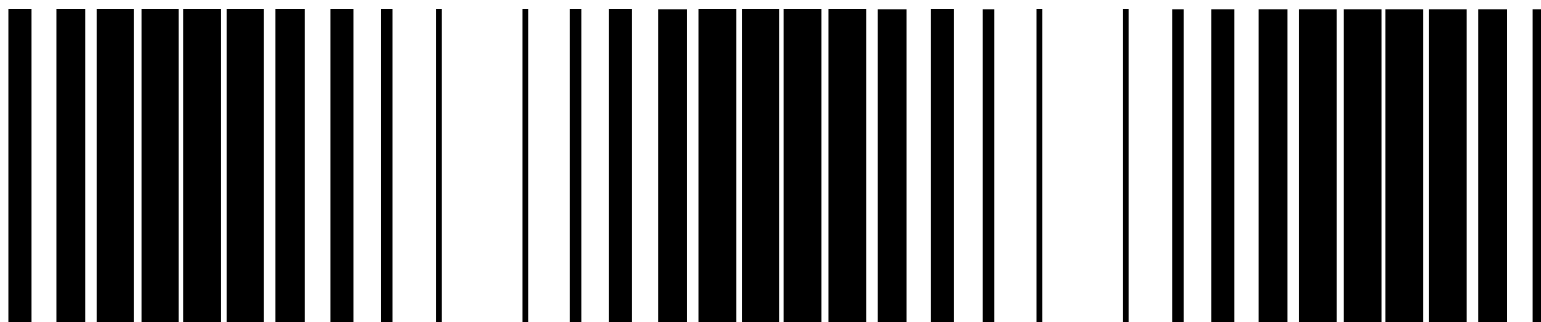1 EPA

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

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

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC

Notice

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Contents

Sources of Information

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

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

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

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

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

Suspended Growth Bioreactors

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U.S. Environmental Protection Agency, Cincinnati, OH

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.

References

1.	Metcalf & Eddy. 1991. Wastewater engineering: Treatment, disposal, and reuse, 3rd ed. In: Tchobanoglous, G., and F.L. Burton, eds. New York, NY: McGraw-Hill.

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.

3.	Bhattacharya, S.K., et al. 1990. Fate and effects of selected RCRA and CERCLA compounds in activated sludge systems. In: Proceedings of the Fifteenth Annual Research Symposium—Remedial Action, Treatment, and Disposal of Hazardous Waste. EPA/600/9-90/006. U.S. EPA, Risk Reduction Engineering Laboratory, Cincinnati, OH.

4.	Govind, R., et al. 1991. Fate and effects of semivolatile organic pollutants during anaerobic digestion of sludge. Water Res. 25:547-556.

5.	Govind, R., et al. 1991. Integrated model for predicting the fate of organics in wastewater treatment plants. Environ. Prog. 10:13-23.

6.	Desai, S.M., R. Govind, and H. Tabak. 1990. Development of quantitative structure-activity relationships for predicting biodegradation kinetics. Environ. Toxicol. Chem. 9:1,092-1,097.

Suspended Growth Reactors

Dolloff F. Bishop or Gregory Sayles

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National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH

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 ft^3)
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 ft^3)
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

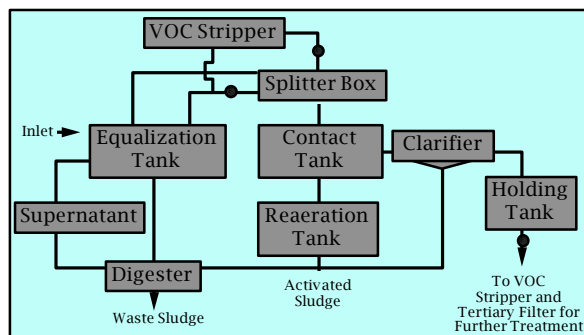Figure 1. Onsite Activated Sludge System

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
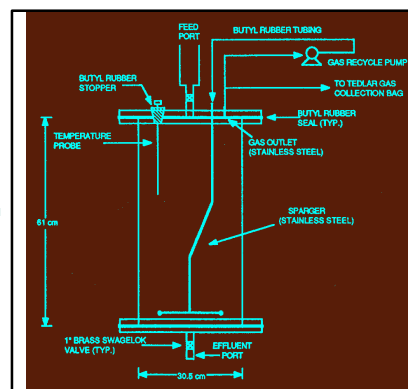
Figure 2. Pilot Digester System

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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National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio

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

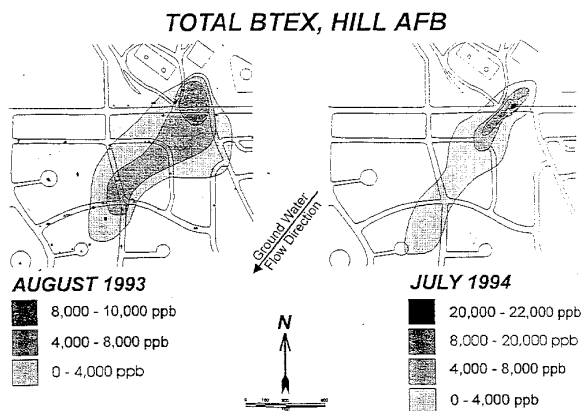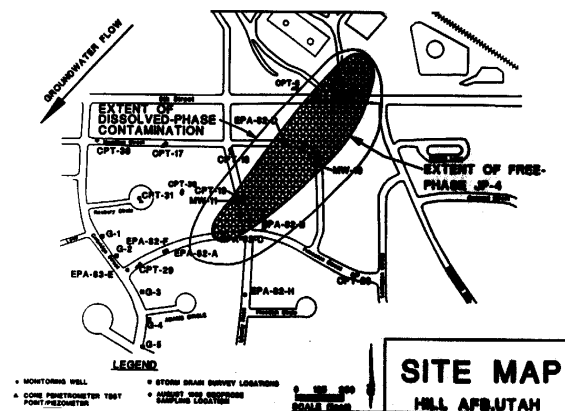## Additional Elements of a Quantitative Assessment of Natural Attenuation

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

SITE MAP
HILL AFB,UTAH

TOTAL BTEX, HILL AFB

AUGUST 1993
- 8,000 - 10,000 ppb
- 4,000 - 8,000 ppb
- 0 - 4,000 ppb

JULY 1994
- 20,000 - 22,000 ppb
- 8,000 - 20,000 ppb
- 4,000 - 8,000 ppb
- 0 - 4,000 ppb

N

Benzene Oxidation Aerobic Respiration

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

$$\Delta G^\circ_r = -3566\ kJ/mole\ Benzene$$

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

TOTAL BTEX   **DISSOLVED OXYGEN**

TOTAL BTEX AND DISSOLVED OXYGEN

8,000 - 10,000 ppb

4,000 - 8,000 ppb

0 - 4,000 ppb

GROUND WATER FLOW DIRECTION

N

3 - 5 mg/L

1 - 3 mg/L

< 1 mg/L

HILL AFB, UTAH   AUGUST 1993

8,000 - 10,000 ppb Total BTEX

4,000 - 8,000 ppb Total BTEX

0 - 4,000 ppb Total BTEX

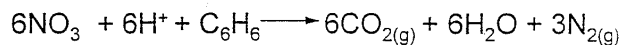Line of Equal Dissolved Oxygen Concentration (mg/L) (Background = 6 mg/L)

N
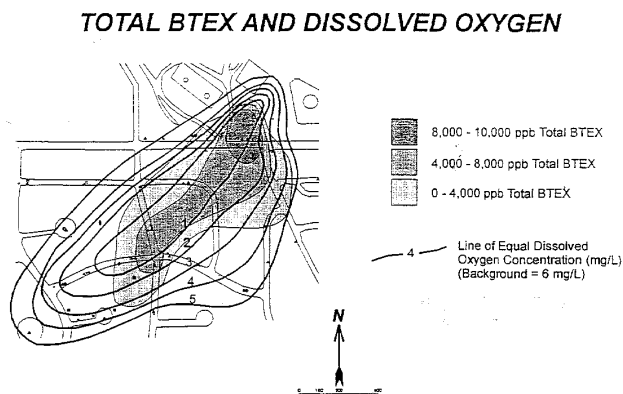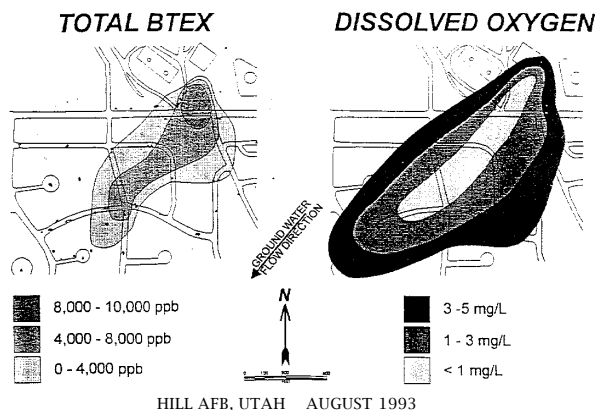
Aerobic Biodegradation

