LETTER OF TRANSMITTAL

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<thead>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Intrinsic Remediation handout</td>
</tr>
</tbody>
</table>

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REMARKS

COPY TO 

Geotrans, inc.

signed  Jim Mercer

FILE: AR300438
**Definition:**

Intrinsic remediation, or natural attenuation: unenhanced physical, chemical and biological processes that act to limit the migration and reduce the concentration of contaminants in the subsurface.

- Effective on soluble petroleum hydrocarbons.
COMMON CHARACTERISTICS OF BTEX PLUMES

(1) The source term changes with time.
(2) Different compounds biodegrade at different rates (frequently, toluene > ethylbenzene, xylenes > benzene).
(3) Most TEX (in large spills) is degraded anaerobically using nitrate, ferric iron, sulfate, and CO₂ as electron acceptors.
(4) Benzene can also degrade anaerobically (anaerobic rates are very slow - anaerobic benzene degraders are probably not present at all sites).
(5) BTEX plumes often appear to sink with distance from the source due to recharge of clean water on top of the plume.
(6) BTEX plumes do not spread out with distance, and may actually become narrower due to enhanced biodegradation at the plume fringe.
(7) Effective first-order decay rates are on the order of 0.001 to 0.01 per day.

INTRINSIC REMEDIATION
Potential Natural Attenuation Mechanisms For Contaminated Groundwater

- Aerobic Biodegradation
- Anaerobic Biodegradation
- Volatilization
- Dispersion (and dilution via recharge)
- Dilution (via discharge to surface water)
- Sorption
- Abiotic Chemical Reactions
AEROBIC BIODEGRADATION

Description
Microbes utilize oxygen as an electron acceptor to convert contaminant mass to CO₂, water, and biomass.

AEROBIC BIODEGRADATION

Application
As a class, petroleum hydrocarbons are biodegradable. The lighter, more soluble members are degraded more rapidly than the heavier, less soluble members. Thus, monaromatic compounds (such as BTEX compounds) are degraded more rapidly than two-ring compounds such as naphthalene, which in turn are more easily degraded than PAHs with three or more rings. Similarly, small aliphatic compounds are degraded more readily than larger aliphatic compounds. Whereas some chlorinated solvents can be degraded under aerobic conditions, others, such as tetrachloroethylene, are completely resistant to aerobic degradation.
# AEROBIC BIODEGRADATION

## Critical Soil Environmental Factors For Microbial Activity

<table>
<thead>
<tr>
<th>Environmental Factor</th>
<th>Optimum Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Conditions</td>
<td>Homogeneous condition; hydraulic conductivity greater than $10^{-3}$ cm/s.</td>
</tr>
<tr>
<td>Available Soil Water</td>
<td>25 - 85% of water holding capacity; -0.01 MPa.</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10%.</td>
</tr>
<tr>
<td></td>
<td>Anaerobic metabolism: $O_2$ concentrations less than 1% in soil gas.</td>
</tr>
</tbody>
</table>

## Critical Soil Environmental Factors For Microbial Activity (cont.)

<table>
<thead>
<tr>
<th>Environmental Factor</th>
<th>Optimum Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox Potential</td>
<td>Aerobes and facultative anaerobes; greater than 50 millivolts; anaerobes: less than 50 millivolts.</td>
</tr>
<tr>
<td>pH</td>
<td>5.5 - 8.5</td>
</tr>
<tr>
<td>Nutrients</td>
<td>Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (Suggested C:N:P ratio of 120:10:1).</td>
</tr>
<tr>
<td>Temperature</td>
<td>15 - 45°C (Mesophiles)</td>
</tr>
<tr>
<td>Microbial Parameters</td>
<td>Adequate cell count and metabolic activities.</td>
</tr>
</tbody>
</table>
AERONIC BIODEGRADATION
Oxygen Requirements

In the absence of microbial cell production, the oxidation (biodegradation) of benzene to carbon dioxide and water is given by:

\[ C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \]

Therefore, 7.5 moles of oxygen are required to metabolize one mole of benzene. On a mass basis, the ratio of oxygen to benzene is given by:

- Molecular Weights:
  - Benzene: \( 6(12) + 6(1) = 78 \text{ gm} \)
  - Oxygen: \( 7.5(32) = 240 \text{ gm} \)

