actively moving down through soil
- Most LTUs, soil piles, compost units are lined to collect leachate

Sampling Program Goals

- Average contaminant concentration to +/- x ppm
- Highest contaminant concentration < x
- Desired confidence limits

Sample Location

- Random
- Stratified random
- Grid, with random start

What Should Monitoring Show?

- Plume type (stable, shrinking, expanding)
- Remediation rates
- Warning of potential impact on sensitive receptors

What is Required To Show That Bioremediation/Natural Attenuation Is "Working?"

- Documented loss of contaminants from site
- Daughter product appearance
- Appropriate geochemistry
- Electron acceptor disappearance/product appearance
- Laboratory assays showing microorganisms from site samples have potential to transform contaminants under expected site conditions

Monitoring – Primary Evidence

Plume behavior (stable, shrinking, expanding)

Monitoring – Primary Evidence

- If the plume is stable or shrinking, this is primary evidence that natural attenuation is occurring
- If the plume is expanding more slowly than GW movement adjusted for retardation, this is evidence that natural attenuation is occurring

Monitoring – Secondary Evidence

- Historical data may not be available to indicate the plume state
- Then, secondary evidence can be used while information on plume state is being accumulated

Monitoring – Secondary Evidence

Electron acceptor/reduction product concentrations

Monitoring – Secondary Evidence

Alkalinity

Monitoring – Secondary Evidence

- Inverse correlation between electron acceptors and contaminant concentrations
- Daughter products

Determining Natural Attenuation Rates

- Mass balance (for any plume type)
- Concentration versus time (for shrinking plumes)
- Concentration versus distance (for stable plumes)

Mass Balance Approach Requirements

- Estimate of source area perpendicular to GW flow
- Estimate of hydraulic conductivity and gradient

Concentration versus Time Approach Requirements

Wells with measurable contaminant outside free product zone

Concentration versus Distance Approach Requirements

Two or three downgradient wells, along direction of GW flow, with at least two wells with measurable contaminant concentrations, differing by several fold

Warning of Impact on Sensitive Receptors

- Sentinel wells located at compliance point between contaminated GW and sensitive receptor
- Location must allow time for remedial measures to be taken before contamination moves past sentinel well to sensitive receptor

Monitoring Frequency – Factors

- Plume status
- Water table fluctuations
- Seasonal variability
- GW velocity
- Distance from plume to sensitive receptor

Monitoring Frequency

One year of quarterly monitoring often sufficient to establish relationship between readily degraded contaminants and electron acceptor/reduction products concentrations

Monitoring Frequency

- More than one year may be necessary to establish whether a plume is stable, shrinking, or expanding
- Previous monitoring efforts may reduce need for more wells, monitoring data

Laboratory Assays for Biodegradation

- Determine biodegradation rates, but may not reliably indicate field rates
- Establish potential for bioremediation, but may not be necessary for simple petroleum contaminants
- Determining need for nutrient, electron acceptor addition

Modeling

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Introduction

A mathematical description of bioremediation establishes a framework for evaluating laboratory treatability data and field data that are useful for determining treatment potential under site and environmental constraints. Mathematical models provide an approach for integrating simultaneous processes of degradation, mass transport, and partitioning within subsurface and surface systems so that an assessment can be made of the presence of target chemicals in leachate, soil, and air. Models provide an estimate of the potential for ground-water and air contamination through a determination of the rate and extent of contaminant transport and biodegradation as related to specific subsurface or surface characteristics. Models also allow identification of those chemicals requiring management to reduce or eliminate risk to human health and the environment. Thus, mathematical models represent tools for ranking design, operation, and management alternatives as well as for the design of monitoring programs for engineered (active) and nonengineered (passive) biological treatment systems.

Model Types

To address the complex processes occurring at a site with regard to bioremediation, four types of models are described: 1) saturated flow, 2) multiphase flow, 3) geochemical, and 4) reaction rate models (1). Saturated flow models are derived from basic principles of conservation of fluid mass and describe the flow path and rate of transport of water and dissolved contaminants (using principles of conservation of chemical mass) through the saturated zone. In special cases, biodegradation reactions, based on simple first-order kinetics, can be incorporated into the model. Often, however, biodegradation processes are too complex to be simply incorporated; therefore, special modeling tools are needed.