Background Dissolved
Oxygen Concentration = 6.0 mg/L

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

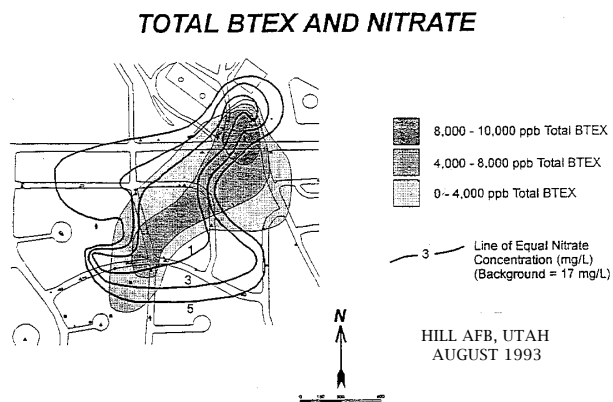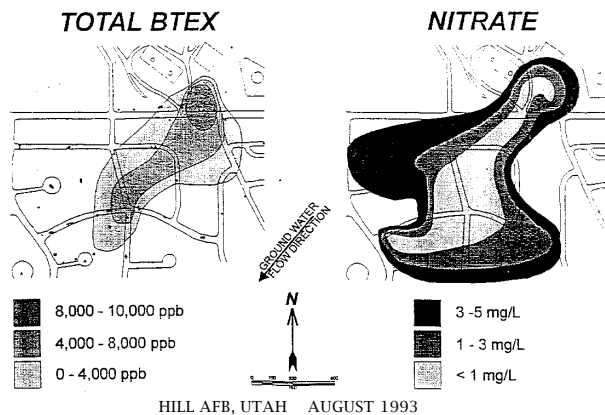Assimilative Capacity - Aerobic Biodegradation
1.92 mg/L
1920 μg/L

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

TOTAL BTEX   **NITRATE**

TOTAL BTEX AND NITRATE

8,000 - 10,000 ppb

4,000 - 8,000 ppb

0 - 4,000 ppb

GROUND WATER FLOW DIRECTION

N

3 - 5 mg/L

1 - 3 mg/L

< 1 mg/L

HILL AFB, UTAH   AUGUST 1993

8,000 - 10,000 ppb Total BTEX

4,000 - 8,000 ppb Total BTEX

0 - 4,000 ppb Total BTEX

Line of Equal Nitrate Concentration (mg/L) (Background = 17 mg/L)

N

HILL AFB, UTAH
AUGUST 1993

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

$$60H^+ + 30Fe(OH)_{3(a)} + C_6H_6 \longrightarrow 6CO_{2(g)} + 30Fe^{2+} + 78H_2O$$
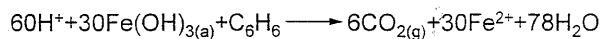
$$\Delta G^\circ_r = -2343 \text{ kJ/mole Benzene}$$

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

8,000 - 10,000 ppb
4,000 - 8,000 ppb
0 - 4,000 ppb

GROUND WATER FLOW DIRECTION

N

0.5 - 5 mg/L
5 - 10 mg/L
10 - 50 mg/L

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TOTAL BTEX AND FERROUS IRON

8,000 - 10,000 ppb Total BTEX

4,000 - 8,000 ppb Total BTEX

0 - 4,000 ppb Total BTEX

—5— Line of Equal Ferrous
Iron Concentration (mg/L)
(Background = 0 mg/L)

N

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

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

$$\Delta G^\circ_r = -340 \text{ kJ/mole Benzene}$$

Mass Ratio of SO_4^{2-} to C_6H_6 = 4.6:1
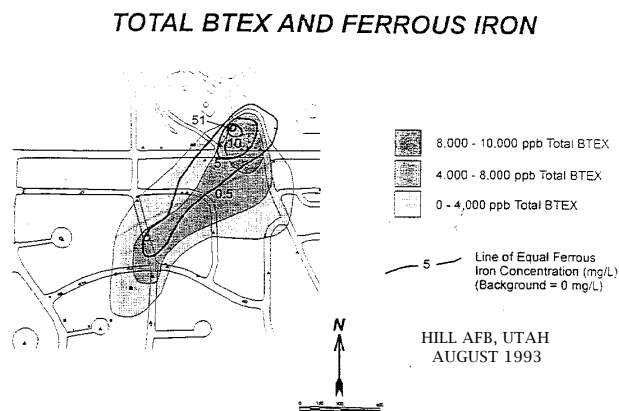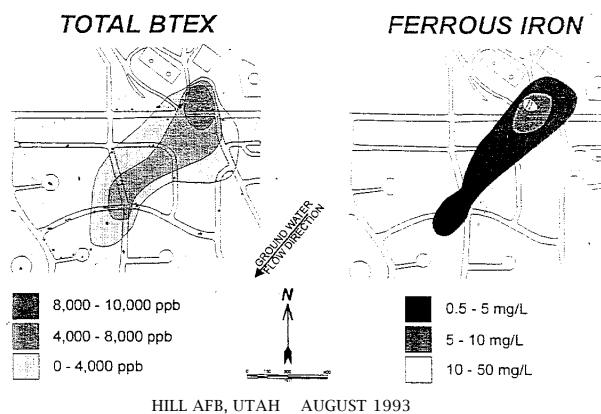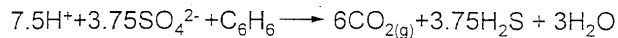
0.22 mg/L C_6H_6 Degraded per mg/L Sulfate Consumed

TOTAL BTEX

SULFATE

TOTAL BTEX AND SULFATE

8,000 - 10,000 ppb
4,000 - 8,000 ppb
0 - 4,000 ppb

40 - 60 mg/L
20 - 40 mg/L
0 - 20 mg/L

HILL AFB, UTAH   AUGUST 1993

8,000 - 10,000 ppb Total BTEX
4,000 - 8,000 ppb Total BTEX
0 - 4,000 ppb Total BTEX

—20— Line of Equal Sulfate
Concentration (mg/L)
(Background = 100 mg/L)
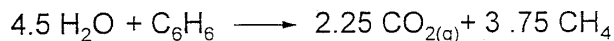
HILL AFB, UTAH
AUGUST 1993
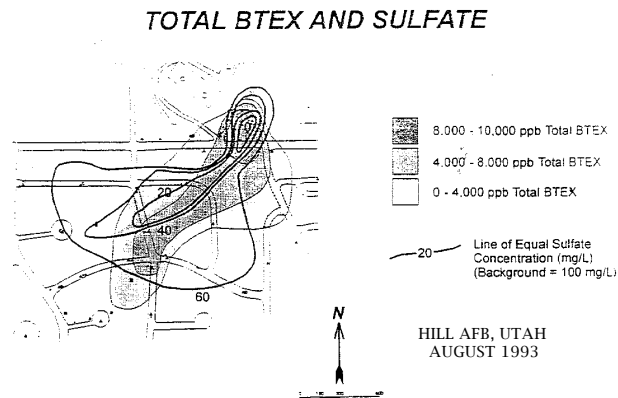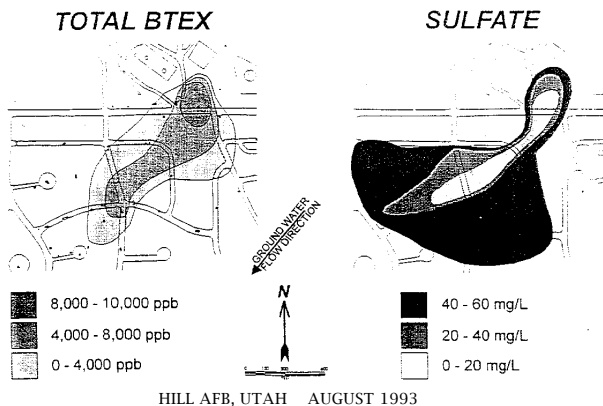
Sulfate Reduction

Background Sulfate
Concentration = 100 mg/L

$$\frac{0.21 \text{ mg/L BTEX}}{1 \text{ mg/L SO}_4^{2-}} \ (100 \text{ mg/L SO}_4^{2-})$$

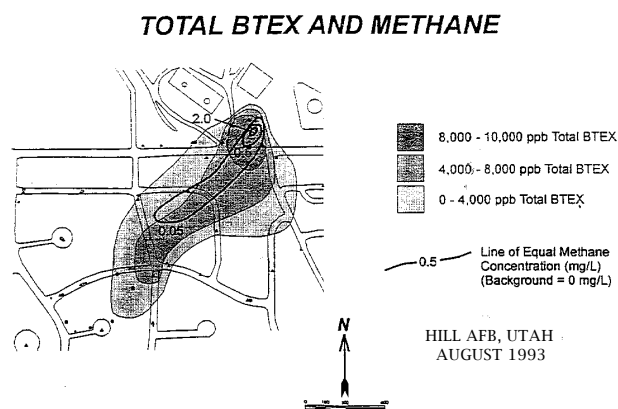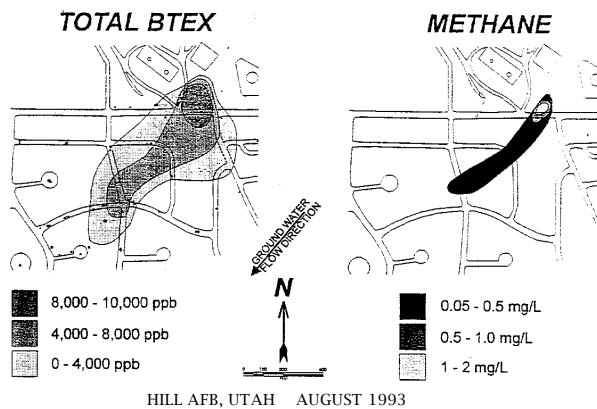Assimilative Capacity - Sulfate Reduction
21 mg/L
21,000 µg/L