- Mass Ratio of Oxygen to Benzene: \( \frac{240}{78} = 3.08:1 \)

In the absence of microbial cell production, 3.08 mg of oxygen are required to completely metabolize 1.0 mg of benzene. Similar calculations can be completed for toluene (3.13 mg oxygen to 1.0 mg toluene), ethylbenzene (3.17 mg oxygen to 1.0 mg ethylbenzene) and the xylenes (3.17 mg oxygen to 1.0 mg xylene). The average mass ratio of oxygen consumed to total BTEX degraded is thus 3.14:1. This means that for petroleum hydrocarbons, a single gram of contaminant requires 3-4 g \( O_2 \) for complete oxidation.
POTENTIAL AEROBIC DECAY RATE

- Total water inflow on plume perimeter
- Dissolved oxygen concentration in inflow
- Stoichiometric factor (ca. 0.3g HC / g O)
- Bioavailability
- Sensitivity to chemical toxicity → inhibition

ANAEROBIC BIODEGRADATION

Description

Some microbes use alternative electron acceptors (e.g., NO₃⁻, SO₄²⁻, Fe³⁺, CO₂) to degrade contaminants.
ANAEROBIC BIODEGRADATION

Application

Some highly chlorinated aliphatic compounds (e.g., tetrachloroethene) are susceptible to anaerobic degradation. As the degree of halogenation in aliphatics decreases, susceptibility to aerobic metabolism increases. Thus, highly chlorinated aliphatic contaminants may be completely degraded under ideal conditions where anaerobic degradation (within the more concentrated portion of a plume) is followed by aerobic degradation at the plume front. Highly halogenated aromatic compounds (e.g., PCBs) are also resistant to aerobic degradation, but may be susceptible to slower anaerobic biodegradation. Cometabolism is a primary process in anaerobic degradation, specifically dehalogenation.

STOICHIOMETRY OF COMMON BIODEGRADATION REACTION

(Wiedemeier et al., 1995)

<table>
<thead>
<tr>
<th>Benzene Biodegradation Reactions</th>
<th>Mass Ratio of Electron Acceptor to Benzene</th>
<th>Mass Ratio of Metabolic By-Products to Benzene</th>
<th>Average Mass Ratio of Metabolic By-Products to Total BTEX(a)</th>
<th>Average Mass Ratio of Metabolic By-Products to Total BTEX(a)</th>
<th>Mass of BTEX Degraded per Unit Mass of Electron Acceptor Used (mg/l)</th>
<th>Mass of BTEX Degraded per Unit Mass of Metabolic By-Product Produced (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.50₂+C₆H₅→6CO₂+3H₂O</td>
<td>3.1:1</td>
<td>3.14:1</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene oxidation / aerobic respiration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6NO₃⁻+6H⁺+C₆H₅→6CO₂+6H₂O+3N₂</td>
<td>4.8:1</td>
<td>4.9:1</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene oxidation / denitrification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6OH⁻+30Fe⁺(OH)₃+C₆H₅→6CO₂+30Fe²⁺+78H₂O</td>
<td>41.1:1</td>
<td>21.5:1</td>
<td>21.8:1</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene oxidation / iron reduction</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>7SH⁻+3.73SO₄²⁻+C₆H₅→6CO₂+3.73H₂S⁴⁻+3H₂O</td>
<td>4.6:1</td>
<td>4.7:1</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene oxidation / sulfate reduction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5H₂O+C₆H₅→2.25CO₂+3.75CH₄</td>
<td>0.77:1</td>
<td>0.78:1</td>
<td>1.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene oxidation / methanogenesis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Simple average of all BTEX compounds based on individual compound stoichiometry. This stoichiometry assumes no cellular mass is produced.
VOLATILIZATION

Description
Low-molecular weight contaminants with high vapor pressures and Henry's law constants volatilize from NAPL and water to the vadose zone.

Application
Attenuation afforded by volatilization is generally very minor. May be significant for highly volatile compounds located at the water table below highly permeable, dry soils. Transport to the vadose zone may enhance aerobic degradation.
DISPERSION (and dilution via recharge)

Description

Variations in flowpath and velocity (and molecular diffusion) cause contaminant spreading and dilution.

