CASE STUDY – Use of zero valent iron (ZVI) to enhance abiotic/biotic chlorinated solvent remediation at a former wastewater treatment facility

Karen Kinsella, Ph.D. and Tanya Justham, M.S.
GZA GeoEnvironmental, Inc.
In-Situ Biological and Chemical Reduction: ISBR (biotic) and ISCR (abiotic)

Combined ISBR (biotic reduction) and ISCR (abiotic reduction) minimizes daughter product accumulation and balances pH

Dehalococcoides

Short-lived chloroacetylenes & acetylene; very little VC

Dr. ZVI
Electron Transfer

Gain electrons: REDUCED

Lose electrons: OXIDIZED

Oxidation/Reduction
REDOX POTENTIAL
Eh, ORP
Lose electrons: OXIDIZED

Zero-Valent Iron
Fe$^0$

Ferric Iron
Fe$^{3+}$

Ferrous Iron
Fe$^{2+}$

Electron Transfer
Electron Transfer

ELECTRON DONOR

+ 

ELECTRON ACCEPTOR

\[ \text{O}_2 \]

[Image of wood] + [Image of oxygen] → [Image of fire]
Electron Transfer

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{BTUs} \]
Microbial Electron Transfer

Something to eat  Something to breathe  A few bacteria

ELECTRON DONOR

+ELECTRON ACCEPTOR

or

SUGAR

or

O₂

or

TCE

PCE
Microbial Electron Transfer

Many bacteria + Waste products: carbon dioxide, water

\[ \text{CO}_2 \]

\[ \text{H}_2\text{O} \]
Abiotic Degradation: Zero-Valent Iron

ELECTRON DONOR

Dr. ZVI

Back off fools! I got excess electrons and ain't afraid to use them

Ferrous Iron

Fe\(^{2+}\)

ELECTRON ACCEPTORS

TCE

PCE

DCE

Short-lived chloroacetylenes and acetylene

Very little VC
In-Situ Biological + Chemical Reduction (ISBR + ISCR)

Biotic/Abiotic Synergies
Minimize daughter product accumulation
Balance pH
Synergistic Biotic/Abiotic Solution

Kinetics

Biotic: more chlorinated degrade faster  
Abiotic: variable degradation rate

Balanced pH

Biotic lowers pH  
Abiotic raises pH

Hydrogen

Fuel for microbial dechlorination
Biotic/Abiotic Synergy continued

Biotic reduction in dissolved phase only

Abiotic not limited by dissolution and desorption

Abiotic reduction can occur within NAPL
Slower process, but ZVI lasts longer

Wilson et al. 1990. EPA/600/6-90/004.
Combined Biotic/Abiotic Dechlorination
Former Wastewater Treatment Facility

WWTF closed in 1980s
Unauthorized discharge of chlorinated solvents with septic system sludge
TCE up to 1,400 ppm in groundwater
DNAPL source found during pilot study temporary monitoring well installations
Combined Biotic/Abiotic Dechlorination
Former Wastewater Treatment Facility

Parent cVOCs detected within the source area groundwater include:

- Tetrachloroethene
- Trichloroethene
- 1,1,1,2-Tetrachloroethane
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- Carbon tetrachloride
Combined Biotic/Abiotic Dechlorination
Former Wastewater Treatment Facility

Two hydrogeologic units:

Upper: Unconfined alluvial sands
Lower: Semi-confined glaciofluvial sands and gravels and glacial till

Potential receptor: Surface water

**Elevated groundwater sulfate**
Combined Biotic/Abiotic Dechlorination

Former WWTF (white circle)
Location of pilot study (orange circle)
Combined Biotic/Abiotic Dechlorination

Additive Blend
- Organic carbon
- Nutrients
- Zero-valent iron
- Emulsifier

Geoprobe® Systems
Combined Biotic/Abiotic Dechlorination

Three degradation mechanisms:

1) Abiotic degradation I
2) Abiotic degradation II
3) Biodegradation
Combined Biotic/Abiotic Dechlorination

Abiotic I

ELECTRON DONOR

ZVI

Back off fools! I got excess electrons and ain’t afraid to use them

ELECTRON ACCEPTOR

TCE
## Combined Biotic/Abiotic Dechlorination

### Abiotic I

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Sample period</th>
<th>NH AGQS</th>
<th>GZ-802US</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Baseline</td>
</tr>
<tr>
<td>Pilot Area Chloroethenes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethene (µg/L)</td>
<td>5</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Trichloroethene (µg/L)</td>
<td>5</td>
<td><strong>384,000</strong></td>
<td><strong>196,000</strong></td>
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<tr>
<td>cis-1,2-Dichloroethene (µg/L)</td>
<td>70</td>
<td><strong>113,000</strong></td>
<td><strong>103,000</strong></td>
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<tr>
<td>Vinyl Chloride (µg/L)</td>
<td>2</td>
<td>&lt;100</td>
<td>&lt;100</td>
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<tr>
<td>Pilot Area Chloroethanes</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (µg/L)</td>
<td>200</td>
<td><strong>39,100</strong></td>
<td><strong>17,600</strong></td>
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<tr>
<td>1,1-Dichloroethene (µg/L)</td>
<td>7</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>1,1-Dichloroethane (µg/L)</td>
<td>81</td>
<td>400</td>
<td><strong>1,100</strong></td>
</tr>
<tr>
<td>Chloroethane (µg/L)</td>
<td>na</td>
<td>&lt;200</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>na</td>
<td>7.65</td>
<td>557</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>500</td>
<td>12.1</td>
<td>34.0</td>
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<tr>
<td>pH (standard units)</td>
<td>na</td>
<td>5.9</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Combined Biotic/Abiotic Dechlorination

**Abiotic II**

**ELECTRON DONOR**

- ORGANIC CARBON

**ELECTRON ACCEPTOR**

- SULFATE
Microbial Sulfate Reduction

**Electron Donor**

- Organic Carbon

**Electron Acceptor**

- Sulfate

Sulfate-Reducing Bacteria

Microbially-Generated Sulfide
Abiotic II Degradation

SULFIDE from SULFATE-REDUCING BACTERIA

+ 

DIVALENT (FERROUS) IRON from ZVI that donated electrons to PCE & TCE

FERROUS SULFIDE
Abiotic II Degradation

ELECTRON DONOR

FERROUS SULFIDE

ELECTRON ACCEPTOR

TCE

PCE
Iron Sulfide = Electron Donor
Permeable Reactive Barrier Formed In-Situ
Abiotic Remediation

Reduction at the iron particle (ZVI) surface
Reduction by ferrous iron in coatings on soil particle surfaces
Combined Abiotic I/II Dechlorination

1\textsuperscript{st} post injection sampling round (1 month):
- TCE
- Iron

2\textsuperscript{nd} post injection sampling round (3 months):
- TCE
- Iron
- Sulfate

4\textsuperscript{th} post injection sampling round (9 months):
- TCE
- Iron
- Sulfate
Combined Biotic/Abiotic Dechlorination

Source Well GZ-802US

Logarithmic Scale

Concentration (ug/L)

Date (Month-Year)

TCE
TCA
Cis 1,2-DCE
VC
Combined Biotic/Abiotic Dechlorination

GZ-TW-2 (downgradient well)

Sample Collection Date (Month-Year)

Concentration (µg/L)

- TCE
- TCA
- VC
- cis-1,2-DCE
Lessons learned:
Combined remedy was effective on a complex source area
pH is penultimate for bioremediation
Sulfate can enhance ZVI remediation
Questions

Tanya.Justham@gza.com
603-232-8765

Karen.Kinsella@gza.com
860-573-9787

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