Benzene Oxidation
Methanogenesis

$$4.5 \text{ H}_2\text{O} + \text{C}_6\text{H}_6 \longrightarrow 2.25 \text{ CO}_{2(g)} + 3.75 \text{ CH}_4$$

$$\Delta G^\circ_r = -135.6 \text{ kJ/mole Benzene}$$

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

TOTAL BTEX

METHANE

TOTAL BTEX AND METHANE

8,000 - 10,000 ppb
4,000 - 8,000 ppb
0 - 4,000 ppb

0.05 - 0.5 mg/L
0.5 - 1.0 mg/L
1 - 2 mg/L

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8,000 - 10,000 ppb Total BTEX
4,000 - 8,000 ppb Total BTEX
0 - 4,000 ppb Total BTEX

—0.5— Line of Equal Methane
Concentration (mg/L)
(Background = 0 mg/L)

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AUGUST 1993

Methanogenesis

Background Methane Concentration = 0 mg/L
Highest Measured Methane Concentration = 2.0 mg/L

$$\frac{1.28 \text{ mg/L BTEX}}{1 \text{ mg/L CH}_4} \ (2.0 \text{ mg/L CH}_4)$$

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

Relative Importance of Biodegradation Mechanisms at 25 Sites

Aerobic Respiration 10%
Denitrification 14%
Iron (III) Reduction 8%
Sulfate Reduction 29%
Methanogenesis 39%
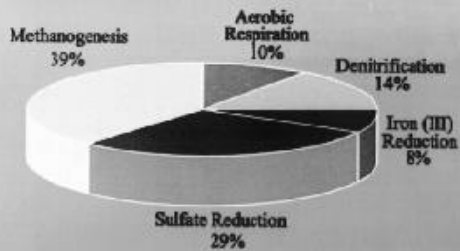
Correcting Attenuation for Dilution or Sorption

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

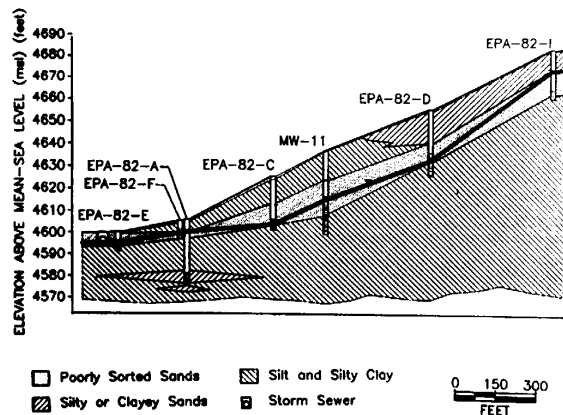## Correcting Attenuation for Dilution or Sorption

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

| | Poorly Sorted Sands | | Silt and Silty Clay |
| | Silty or Clayey Sands | | Storm Sewer |

0   150   300
FEET

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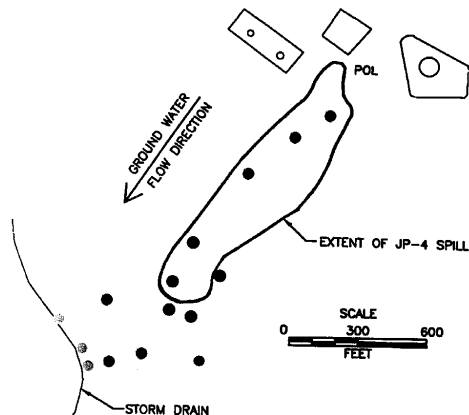
Near Source
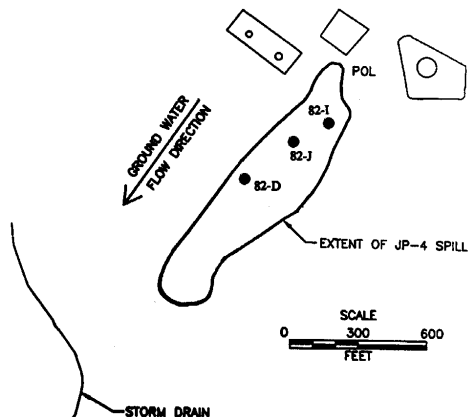
	82-I	82-J	82-D
	----- (mg/liter) -----		
Oxygen	0.0		0.2
Nitrate	<0.05	<0.05	<0.05
Sulfate	<0.5	<0.5	<0.5
Iron II	10.3	1.3	7.4
Methane	1.9	0.05	0.002
Alkalinity	491	430	657

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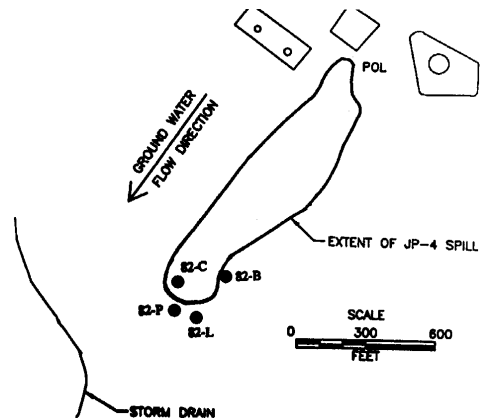
	82-P	82-L	82-B
	----- (mg/liter) -----		
Oxygen	0.1	0.3	0.4
Nitrate	<0.05	<0.05	0.15
Sulfate	<0.5	<0.5	74
Iron II	0.2	2.4	0.1
Methane	0.004	0.018	0.001
Alkalinity	792	730	428

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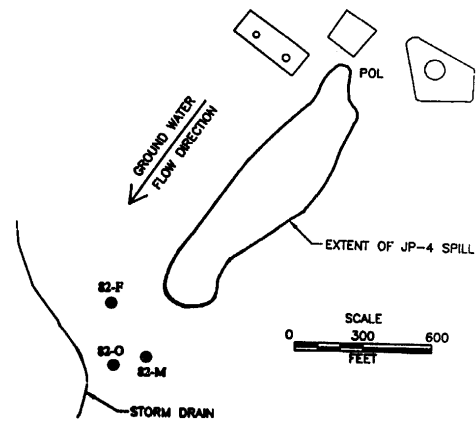
	82-F	82-O	82-M
	----- (mg/liter) -----		
Oxygen	0.1	0.2	0.2
Nitrate	1.7	1.6	1.8
Sulfate	52	37	35
Iron II	0.5	<0.05	<0.05
Methane	0.58	0.001	0.12
Alkalinity	490	566	666

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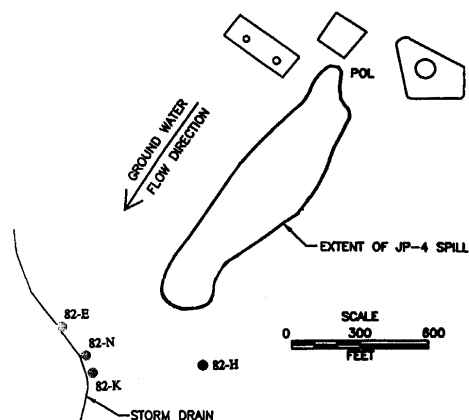
	82-E	82-N	82-K	82-H
	----- (mg/liter) -----			
Oxygen	3.7	2.0	2.0	5.9
Nitrate	4.4	1.1	4.4	1.5
Sulfate	37	43	60	62
Iron	<0.05	<0.05	<0.05	<0.05
Methane	0.001	0.004	0.003	0.001
Alkalinity	375	256	498	492

	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
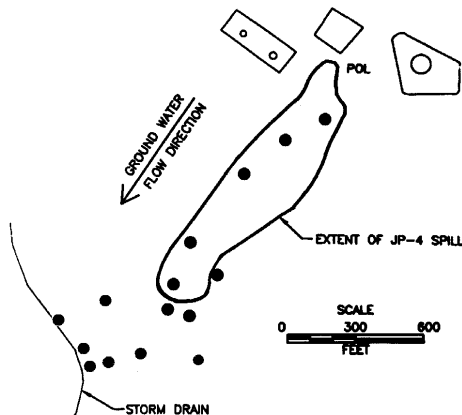
Natural Attenuation of Chlorinated Solvents

Mechanism of Chloroethene Biotransformation
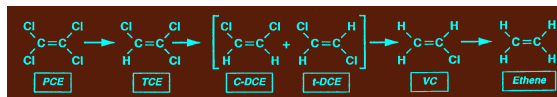
Reductive dehalogenation:
- Oxidation/reduction reaction where electrons are transferred from donor to chlorinated hydrocarbon acceptor
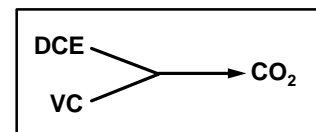
Co-metabolic process:
- Organisms growing on alternate carbon sources

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 Biotransformations for Chloroethenes
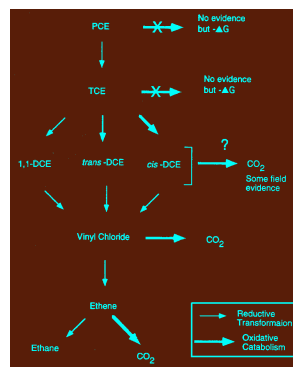
Patterns of Natural Attenuation Sites