Application

Dispersion affects all solutes and reduces the high concentrations within a plume of contaminated groundwater by spreading contaminants into less contaminated areas. Dispersion does not remove contaminant mass, but may promote aerobic degradation by spreading contaminants into more oxygenated groundwater.
DILUTION (via discharge to surface water)

Description

Contaminants dissolved in groundwater discharge to and are diluted in surface water.

Application

At some sites, contaminant plume growth is limited by groundwater flow and discharge to streams, rivers, lakes, or oceans where dilution may reduce contaminant concentrations to acceptable levels.
SORPTION

Description
Contaminants partition between groundwater and the porous medium. Sorption of organic compounds is typically controlled by the organic carbon content of the soil.

SORPTION

Application
Sorption retards contaminant plume migration. However, to the extent that sorption is reversible, it does not permanently remove contaminants from groundwater as desorption may occur. Retardation may facilitate more effective degradation or other attenuation processes.
**ABIOTIC CHEMICAL REACTIONS**

**Description**

Hydrolysis, radionuclide decay, or other reactions occur in groundwater to reduce contaminant mass.

**Application**

Significant for some organic and inorganic contaminants under favorable conditions.
Microbes degrade contaminants because in the process they gain energy that allows them to grow and reproduce. Microbes get energy from the contaminants by breaking chemical bonds and transferring electrons from the contaminants to an electron acceptor, such as oxygen.

The driving force of degradation is electron transfer, which is quantified by the free energy of the reaction. Coupled redox reactions are expected to occur in order of their thermodynamic energy. Once available oxygen is depleted and anaerobic conditions dominate the interior regions of a contaminant plume, anaerobic microorganisms can utilize other electron acceptors in the following order of preference: nitrate, manganese, ferric iron, sulfate and carbon dioxide.
ELECTRON ACCEPTORS IN BIOTRANSFORMATION PROCESSES

<table>
<thead>
<tr>
<th>Microbial Process</th>
<th>Electron Acceptor</th>
<th>Reaction(^a)</th>
<th>Free Energy Change ((\Delta G^\circ)) at pH 7 (kcal/equivalent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td>O(_2)</td>
<td>CH(_2)O + O(_2)(g) = CO(_2)(g) + H(_2)O</td>
<td>-29.9</td>
</tr>
<tr>
<td>Denitrification</td>
<td>NO(_3^-)</td>
<td>CH(_2)O + 0.8 NO(_3^-) + 0.8 H(+) = CO(_2)(g) + 0.4 N(_2)(g) + 1.4 H(_2)O</td>
<td>-26.4</td>
</tr>
<tr>
<td>Mn(IV) Reduction</td>
<td>Mn(IV)</td>
<td>CH(_2)O + 2 MnO(_2)(s) + 2 HCO(_3^-) + 2 H(+) = CO(_2)(g) + 2 MnCO(_3)(s) + 3 H(_2)O</td>
<td>-23.3</td>
</tr>
<tr>
<td>Fe(III) Reduction</td>
<td>Fe(III)</td>
<td>CH(<em>2)O + 4 FeOO(</em>)H(_)(s) + 4 HCO(_3^-) + 4 H(+) = CO(_2)(g) + FeCO(_3)(s) + 7 H(_2)O</td>
<td>-10.1</td>
</tr>
<tr>
<td>Sulfate Reduction</td>
<td>SO(_4^{2-})</td>
<td>CH(_2)O + 0.5 SO(_4^{2-}) + 0.5 H(+) = CO(<em>2)(g) + 0.5 HS(</em>-)(^+) + H(_2)O</td>
<td>-5.9</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>CO(_2)</td>
<td>CH(_2)O + 0.5 CO(_2)(g) = CO(_2)(g) + 0.5 CH(_4)(g)</td>
<td>-5.6</td>
</tr>
</tbody>
</table>

\(\Delta G^\circ\) oxidation and reduction half-reactions for the combinations listed were obtained from Stumm and Morgan (1981).

