Presentation Outline

• What are we trying to do?
• How is it supposed to work?
• What are the benefits?
• What are the unique challenges?
What Are We Trying to Do?

- By Modifying In Situ Conditions we can Enhance **Ongoing** Degradation of CVOCs – Important because:
  - Natural Degradation Rates are Often Not Sufficient for Remediation Goals.
- Natural Rates are Generally Limited By:
  - Absence of anaerobic groundwater environment,
  - Lack of cometabolic substrate (organic carbon source).
Industrial Site, New Jersey
Reactive Zone Bulk Attenuation Rates

- **Natural Rate**
- **Enhanced Rate**
- **Trendline**

<table>
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<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
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<tbody>
<tr>
<td>PCE</td>
<td></td>
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ARCADIS
**PCE Degrades to TCE**

\[
\begin{align*}
\text{PCE} & \quad \text{Cl} \quad \text{C} = \text{C} \quad \text{Cl} \quad \text{Cl} \\
\text{TCE} & \quad \text{H} \quad \text{Cl} \\
& \quad \text{H} \quad \text{C} = \text{C} \quad \text{Cl} \\
& \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

**Full Degradation**

\[
\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{ETHENE} \rightarrow \text{ETHANOL} \rightarrow \text{CO}_2
\]

**Reductive Dechlorination of Tetrachloroethene**
MICROBIAL CHEMICAL PHYSICAL PROCESSES IN SITU REACTIVE ZONE TREATMENT PROCESSES DISCHARGE REAGENT(S) MICROBIAL CHEMICAL PHYSICAL PROCESSES IN SITU REACTIVE ZONE
How Is It Supposed to Work?

• Addition of easily degradable carbohydrate provides:
  – Source of Organic Carbon
  – Depletion of oxygen
  – Creation of anaerobic reduced environment
• Carbohydrate added through periodic solution injections.
• Zone of enhanced CVOC degradation.
Required Elements

- Carbon Source (Electron Donor)
  - Natural, Supplemental (Molasses)
- Electron Acceptors
  - Nitrate, Iron, Sulfate, Etc.
- Reducing Environment
  - Low Redox Potential (< -100 mV)
- Demonstrated End-Products
Carbohydrate Solution Injection
IN SITU REACTIVE ZONE

Reactive Zones

Injection Wells

Contaminant Plume
Creating a Biological Reactive Zone

- Degradable carbon (electron donor) injection
- Days Travel in Groundwater
- Redox Recovery Zone
- O₂-reducing
- NO₃-reducing
- Mn-reducing
- Fe-reducing
- SO₄-reducing
- CO₂-reducing

ARCADIS
### Microbial Respiration Processes & Redox Regimes

<table>
<thead>
<tr>
<th>Redox</th>
<th>Respiration</th>
<th>e\textsuperscript{-} Acceptor</th>
<th>By-Products</th>
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<td>+ 200 mv</td>
<td>Aerobic</td>
<td>O\textsubscript{2}</td>
<td>CO\textsubscript{2}</td>
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<td>Denitrification</td>
<td>NO\textsubscript{3}\textsuperscript{2-}</td>
<td>NO\textsubscript{2}\textsuperscript{-}, N\textsubscript{2}, NH\textsubscript{3}</td>
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<tr>
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<td>Mn\textsuperscript{2+}</td>
</tr>
<tr>
<td></td>
<td>Iron Reduction</td>
<td>Fe\textsuperscript{3+}</td>
<td>Fe\textsuperscript{2+}</td>
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<tr>
<td></td>
<td>Sulfidogenesis</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>H\textsubscript{2}S</td>
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<tr>
<td>- 400 mv</td>
<td>Methanogenesis</td>
<td>CO\textsubscript{2}</td>
<td>CH\textsubscript{4}</td>
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</table>
Encroachment of the Aerobic Fringe