Multiphase flow models describe systems where two or more fluids exist together in a porous medium. With regard to unsaturated flow, water and air are two fluids that exist together. Addition of gasoline represent a third fluid within the unsaturated zone. Dense nonaqueous phase liquids (DNAPLs) often occur within the saturated zone and are immiscible (nonmixing) with water. Complex interactions among water, air, NAPLs, and solids renders multiphase flow models that are more complex and less accurate due to the relatively large number of transport parameters required.

Geochemical models identify how thermodynamics of chemical reactions in the subsurface control the speciation of target chemicals. Geochemical models are primarily concerned with inorganic contaminants, for example, metal mobility. The lack of application to bioremediation of such models is due to 1) lack of incorporation of organic chemicals, 2) equilibrium orientation (rather

than kinetic orientation of biodegradation models), and 3) high complexity and cost without the incorporation of biological components.

Reaction rate models, including biological models, describe the rate of microbial transformation of target organic chemicals. Biodegradation rate expressions can be incorporated into a model that takes into account the rate of reaction as a function of active biomass present, contaminant concentration, and electron acceptors present. Determination of appropriate rate expressions, especially for the description of co-oxidation or co-metabolism, is an area of current development.

Biodegradation models are most easily combined with flow models when one rate-limiting material can be identified. The rate-limiting material often is the primary electron donor or electron acceptor. The biodegradation of petroleum hydrocarbons can often be modeled with oxygen as the rate-limiting parameter.

Modeling Biodegradation

Main approaches used for modeling biodegradation include 1) first-order degradation models, 2) biofilm models, 3) instantaneous reaction models, and 4) dual-substrate Monod models. Additional information regarding these modeling efforts is given in Bedient and Rifai (2). Where a biofilm approach is used, as often occurs in the subsurface, three processes are described: 1) mass transport from the bulk liquid, 2) biodecomposition within the biofilm, and 3) biofilm growth and decay.

Borden and Bedient (3) developed the first version of the BIOPLUME model. They developed a system of equations to simulate the simultaneous growth, decay, and transport of microorganisms combined with the transport and removal of hydrocarbons and oxygen. Simulation indicated that any available oxygen in the region near the hydrocarbon source will be rapidly consumed. In the body of the plume, oxygen transport will be rate limiting, and the consumption of oxygen and hydrocarbon can be approximated as an instantaneous reaction.

Rifai and others (4, 5) expanded the original BIOPLUME and developed a numerical version (BIOPLUME II) by modifying the U.S. Geological Survey (USGS) two-dimensional method of characteristics (6). Transport of oxygen and contaminants in the subsurface is simulated, and biodegradation is approximated by the instantaneous reaction model. The only input parameters to BIOPLUME II that are required to simulate biodegradation are the amount of dissolved oxygen in the aquifer prior to contamination and the oxygen demand of the contaminant determined from a stoichiometric relationship. Other parameters are the same as required for the USGS model (6). BIOPLUME II was used to model biodegradation of aviation fuel at the U.S. Coast Guard Station in Traverse City, Michigan.

Unsaturated zone modeling has been presented in Stevens et al. (7), where the model developed by the U.S. Environmental Protection Agency, Regulatory and Investigative Treatment Zone (RITZ), was expanded. The Vadose Zone Interactive Processes (VIP) model allows for the prediction of the dynamic behavior of chemicals in the unsaturated zone under variation of temperature, precipitation, and waste spill frequency (7). The VIP model accounts for biodegradation, effect of

oxygen concentration on biodegradation rate, volatilization, sorption/desorption, advection, and dispersion of target chemicals within a vadose zone system.

The BIOSCREEN model is an easy-to-use screening tool for simulating natural attenuation of dissolved hydrocarbons at petroleum release sites (8). The software uses a Microsoft Excel spreadsheet environment and is based on the Domenico analytical solute transport model. BIOSCREEN has the ability to simulate advection, dispersion, adsorption, and aerobic decay as well as anaerobic reactions, which have been shown to be the dominant biodegradation processes. BIOSCREEN included three types of models: 1) solute transport without decay, 2) solute transport with first order decay, and 3) solute transport with biodegradation assuming an "instantaneous" biodegradation reaction. It is possible to modify BIOSCREEN to simulate intrinsic remediation of chlorinated hydrocarbons.