TERMINAL ELECTRON ACCEPTOR

Sequence of Redox Reactions
**REDOX POTENTIALS FOR VARIOUS ELECTRON ACCEPTORS**

At pH = 7 and T = 25°C:

- O₂ + 4H⁺ + 4e⁻ → 2H₂O (Eₚ = +2.0)
- 2NO₃⁻ + 12H⁺ + 10e⁻ → N₂ + 6H₂O (Eₚ = +0.74)
- MnO₂(S) + HCO₃⁻ + 3H⁺ + 2e⁻ → MnCO₃(S) + 2H₂O (Eₚ = -0.52)
- Fe₃O₄(s) + HCO₃⁻ + 2H⁺ + e⁻ → FeCO₃ + H₂O (Eₚ = -0.59)
- SO₄²⁻ + 2H⁺ + 2e⁻ → H₂S + 2H₂O (Eₚ = -0.22)
- CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O (Eₚ = -0.24)

**TERMINAL ELECTRON ACCEPTOR**

Chemical Species in Bulk Groundwater:

- SO₄²⁻
- NH₃
- NO₃⁻
- Fe(II)
- Mn(II)
- H₂S
- CH₄

**VADOSE ZONE**

Groundwater Flow

- Aerobic
- Denitrification
- Mn(IV) & Fe(III) Reduction
- Sulfate Reduction
- Methanogenesis

Organics:
- Chlorobenzenes
- Chlorophenols
- Polyaromatic hydrocarbons
- PAHs
- Chlorophenyl biphenyl chlorobenzenes

Possible Microbially-mediated changes in chemical species, redox conditions, and organic contaminant transformations in the direction of groundwater flow.
**EVALUATING INTRINSIC REMEDIATION**

**PHASE I**
Plan and conduct site assessment activities to obtain the data necessary to evaluate natural attenuation.

**Measure**
- Hydraulic head, hydraulic conductivity, and the fraction of organic carbon distributions to estimate the directions and velocities of groundwater flow and contaminant transport. Define contaminant source areas, contaminant distributions and properties, and migration pathways. Measure dissolved oxygen (D.O.) concentrations inside, outside, and upgradient of the contaminant plume to determine sufficient D.O. (3.4 to 2 mg/l) is available for aerobic biodegradation. Establish an inverse correlation exists between D.O. and dissolved contaminant concentrations. Place monitoring points along the plume axis and at its leading edge to determine if the plume is advancing, shrinking, or stable. Analyze groundwater sampled inside and outside of the plume for geochemical indicators (e.g., pH, redox potential, CO₂) of degradation and for degradation products. Consider using laboratory microcosm and modeling analyses to study contaminant degradation.

**Procedures**
- Place monitoring points along the plume axis and at its leading edge to determine if the plume is advancing, shrinking, or stable.
- Analyze groundwater sampled inside and outside of the plume for geochemical indicators (e.g., pH, redox potential, CO₂) of degradation and for degradation products.
- Consider using laboratory microcosm and modeling analyses to study contaminant degradation.

<table>
<thead>
<tr>
<th>EVALUATING INTRINSIC REMEDIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Stable Plume</strong></td>
</tr>
<tr>
<td><strong>Surface</strong></td>
</tr>
<tr>
<td>Vadose</td>
</tr>
<tr>
<td>GW Flow, BTEX ppb</td>
</tr>
<tr>
<td>Conditions:</td>
</tr>
<tr>
<td>- Groundwater flow slow</td>
</tr>
<tr>
<td>- Low-permeability soils</td>
</tr>
<tr>
<td>- Monitoring wells at plume</td>
</tr>
<tr>
<td>- Edges contain detectable</td>
</tr>
<tr>
<td>- Dissolved oxygen</td>
</tr>
<tr>
<td>- Small changes in plume</td>
</tr>
</tbody>
</table>

| **B. "Shrinking" Plume**         |
| **Surface**                      |
| Vadose                           |
| GW Flow, BTEX ppb               |
| Conditions:                     |
| - Groundwater flow faster        |
| - Higher-permeability soils      |
| - Higher levels of dissolved     |
| - Oxygen observed                |
| - Plume boundary narrows         |
| - With time                      |

Levels of Intrinsic Bioremediation in Aquifers
Disappearance of Benzene and Toluene Relative to Chloride in a Field-Scale Injection Test.

Concentrations of the crude oil components toluene, ethylbenzene, and benzene at various distances from the center of the Bemidji, Minnesota, oil spill. These concentrations have remained relatively stable at the levels shown here since 1987.
EVALUATING INTRINSIC REMEDIATION

PHASE 2
Examine primary and secondary indicators to evaluate the extent of natural attenuation.

Significant natural attenuation is indicated if the plume is shrinking, at steady-state, or advancing more slowly than expected.