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
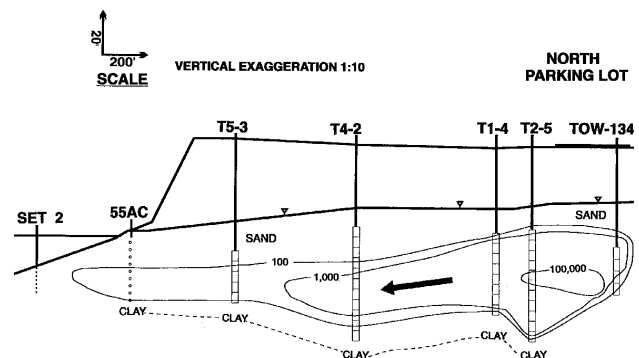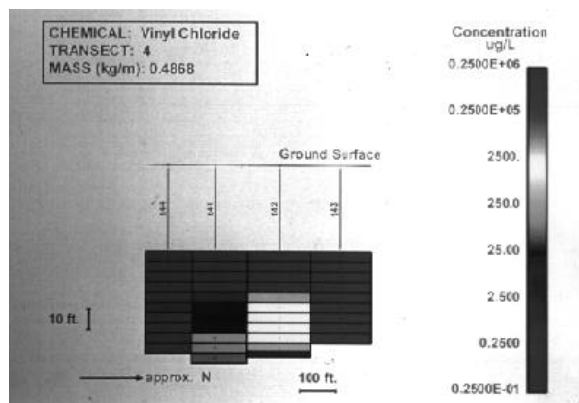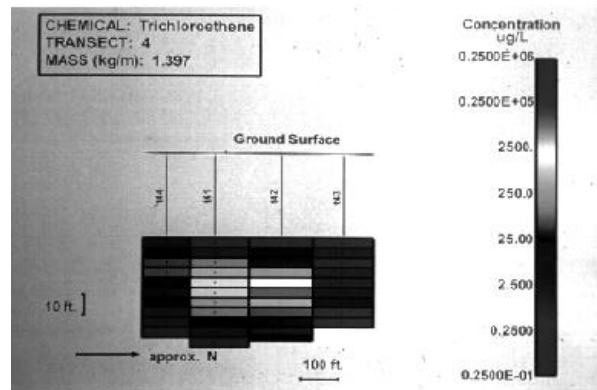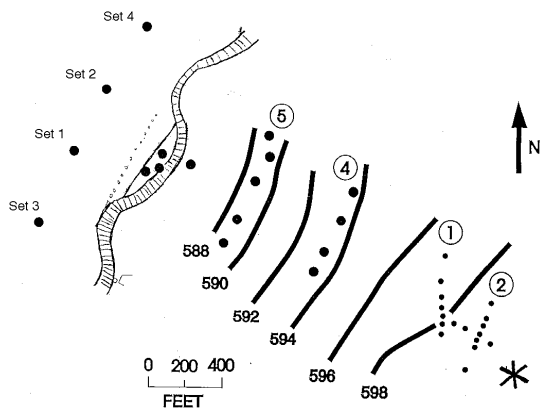
Methods to Estimate Rate Constants

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)

Distance from Transect 2 (m)
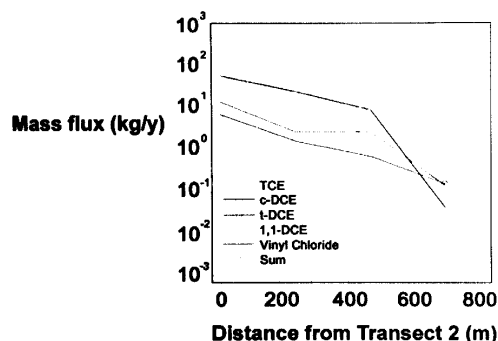
Chemical Mass Flux for the Sum of the Chlorinated Ethenes

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
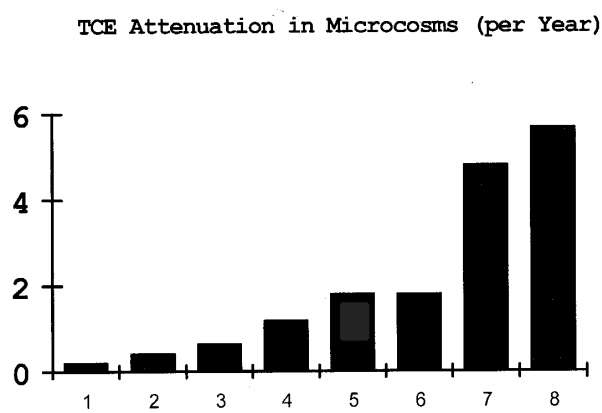
For TCE from transect 2 to 4

Δt = 340 weeks

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

c_j = 6.70 x 10^{-3} kg/m^3

λ = -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

TCE Attenuation in Microcosms (per Year)

TCE Attenuation in the Field (per Year)

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.

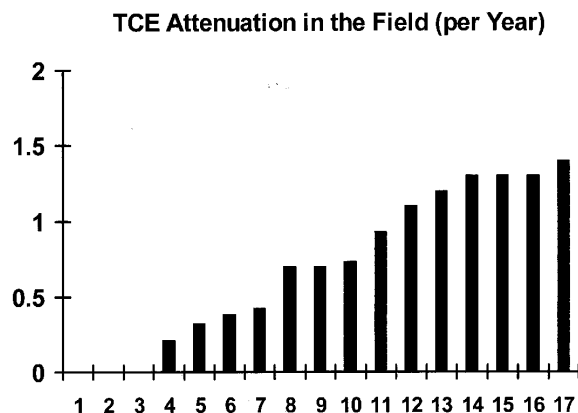Information needed:
  Hydraulic conductivity from aquifer test.
  Hydraulic gradient from water table
    elevations in monitoring wells.
  Effective porosity from Freeze and Cherry.

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.

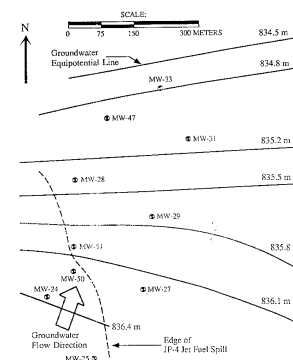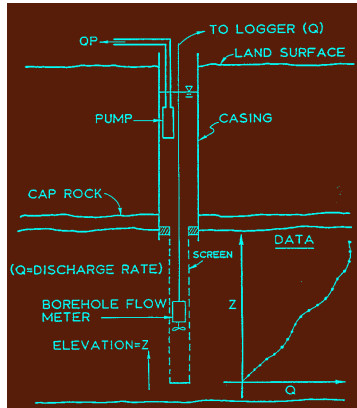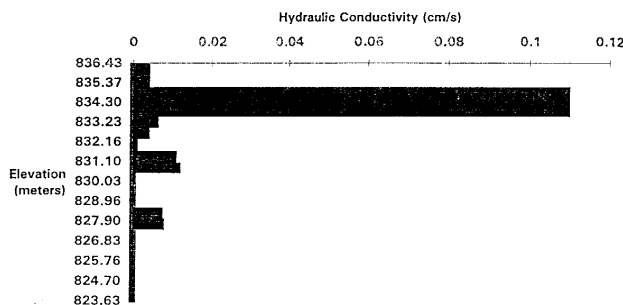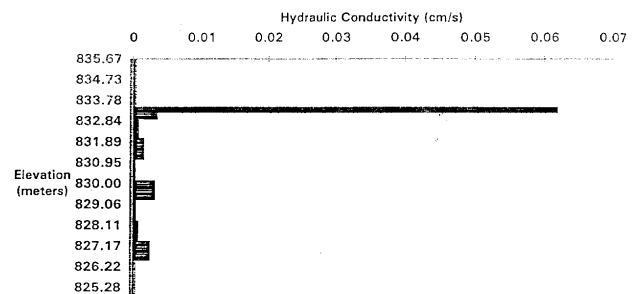Apparatus and Geometry Associated with a Borehole Flowmeter Test

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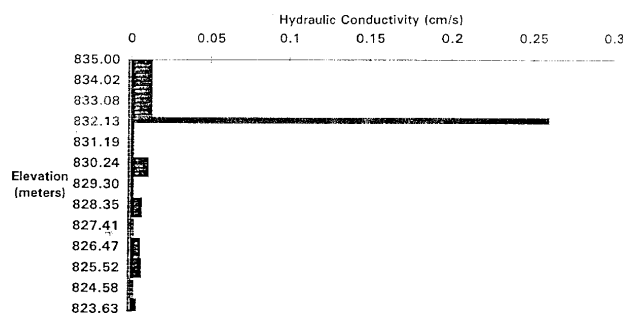
Vertical distribution of hydraulic conductivity in the aquifer sampled by well MW-31

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

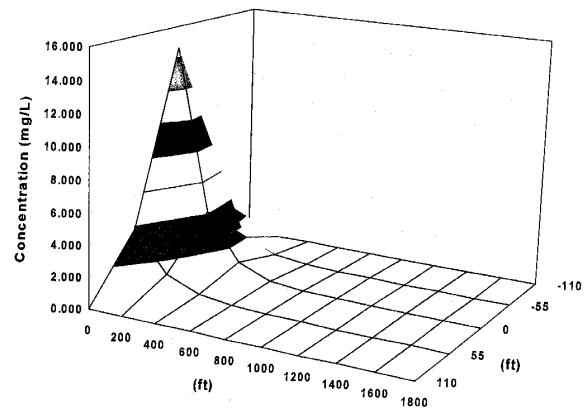| Monitoring Well	Average Hydraulic Conductivity (cm/sec)	Hydraulic Conductivity of Most Transmissive Interval (cm/sec)
MW-27	0.0074	0.11
MW-28	0.0046	0.022
MW-29	0.0028	0.062
MW-31	0.013	0.26
MW-45	0.0032	0.0056
MW-46	0.018	0.40

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.
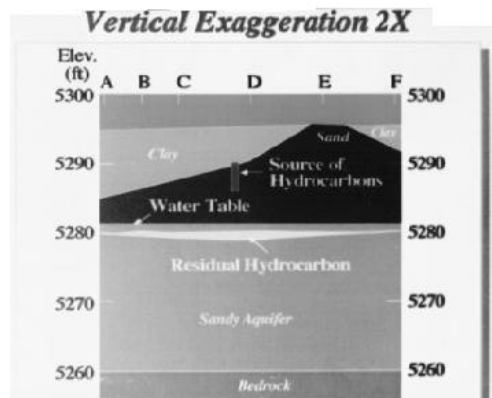
Will the Plume Return?