With regard to the application of all models, the limitations must be identified and constraints addressed. For all models, validity must be established on a site-by-site basis. No "off-the-shelf" models are available for use on a routine basis regarding biodegradation. In addition, measurement of input parameters often are extensive and sometimes are expensive (1). While modeling has several limitations, the approach is a useful tool for understanding the dynamic changes that occur in field sites during bioremediation.

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Modeling

Quantifying Biodegradation of Subsurface Pollutants

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Modeling

- Provides framework for organizing information about a site
- Provides an approach for integration of degradation, transport, and partitioning processes
- Useful tools for managing field sites and evaluating bioremediation

Modeling

Evaluation of In Situ Bioremediation

- Contaminant loss explained by abiotic reactions?
- Contaminant loss explained by biological reactions using reasonable processes

Model Types

• Saturated flow	Water
• Multiphase flow	Two or more fluids together
• Geochemical	Speciation/ thermodynamics
• Reaction rate	Biological, chemical

Challenges

- Physical, chemical, and biological processes must be incorporated
- Lack of field data on biodegradation
- Lack of numerical schemes that accurately simulate relevant processes

Biodegradation Kinetics Main Approaches for Modeling

- First-order degradation models
- Biofilm models (including kinetic expressions)
- Instantaneous reaction models
- Dual-substrate monod models

Biofilm Model Processes

- Mass transport from the bulk liquid
- Biodecomposition within the biofilm
- Biofilm growth and decay

Bioplume Model

- Borden and Bedient (1986)
- Microorganism growth, decay, and transport
- Hydrocarbon transport and removal
- Oxygen transport and removal

Bioplume Model

- Oxygen near hydrocarbon source rapidly depleted
- Oxygen transport limiting in the body of the plume
- Consumption of oxygen and hydrocarbon considered instantaneous

Bioplume Model

Major Sources of Oxygen

- Transverse mixing
- Advective fluxes
- Vertical exchange with unsaturated zone

Bioplume II

- Rifai et al. (1987, 1988)
- Improvement
- Simulate transport of oxygen and contaminants

Bioplume Applications

- Conroe, Texas site—PAH contamination
- Traverse City, Michigan—aviation fuel

Unsaturated Zone Modeling

Vadose Zone Interactive Processes (VIP)

- EPA model
- Grenney and Stevens (1988–1989)
- Enhancement of Ritz model (EPA)
- Regulatory and Investigative Treatment Zone

Unsaturated Zone Modeling

Vadose Zone Interactive Processes (VIP)

- Biodegradation
- Effect of O_2 concentration on biodegradation
- Volatilization
- Sorption/desorption
- Advection
- Dispersion

Unsaturated Zone Modeling

Vadose Zone Interactive Processes (VIP)

- Dynamic behavior under variable conditions of:
  - Precipitation
  - Temperature
  - Spill frequency

Model Applications

- Mass of parent compound remaining with time and distance
- Apparent mass of parent compound remaining with time and distance
- Predict effects of source removal on lifetime of plume

Bioscreen Model

- U.S. Air Force
- Microsoft Excel spreadsheet environment
- Based on Domenico analytical solute transport model

Bioscreen Model

- Simulate natural attenuation of dissolved hydrocarbons at petroleum release sites
- Can be modified to simulate natural attenuation of chlorinated hydrocarbons

Bioscreen Model

Processes Simulated

- Advection
- Adsorption
- Dispersion
- Aerobic decay
- Dominant anaerobic reactions

Bioscreen Model

Includes 3 Model Types

1. Solute transport without decay
2. Solute transport with first-order decay
3. Solute transport with biodegradation assuming as "instantaneous" biodegradation reaction

Limitations of Models

- Validity must be established on "site-by-site" basis
- No "off-the-shelf" models are available for evaluating bioremediation on a routine basis
- Measurement of input parameters often extensive and/or expensive