Degradation of certain compounds may be evidenced by retarded migration, the detection of degradation products, or an increase in the ratio of nondegradable to degradable compounds with time or distance from source area. Aerobic biodegradation is probably occurring if D.O. concentrations inside the plume are depleted relative to background D.O. concentrations. Similarly, nitrate or sulfate concentrations in a contaminated zone that are less than background may evidence anaerobic biodegradation via denitrification and sulfanogenesis, and elevated concentrations of metabolic byproducts (e.g., ferrous iron and methane) can result from hydrocarbon biodegradation via ferric hydroxide reduction and methanogenesis.

CHC TRANSFORMATION PATHWAYS

1,1,1-TCA → 1,1-DCA
1,1-DCE
1,1-DCE → 1,1-DCA

PCE → TCE
TCE → Vinyl Chloride
Cl2,2-DCE
Cl2,2-DCE → Vinyl Chloride

1,2-DCA → Vinyl Chloride

Chloroethane
TCA Degradation

TCA

A

B

1,1-DCE

July 8, 1987
5 ppb

B

1,1-DCA

July 8, 1987
6 ppb

B

A

ETHANOL

ACETIC ACID

CO₂

TCE Degradation

TCE

July 8, 1987
5 ppb

B

1,1-DCE

July 8, 1987
7 ppb

B

t-1,2-DCE

Jan 30, 1991
100 ppb

B

c-1,2-DCE

Jan 30, 1991
700 ppb

B

VC

July 8, 1987
2 ppb

B

CA

Acetate

1,1-DCE can undergo aerobic degradation to form VC, which can then serve as an electron donor for other reactions. 
1,1-DCE and 1,2-DCE can undergo anaerobic degradation to form VC. 
1,1-DCE and 1,2-DCE are not regulated by the EPA. 
1,1-DCE and 1,2-DCE can undergo aerobic degradation to form VC. 
1,1-DCE and 1,2-DCE can undergo anaerobic degradation to form VC. 
1,1-DCE and 1,2-DCE are not regulated by the EPA.
EVALUATING INTRINSIC REMEDIATION

Chemical Degradation of 1,1,1-Trichloroethane (TCA).

20
EVALUATING INTRINSIC REMEDIATION

Chemical and Microbial degradation of TCA.

Reductive dechlorination of trichloroethylene (TCE) under hypothesized anaerobic field or laboratory conditions.
CHLORINATED ALIPHATIC HYDROCARBONS (CAH), ETHENE, AND METHANE CONCENTRATION PROFILE VERSUS DEPTH IN BORE T1-6 (Semprini et al., 1995)

EVALUATING INTRINSIC REMEDIATION

PHASE 3
Implement a monitoring program to confirm natural attenuation.

Monitor wells for target compounds and degradation products at the leading edge and along the longitudinal axis of the plume to assess whether the plume is shrinking, stable, or advancing. If necessary and cost-effective, conduct more intensive studies to evaluate natural attenuation. Such studies may include developing mass-balance analyses to assess the mass histories of contaminants and their break-down products, detailed flow and transport modeling, laboratory microcosm studies, and analysis of secondary geochemical indicators of natural attenuation processes.
AEROBIC AND ANAEROBIC METABOLISM

<table>
<thead>
<tr>
<th>Process</th>
<th>Electron Acceptor</th>
<th>Metabolic Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td>O₂</td>
<td>CO₂, H₂O</td>
</tr>
<tr>
<td>Denitrification</td>
<td>NO₃</td>
<td>CO₂, N₂</td>
</tr>
<tr>
<td>Iron Reduction</td>
<td>Fe³⁺</td>
<td>CO₂, Fe²⁺</td>
</tr>
<tr>
<td>Sulfate Reduction</td>
<td>SO₄²⁻</td>
<td>CO₂, H₂S</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td></td>
<td>CO₂, CH₄</td>
</tr>
</tbody>
</table>

INTRINSIC REMEDIATION OF TCE

(1) Redox conditions (< 750 mV for anaerobic)
(2) Dissolved oxygen (< 1 mg/l for anaerobic)
(3) Anaerobic transformation products
   - 1,1-DCE
   - 1,2-DCE
   - 1,1,2-Trichloroethane
   - Vinyl Chloride
   - Ethane
(4) Methane (produced during methanogenesis)
(5) Sulfate (used during sulfanogenesis)
(6) Nitrate (used during denitrification)
(7) Ferrous Iron (produced during iron reduction)
   (Fe²⁺)
(8) Manganese (II) (produced during manganese reduction)
(9) Chloride (produced during dechlorination)
PHASE 4

Reevaluate the site after monitoring to determine the final corrective action.