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

TPH (mg/kg) or
Hydrocarbon Vapors (ppm as Hexane)
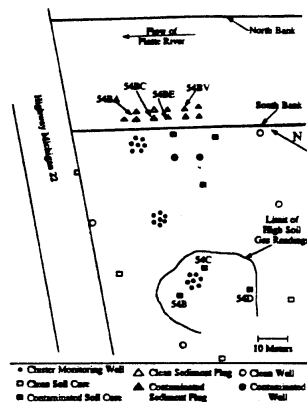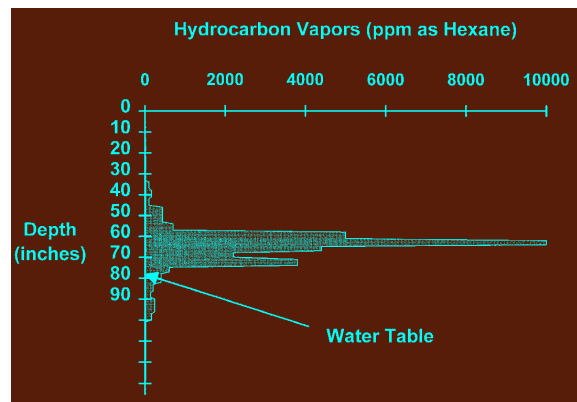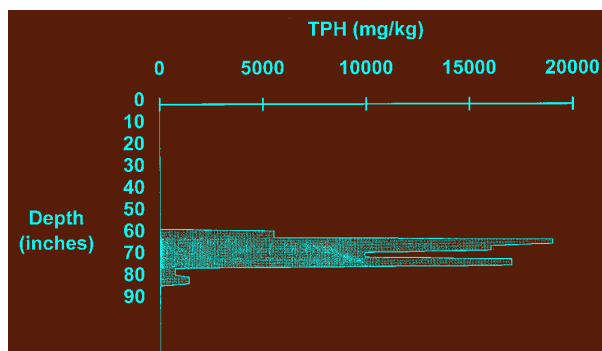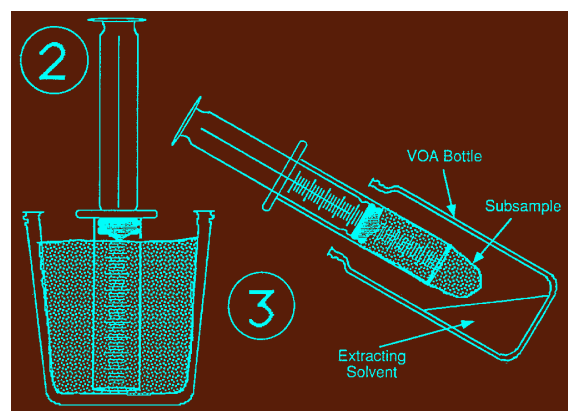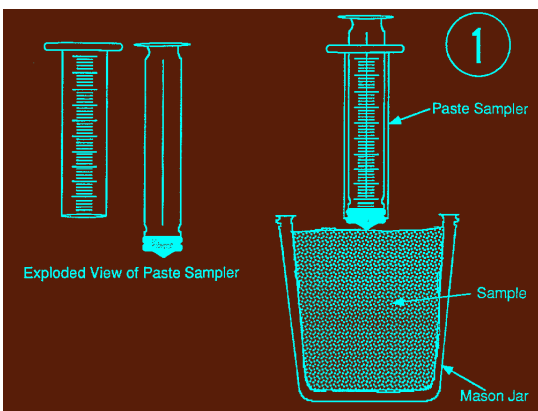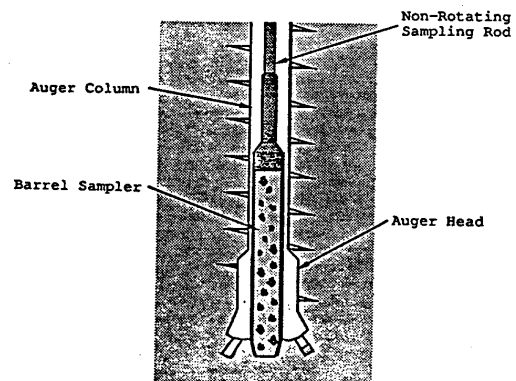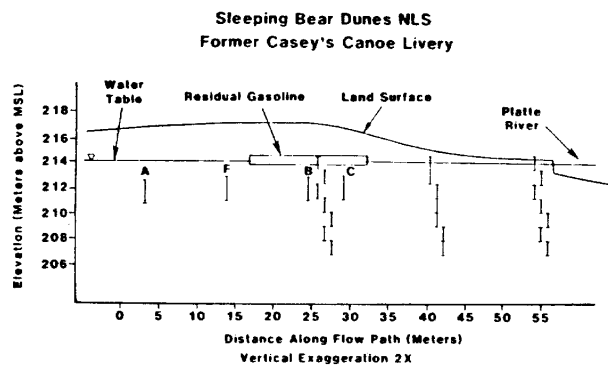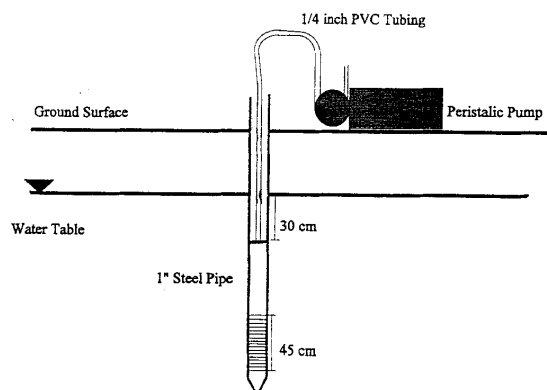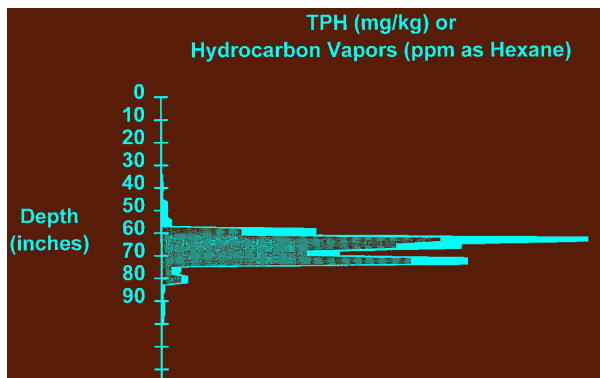
Calibration of Aquifer Test Using a Geoprobe

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
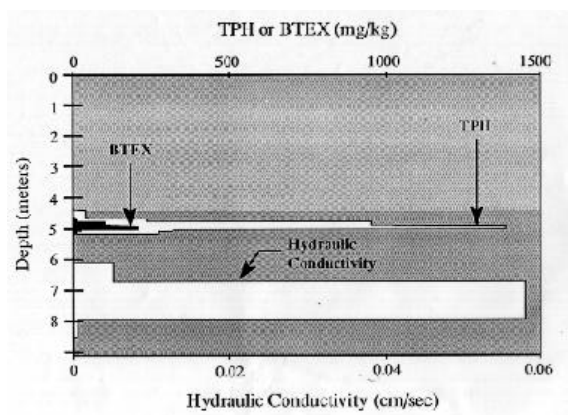
Fuel Derived Organic Compounds at the Public Services Site

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)
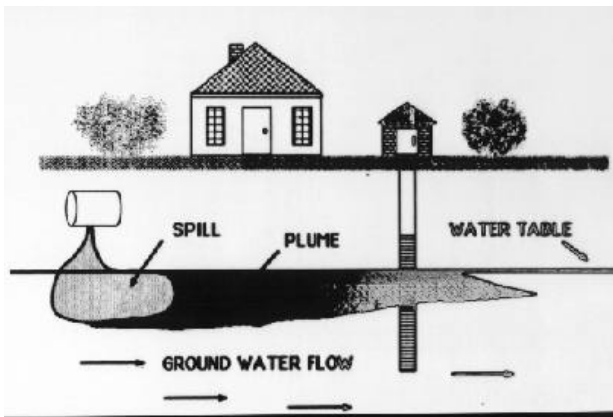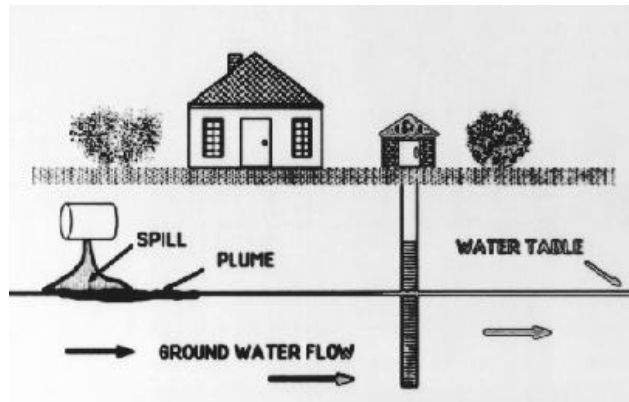
Where Should It Work?