Methanogenic

SO$_4^{2-}$ Reduction

Fe$^{3+}$/Mn$^{4+}$ Reduction

NO$_3^-$ Reduction

Aerobic Zone

O$_2$

Source Area

Groundwater Flow Direction

Encroachment of the Aerobic Fringe

1. Aerobic Zone
2. Transient Anaerobic Zones
3. Core Anaerobic Zones

Geochemical Mapping (Baseline Analysis): Conceptualization of the Dominant Terminal Electron Acceptor Process (TEAP) in Advancing Plume
Reductive Dechlorination

- Hydrogenolysis
- Cometabolic Pathways
- Dehalorespiration
Hydrogenolysis

Production of H Atoms Influence the Rate
Supply and Demand of NAD Species

Fermentative loss:

NADH + pyruvate

\[ \text{Glu-6P} \rightarrow \text{Glu-6P} \]

NAD+ → NADH

Acetyl-CoA → pyruvate

ATP → ADP

CO₂

Krebs

H⁺

Redox (mV) defines the active couple

NADH + acetyl CoA → acetaldehyde

H⁺

H⁺

NADH + acetyl CoA → H⁺

ethanol

Lactic acid
Hydrogen Production

Hydrogen Concentration

O₂ Depletion  NO₃ Depletion  Fe (iii) Depletion  SO₄²⁻ Depletion  Methanogenic Conditions  End of Remediation
Cometabolic Degradation

Fortuitous Degradation of CVOCs
Dehalorespiration

\[ C_6 H_{12} O_6 + Fe^{3+} \rightarrow CO_2 + H_2O + Fe^{2+} \]
What are the Benefits?

• Often takes advantage of existing site conditions.
• Uses readily available reagents.
• Degradation not mass-transfer.
• Proactive & aggressive in situ treatment.
• Low site impact.
• Flexible - immediate scale-up with minimal effort.
• Proven technique.
• Less costly & more reliable than pump & treat.
What Are the Unique Challenges?

• Can treatment achieve clean up standards?
• Is there a potential for toxic by-products?
• Will you mobilize CVOCs?
• Do you need to add bacteria?
• What if the site has fine-grained soils?
Can Treatment Achieve Clean up Standards?
California Site: CAH Data
Is There a Potential for Toxic By-Products
Superfund Site - Pennsylvania
Will You Mobilize CVOCs?
Source Area Results (Molar Basis)

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<th>Concentration (umoles/L)</th>
<th>Aug-01</th>
<th>Sep-01</th>
<th>Oct-01</th>
<th>Nov-01</th>
<th>Dec-01</th>
<th>Jan-02</th>
<th>Feb-02</th>
<th>Mar-02</th>
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<table>
<thead>
<tr>
<th>Source Area</th>
<th>Results (Molar Basis)</th>
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<td>Jan-02</td>
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<tr>
<td>Feb-02</td>
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Sum umoles/l: 24
Graph of sorbed vs total mass

Effect of Koc on $\frac{\text{Mass}_{\text{sorbed}}}{\text{Mass}_{\text{total}}}$

Organic Carbon Fraction ($f_{\text{OC}}$)

Percent Sorbed

- $K_{\text{OC}} = 265$ (PCE)
- $K_{\text{OC}} = 94$ (TCE)
- $K_{\text{OC}} = 36$ (cis-1,2-DCE)
Do You Have to Add Bacteria?

- Microbial Conditioning
- Electron Donor (only) Amendment
- Bioaugmentation (Microbe and Donor Amendment)
Remediation in Fine-grained Material Site Layout
Initial Carbon Injection

GROUT PUMP
MOLASSES SOLUTION MIX TANK

CLAY/SILT

1" PVC TEMPORARY WELL (Direct Push, No Seals)

SILT/SAND

CLAY/SILT
Initial Carbon Injection
Groundwater Remediation Results Monitoring Well MW-13
PCE Transformation Over Time – Monitoring Well MW-13
Tetrachloroethylene Plume
Summary

• Low levels can be achieved.
• Toxic by-products can be controlled or mitigated.
• Mobilization of CVOCs can be controlled.
• Bacteria present in subsurface.
• Properly engineered systems can address complicated hydrogeology.