After acquiring sufficient data, it should be possible to determine if natural attenuation will prevent contaminants from impacting sensitive receptors, or if other remedial technologies, such as pump-and-treat, are needed.

EVALUATING INTRINSIC REMEDIATION

METHODS OF DEMONSTRATING BIODEGRADATION

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminant Attenuation</td>
<td><em>laboratory</em>: reliable, depending on controls; volatilization often a problem</td>
</tr>
<tr>
<td></td>
<td><em>field</em>: not as reliable, often many uncontrolled abiotic loss mechanisms</td>
</tr>
<tr>
<td>Electron Acceptor Loss</td>
<td><em>laboratory and field</em>: may indicate non-contaminant organic matter is degrading (particularly in the presence of enhanced N, P); adequate controls often not possible in the field.</td>
</tr>
<tr>
<td>14CO2 Capture</td>
<td><em>laboratory</em>: usually the most reliable indicator of mineralization if good controls are used</td>
</tr>
<tr>
<td></td>
<td><em>field</em>: not practical for use in field situation - capture CO2 very difficult</td>
</tr>
<tr>
<td>Growth of Contaminant Degrading Microbes</td>
<td><em>laboratory and field</em>: offers reliable supporting evidence of biodegradation, though not conclusive proof alone, especially at field scale</td>
</tr>
</tbody>
</table>
### EVALUATING INTRINSIC REMEDIATION

#### METHODS OF DEMONSTRATING BIODEGRADATION (Cont.)

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutrient Removal ( (N, P) )</td>
<td>\textit{laboratory}: reliable indicator of biotic activity where not completing substrates and adequate controls are used. \textit{field}: supporting evidence only; not reliable where alternate substrates are available.</td>
</tr>
<tr>
<td>Intermediate Metabolite Production</td>
<td>\textit{laboratory and field}: reliable indicator of biodegradation; controls to insure metabolite was not indigenous to the site are necessary.</td>
</tr>
<tr>
<td>Degradable Nondegradable Contaminant Ratios</td>
<td>\textit{laboratory}: most common is the ( C_{17} )/pristane ratio; for petroleum reliability hinges on pristane persistence in medium.</td>
</tr>
<tr>
<td>Growth of Noncontaminant Degrading Microbes</td>
<td>\textit{laboratory and field}: growth of protozoan gazers has been used as an indirect measure of bacterial growth; reliability compromised by protozoan feeding on non-contaminant degrading bacteria.</td>
</tr>
</tbody>
</table>

### EVALUATING INTRINSIC REMEDIATION

#### MEASURES TO DEMONSTRATE BIODEGRADATION

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide Content of Soil Gas</td>
<td>Soil gas carbon dioxide may be produced by the degradation of petroleum hydrocarbons.</td>
</tr>
<tr>
<td>Methane Content of Soil Gas</td>
<td>Methane is a product of the anaerobic degradation of petroleum hydrocarbons.</td>
</tr>
<tr>
<td>Ferrous (Fe(^{+2})) in Groundwater</td>
<td>May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese.</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>Depressed concentrations inside contaminant plume may indicate aerobic biodegradation; concentrations less than 1 mg/L generally indicate an anaerobic pathway.</td>
</tr>
<tr>
<td>Nitrate (NO(_3)(^{-1})) in Groundwater</td>
<td>Substrate (carbon source) for microbial respiration if oxygen is depleted.</td>
</tr>
<tr>
<td>Sulfate (SO(_4)(^{-2})) in Groundwater</td>
<td>Substrate (carbon source) for anaerobic microbial respiration.</td>
</tr>
</tbody>
</table>
### Dissolved Sulfide (S\(^2\)) in Groundwater
Product of sulfate-based anaerobic microbial respiration; analyze in conjunction with sulfate analysis.

### Methane in Groundwater
The presence of methane indicates strongly reducing conditions and suggests BTEX degradation via an anaerobic pathway utilizing carbon dioxide (carbonate) as the electron acceptor (methanogenesis); a redox potential measurement of less than -200 mV could be indicative of methanogenesis.