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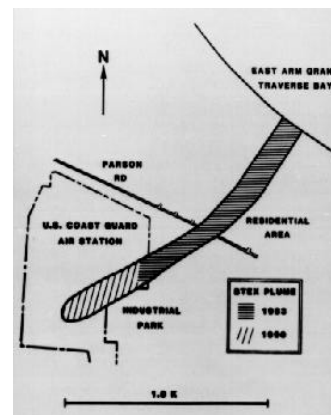
- How far will a plume move if it is subject to Natural Attenuation?
- How far will ground water move in 10 years?
- How fast is water moving through the source of ground-water contamination?

- 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

John Wilson
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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

Capped Landfill Lysimeters

CAP 1 No moisture addition
CAP 2 No moisture addition
CAP 3 No moisture addition
CAP 4 Abiotic control without moisture
CAP 5 Abiotic control without moisture
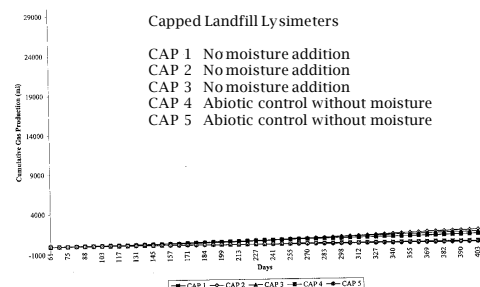
Figure 2. Cumulative Gas Production for Uncapped Columns

Uncapped Landfill Lysimeters

UNC 1 (rainfall)
UNC 2 (rainfall)
UNC 3 (rainfall)
UNC 4 Abiotic control
UNC 5 Abiotic control
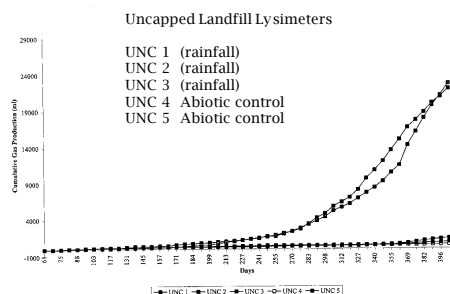
Figure 3. Distribution of Tetrachloroethylene for CAP 3

Mass Biodegraded 78%
Mass in Carbon 9%
Mass Remaining in Soil 13%
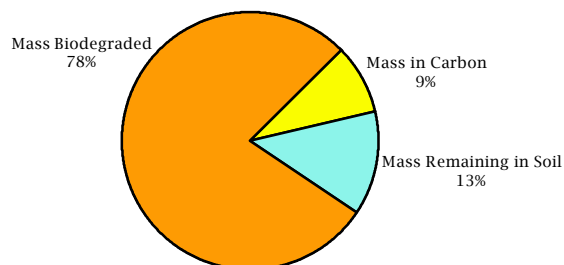
Figure 4. Distribution of Tetrachloroethylene for UNC 3

Mass Biodegraded 89%
Mass in Leachate 0%
Mass in Carbon 8%
Mass Remaining in Soil 3%
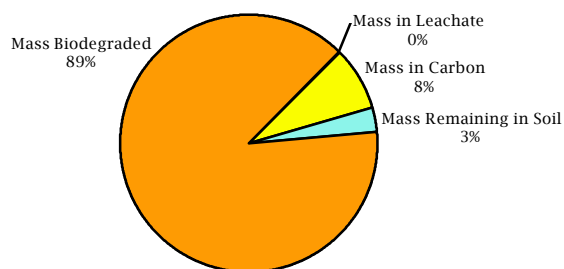
Natural Attenuation Research Approach

- 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

Dolloff F. Bishop
Office of Research and Development, National Risk Management Research Laboratory,
U.S. Environmental Protection Agency, Cincinnati, OH

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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14.   Safe, S. 1992. Toxicology structure-function relationship and human environmental health impacts of polychlorinated biphenyls: Progress and problems. Environ. Health Perspec. 100:259-268.

15.   Abramowicz, D.A., and D.R. Olson. 1995. Accelerated biodegradation of PCBs. Chemtech. 24:36-41.
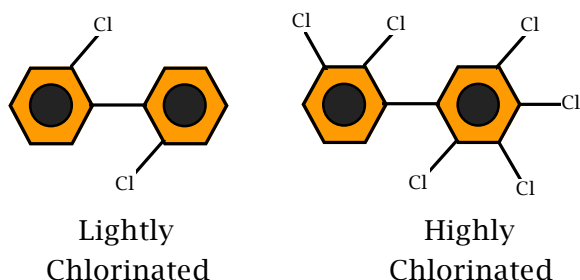
Natural Attenuation of Sediments

Dolloff F. Bishop

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

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

4-Ring (Pyrene)

2-Ring (Naphthalene)

5-Rings (Perylene)

3-Rings (Anthracene)

Figure 2. Representative PCB Congeners

Lightly
Chlorinated

Highly
Chlorinated
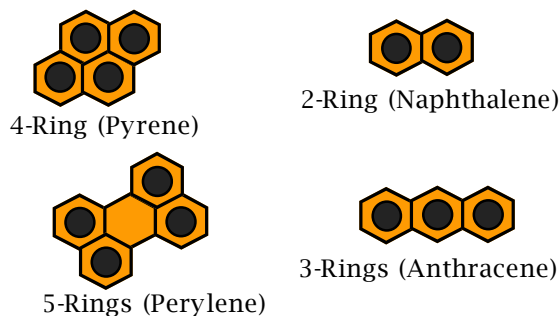
Sediment Conditions

- 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

John Wilson
Office of Research and Development
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Ada, OK

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
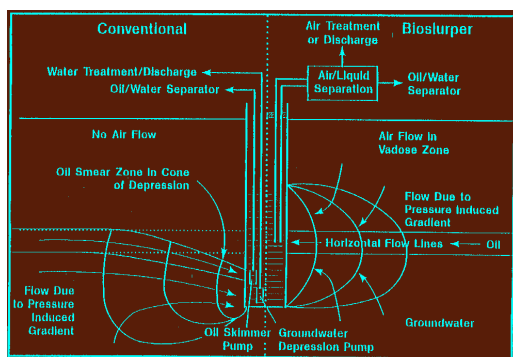- Amount of free product related to location of water table
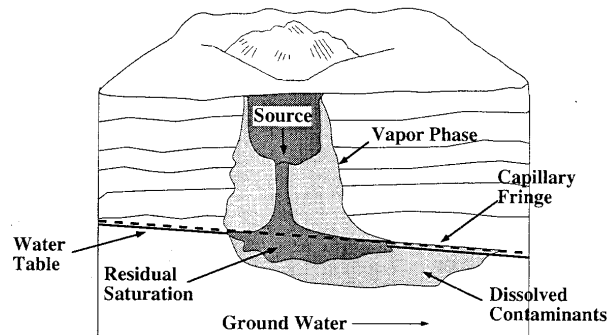
Relationship Between Free Product in Monitoring Wells and Contaminant Mass in Aquifer

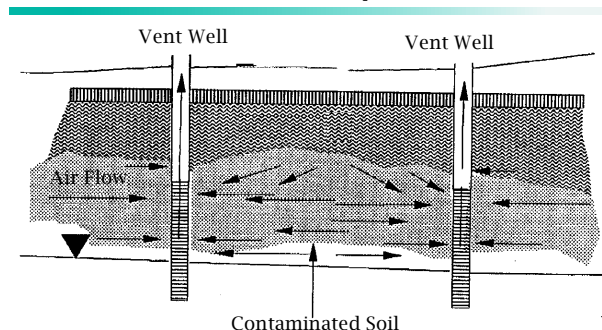- Free product is greatest when water table is low
- Free product can disappear when water table is high

Methods To Remove Nonaqueous Phase Liquids

- Free product recovery
- Bioslurping
- Soil vacuum extraction

LNAPL Remediation

Soil Vent System

**Plattsburg AFB
Fire Protection Training Area**

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)

25000

20000

15000

10000

5000

0

0   5000   10000   15000

Fluorescence Intensity

■ TPH near water table
○ TPH shallow

Total Petroleum Hydrocarbons (mg/kg)

Elevation (feet)

260
250
240
230
220
210
200

04 PTR   06 PTR   08 PTR   10 PTR   Pit 1   02 PTR   40 PTR   12 PTR   44 PTR   46 PTR

0   150   300   450   600
(Feet)

Total Petroleum Hydrocarbons (mg/kg)

Elevation (feet)

260
250
240
230
220
210
200

30 PTR   14 PTR   Pit 1   02 PTR   64 PTR   54 PTR

0   150   300
(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

0 50 100 150 200
Feet

PLAT-ABC-001-012493

Bottom Line

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

Air Sparging/ Air Injection

John Wilson
Office of Research and Development
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