### Ethane, Ethene in Groundwater
Ethane and ethene are products of the biotransformation of chlorinated hydrocarbons under anaerobic conditions. The presence of these chemicals and other intermediate daughter products (DCE isomers, VC) may indicate that anaerobic degradation is occurring.

### Carbon Dioxide in Groundwater
The presence of free carbon dioxide dissolved in groundwater is unlikely because of the carbonate buffering system of water, but if detected, the carbon dioxide concentrations should be compared with background to determine whether they are elevated; elevated concentrations of carbon dioxide could indicate an aerobic mechanism for bacterial degradation for petroleum.
EVIDENCE OF INTRINSIC REMEDIATION

- Stable or decreasing contaminant plume with time
- Disappearance of a degradable contaminant relative to a "conservative" tracer (e.g., for gasoline contamination, smaller BTEX plume relative to MTBE)
- Correlation of low concentrations of electron acceptors with high contaminant concentrations (i.e., reduced oxygen, nitrate and sulfate concentrations within the contaminant plume relative to their background concentrations)
- Appearance of degradation products (e.g., accumulation of dissolved iron and the production of carbon dioxide, hydrogen sulfide, methane and specific degradation products)
- Ratios of microbial numbers between impacted area and upgradient area that reflect enrichment of the indigenous microbial community by microorganisms with the desired metabolic capabilities
- Microcosm studies to estimate rates of biodegradation in the lab; modeling studies to estimate rates of biodegradation in the field

PHENOMENOLOGICAL MODELS FOR IN SITU BIOREMEDIATION

<table>
<thead>
<tr>
<th>Reference(s)</th>
<th>Transport</th>
<th>Genetics</th>
<th>Species</th>
<th>Sorption</th>
<th>Phases</th>
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### Modeling Intrinsic Remediation

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<td>Brusseau et al. (1992a)</td>
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</tbody>
</table>

### Notes
- Spatial dimensionality: one-, two-, and three-dimensionality, respectively.
- First order; M = Monod; DM = double Monod; TM = triple Monod.
- F = instantaneous fast reaction between substrate and electron acceptor.
- I = inhibition; C = cometabolism.
- CS = substrate (contaminant); E = electron acceptor or nutrient; M = microorganisms.
- E = equilibrium sorption; NE = nonequilibrium sorption; • = not considered.
- D = dissolved; I = insoluble; G = gaseous.
- Oxygen transfer from the unsaturated to saturated zone.
- Theoretical development.
- Microbial transport.
- External mass transfer between bulk liquid and biological phases.
- Multiple substrates or metabolites.
- Two-zone model.
- Multiple microorganisms.
- Internal mass transfer resistance within a biofilm.
- Water loss by plant transpiration.
- Spatial heterogeneity in hydraulic conductivity.
Observed degradation rate dependence of aromatic hydrocarbons (BTEX) on initial substrate concentration under aerobic, denitrifying, and methanogenic conditions. All points were measured in the laboratory.

Field measured half-lives tend to be 4-10 times longer than laboratory-determined values, presumably due to scale-dependent rate limitations.

A rate dependence on initial substrate concentration is consistent with Monod Kinetics.
During the past few months a substantial amount of information has been published in the literature and released in scientific meetings on the intrinsic remediation of soil and ground water (References 1, 2, 3, 4). Dames & Moore believes strongly that conditions at ORS are indicative of ongoing natural processes that, on the one hand, serve to remediate the contaminated ground water beneath the site, and on the other, virtually assure that benzene contaminated ground water is contained and could never reach the Coraopolis well field. The importance of this conclusion is that Alternative 3 in the Feasibility Study now emerges as the only alternative that, in addition to being environmentally protective, meets EPA's cost effectiveness criteria. It should therefore be selected as the preferred remedy in the forthcoming Record of Decision for the ORS.

Intrinsic remediation is defined as the aggregate beneficial effect of the action of a combination of natural attenuation processes on the evolution of a contaminant plume in a given medium. Much of the information now available on intrinsic remediation is explicitly applicable to media contaminated with petroleum constituents such as benzene. Of particular interest at ORS are the natural phenomena of biodegradation and dilution (Reference 5). Dames & Moore has already made a convincing demonstration (Alternative 4) that a remedial action based, in part, on the latter would be an appropriate plume management strategy. Ongoing and future biodegradation is now believed to be an even more important characteristic of the site.