Monitoring Probe · Vapor Extraction Well · Air Sparger Well · Monitoring Probe

Vent Radius · Sparge Radius

Vent Radius = f(Vacuum)
Sparge Radius = f(Depth)(Pressure)

Contaminated Soil

Depth

Air · Water · Soil Particle · Transient Air Filled Porosity
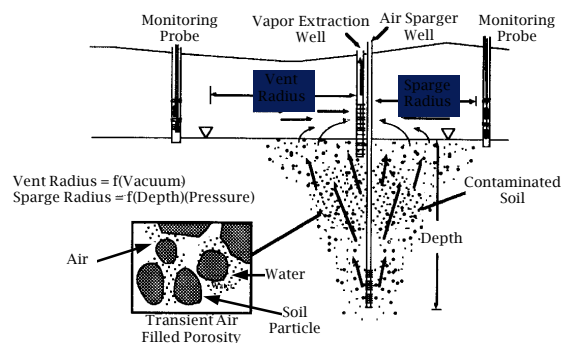
Effects of Air Sparging

- 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

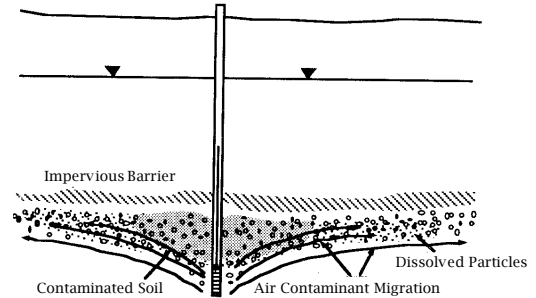## Inhibited Vertical Air Flow Due to Impervious Barrier

Impervious Barrier

Contaminated Soil   Air Contaminant Migration   Dissolved Particles

Channeled Air Flow Through Highly Permeable Zone

High Permeability Zone   Air/Contaminant Migration
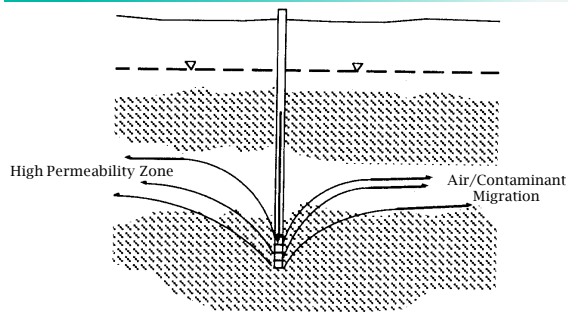
Case Studies on Air Sparging or Air Injection

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

RUBBER BOOT

5" DIA PVC

4" DIA PVC

PACKER

WELL SCREEN
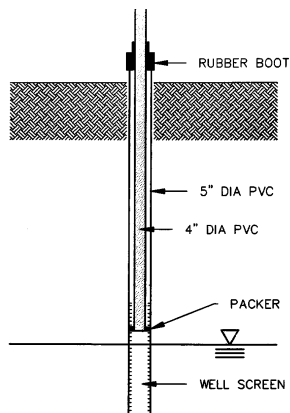
Soil Gas Hydrocarbons at Four Meter Depth for Injection Only Plot

Vertical Profile Oily Phase Residue in Bioventing South Plot
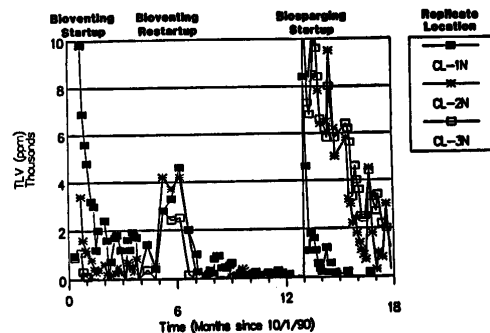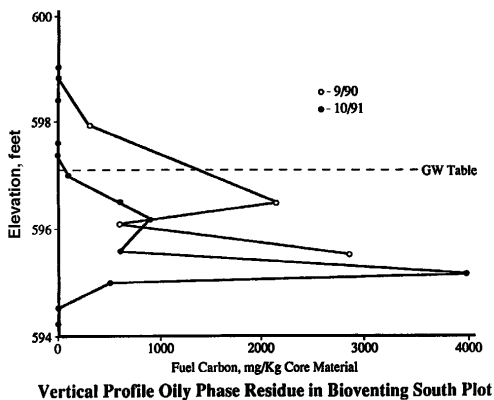
CHANGE IN TPH IN NORTH PLOT DURING PROJECT

	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

Prior to Remediation   During Remediation

Total TPH Concentration, Fire Station Site
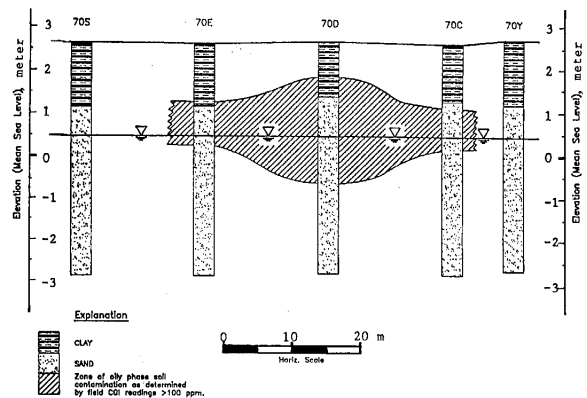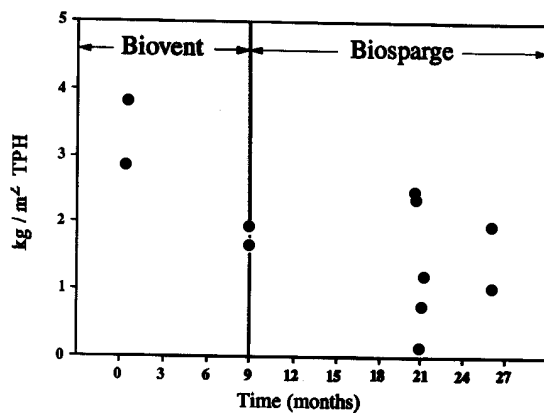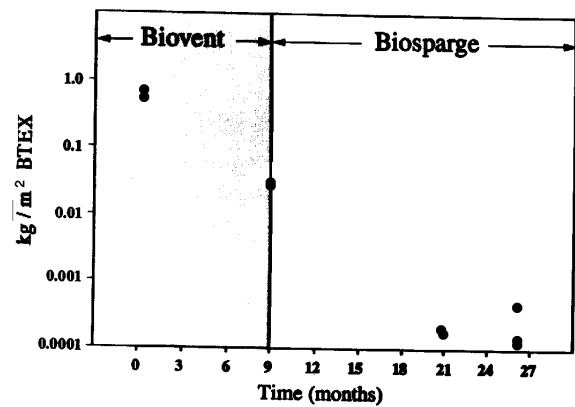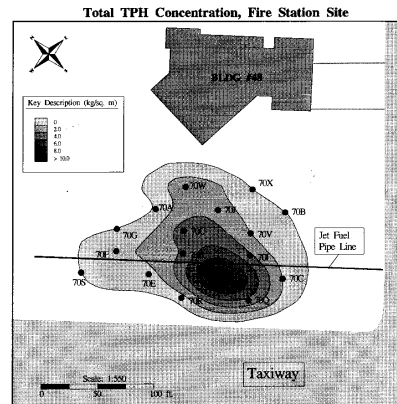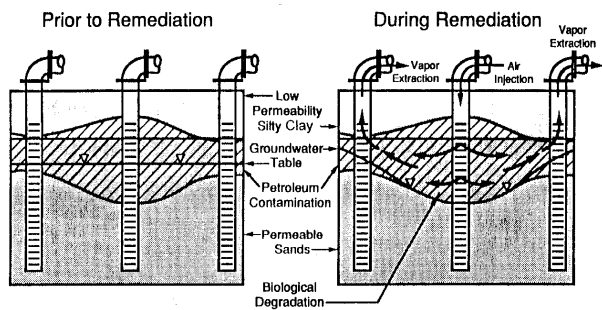
Baseline Total BTEX,
Fire Station Site
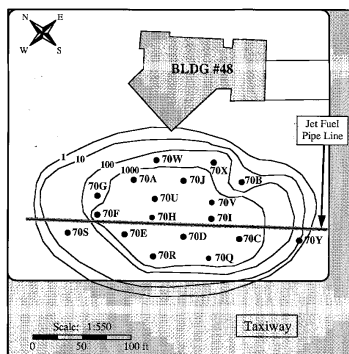
6th Period BTEX,
Fire Station Site

Benzene (mg/km)

Depth (feet)

- Benzene before (mg/kg)
- Benzene after (mg/kg)
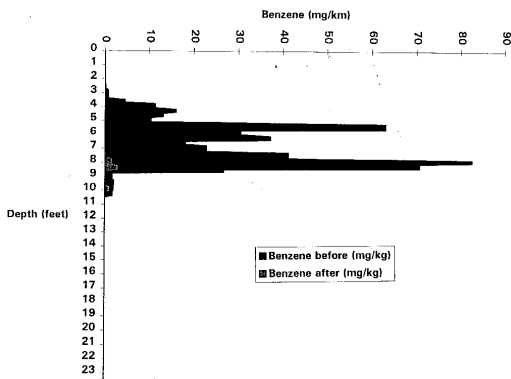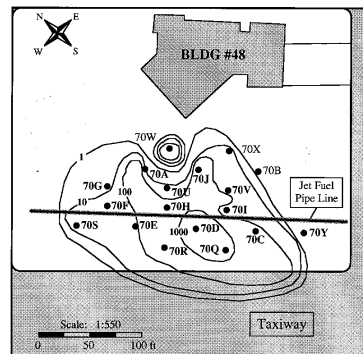
Monitoring wells screened from 7 to 10 meters
below grade, 15 and 30 meters down gradient
of the NAPL

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

K at 70DC (cm/sec)

Sleeve Friction Stress (psi)	15 10 5 0
Tip Stress (psi)	750 1500
Friction Ratio (%)	0 2 4 6

Misc. Fill
Sandy Soil
Organic Clay
Sand
Sandy Clay

MTBE (ug/liter)

Hydraulic Conductivity (cm/sec)
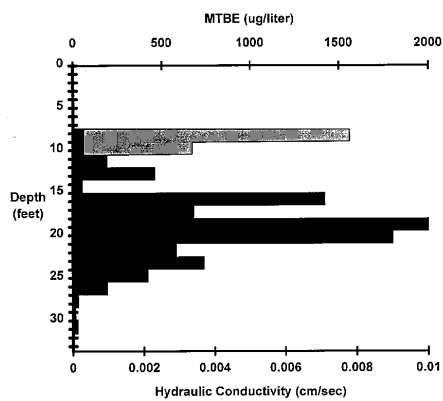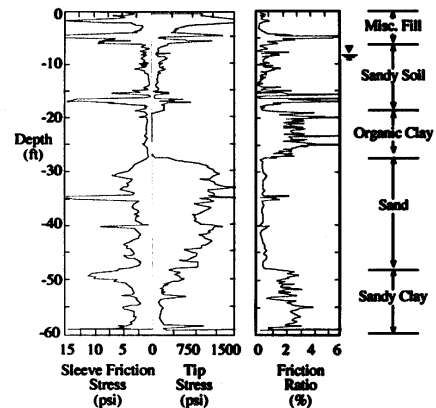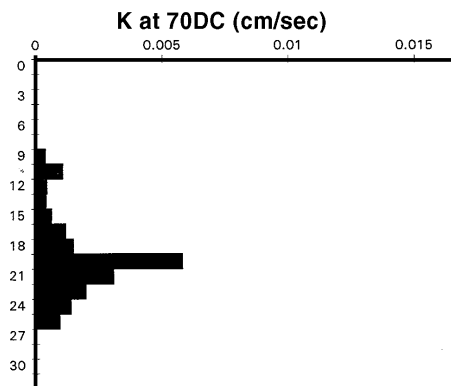
Conditions of Sparge Efficiency Test

- 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

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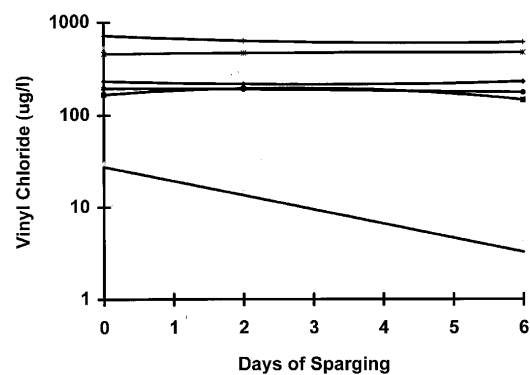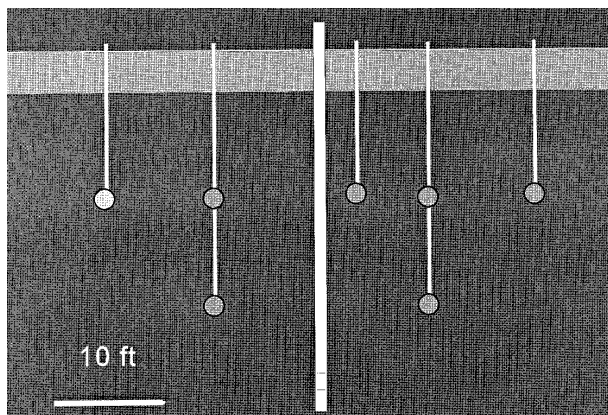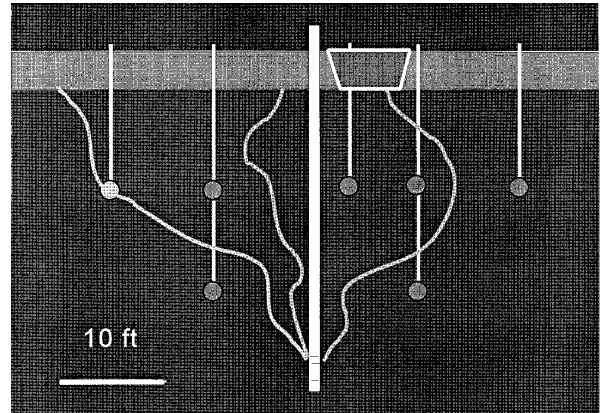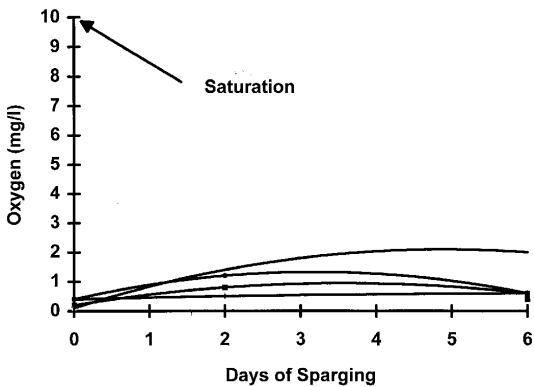
Why didn't air sparging strip Vinyl Chloride and increase the concentration of Oxygen?

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

Incineration 2
Thermal Desorption 3
Landfarming 7
Landfilling 34
Soil Vapor Extraction 9
Biopiles 16
Natural Attenuation 20

Adapted from Dana Tulis, EPA UST/LUST National Conference Talk, March 11, 1996
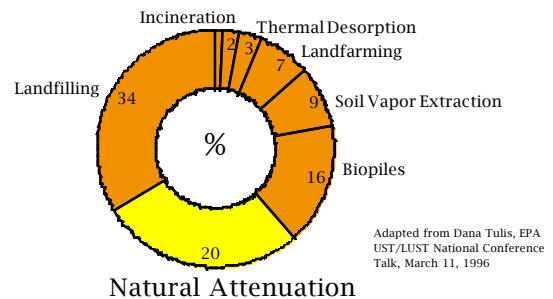
Use of Groundwater Cleanup Technologies at UST Sites

Dual-Phase Extraction 2
Biosparging 4
In Situ Bioremediation 4
Pump-and-Treat 29
Air Sparging 13
Natural Attenuation 48

Adapted from Dana Tulis, EPA UST/LUST National Conference Talk, March 11, 1996
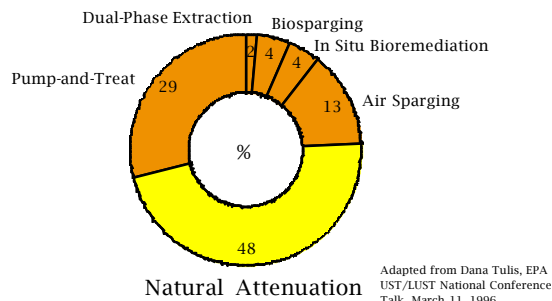
Programs That May Look at Natural Attenuation in Cleanup

- 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
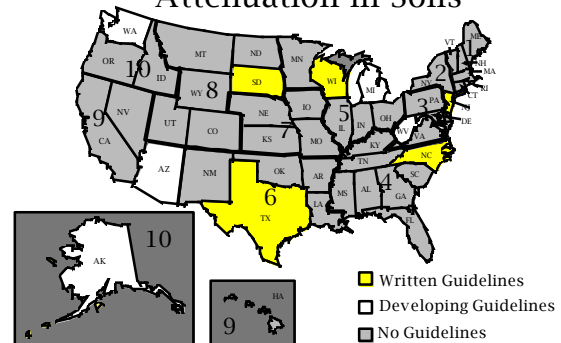
States With Formal Guidance on Soils Using NA

- Texas
- Wisconsin

States Developing Soils Guidance With NA

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

State Guidelines on Natural Attenuation in Soils

- ☐ Written Guidelines
- ☐ Developing Guidelines
- ☐ No Guidelines

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

Written policies and guidelines
Developing policies and guidelines
Informal policies and guidelines
Informal guidelines/Do not consider non-UST waste
Do not have any formal policy
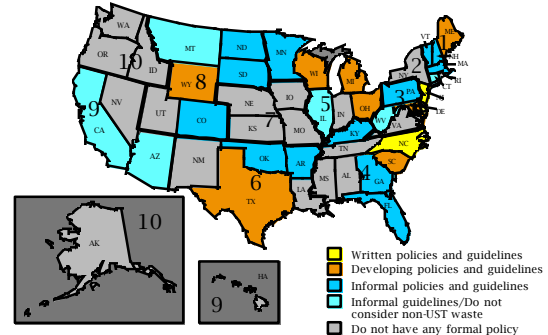
Conclusion

- 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