It has been found that many organic chemicals are amenable to biodegradation in the environment. The process relies on naturally occurring microbes to metabolize the material using either oxygen or another terminal electron acceptor. If oxygen is used, the process is considered aerobic; if not, it is anaerobic. Examples of non-aerobic receptors are iron and manganese which are abundant naturally in the aquifer at ORS. In many cases it has been found that a plume of contaminated ground water will be surrounded by a halo of active aerobic biotransformation that eventually prevents the further growth of the plume and begins to cause it to shrink.
in the heart of the plume, conditions may not favor aerobic activity because of oxygen depletion and the other electron receptors become important, providing the necessary conditions for anaerobic biotransformation.

Aerobic biotransformation of benzene is relatively rapid and the bi-products of metabolism are water and carbon dioxide. Anaerobic reactions are less rapid, but non the less significant. Having depleted the oxygen in a portion of the aquifer, additional benzene will be metabolized using the following electron receptors preferentially in order: nitrate, manganese, iron and sulfate. As indicated above, there is an abundance of both iron and manganese in the glacial outwash deposits that form the aquifer in the Ohio River Valley. These metabolic reactions produce soluble carbonates of iron and manganese in addition to carbon dioxide and water. The elevated levels of dissolved manganese that have been observed in monitoring wells at ORS may be the most compelling evidence that biotransformation is a long established and active process at the site.

The apparent stability of the benzene plume at ORS over a period of several decades and the elevated levels of electron acceptors in the ground water suggests strongly that one or more natural attenuation processes are occurring within the water-bearing zone, and that little or no potential for migration of this contamination exists. A positive demonstration that intrinsic remediation is occurring within the ORS water-bearing zone eliminates the need to install and operate a costly pumping and treatment system that would merely replicate the natural processes, but in a far less efficient and reliable manner.

There are simple and inexpensive methods for rapidly assessing the status of intrinsic remediation that is apparently occurring in the ORS ground water. One of the simplest of these is the collection of data, using existing monitoring wells, on the dissolved oxygen content and the redox potential of the ground water, and the correlation of this data with benzene concentrations at specific locations within the plume. If aerobic biodegradation of benzene is occurring, the concentrations of the contaminant and dissolved oxygen at given points within the plume should stand in rough inverse proportion. Measurement of the levels of electron acceptors, carbon dioxide levels and other simple indicator parameters will further serve to help describe the ongoing anaerobic reactions. Ultimately, a predictive model could be developed that would provide guidance to long term monitoring needs.
We have recently discussed the current situation with an acknowledged expert on intrinsic remediation processes, Dr. James Mercer, who has agreed to review the ORS data and to provide an evaluation of the potential importance of intrinsic remediation as a component of the overall site remedy, and to guide us in the collection and interpretation of additional data. Dr. Mercer is well known in the field of hydrogeology, and he has recently co-authored a study of ground water biodegradation commissioned by the American Petroleum Institute. His preliminary findings relative to ORS, based on the existing data, will be available in mid March.

Since the appropriate form and content of the ground water protection remedy for ORS are believed to be the subjects of continuing discussion within the agency at this time, we wish to take this opportunity to bring the issue of intrinsic remediation for ORS ground water to your attention, and urge that it be considered thoroughly before EPA selects the final ground water remedy for the site. We appreciate the fact that the agency has given substantial consideration to our prior technical communications regarding the bases for selection of ground water remedial action objectives and ground water protection system configurations and parameters. Since recently we have become convinced that the general state of understanding regarding intrinsic remediation makes it feasible to evaluate this process on an equivalent basis with other engineered ground water remediation processes we request that EPA provide adequate opportunity and time for full evaluation of this important development.

Dames & Moore, on behalf of Neville Land Company, requests the opportunity to discuss further with EPA our views on the potential for intrinsic remediation, and its application as an element of the ORS remedy.

Very truly yours,

DAMES & MOORE

Mark E. Stella
Project Manager

Stuart Edwards, P.E.
General Manager, Northeast Region
References:

1. Kemblowski, M.W., Y Ma, and E Johnson. Modeling aerobic biodegradation of dissolved hydrocarbons in heterogeneous geologic formations, Utah State University, Health and Environmental Sciences Department, Department Report No. DR 200, 1995


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Anthony J. Burlando