Enhanced Bioremediation Field Experience: Using Observed Half Lives in Design and Prediction

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Questions

• What treatment results do we expect?
• How can we use lab and field data for realistic design and prediction?
Outline of Presentation

• Lab Half Lives
• Field Half Lives
• Half Life Trends over Time
• Comparison between Lab and Field Data
• Extrapolation of Data to Design
• Use of Data in Prediction of Cleanup Time
• Conclusions
• Future Work
Substrate Composition

EHC is composed of:

- Controlled-release, food grade, complex carbon
- Micro-scale zero valent iron (5 - 10 µm)
- Major, minor, and micronutrients
- Food grade organic binding agent
EHC Conceptual Designs

**Source Area/Hotspot Treatment**
- Dosing: 0.15 to 1% wt/wt
- Spacing: 5 to 15 ft (DPT)

**Injection PRB for Plume Control**
- Dosing: 0.4 to 1% wt/wt
- Spacing: 5 to 10 ft (DPT)

**Plume Treatment**
- Dosing: 0.05 to 0.2% wt/wt
- Line Spacing: 100 ft / 1 year gw travel distance
Laboratory Column Approach

Column test results analyzed using 1D equation (first order decay), appropriate for anaerobic biodegradation of VOCs in aquifers (Alvarez and Illman, 2006) and abiotic degradation with ZVI (Gillham and O’Hannesin, 1994):

\[ C = C_0 e^{-kt} \]

Where:
- \( t \) = residence time [T]
- \( C \) = effluent concentration \([M/L^3]\)
- \( C_0 \) = inflowing concentration \([M/L^3]\)
- \( k \) = decay constant \([1/T]\)
Laboratory Column Half Lives

<table>
<thead>
<tr>
<th>Substance</th>
<th>Half Life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE (3%)</td>
<td>107</td>
</tr>
<tr>
<td>Chloroform (30%)</td>
<td>86</td>
</tr>
<tr>
<td>TCE (0.5%)</td>
<td>64</td>
</tr>
<tr>
<td>PCE (0.5%)</td>
<td>69</td>
</tr>
<tr>
<td>Chloroform (0.5%)</td>
<td>17</td>
</tr>
<tr>
<td>TCE (1%)</td>
<td>26</td>
</tr>
<tr>
<td>PCE (1%)</td>
<td>17</td>
</tr>
<tr>
<td>Chloroform (1%)</td>
<td>10</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (30%)</td>
<td>140</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane (1%)</td>
<td>20</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>40</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane (30%)</td>
<td>120</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (1%)</td>
<td>22</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (30%)</td>
<td>132</td>
</tr>
</tbody>
</table>

Explanation
PCE (3%) - VOC (application rate for lab)
Laboratory Column Half Lives vs. Time

- TCE (0.5%)
- TCE (0.5%)
- PCE (3%)
- PCE (3%)
- PCE (1%)
- TCE (1%)

The graph shows the half-life of different compounds over time, with the x-axis representing time in days and the y-axis representing half-life in hours.
Degradation Kinetics and Yield Rates

- 35 days: 1,2-DCA CA 100% (mol)
- 64 days: 1,2-DCA CA 42% (mol)
- 223 days: 1,2-DCA CA 0%

Graph showing concentration over time for different samples: Feed, Control, Iron Column, BHC column, and EHC Soil Jar.
Degradation Kinetics and Yield Rates

1,2-DCA

Yield (%)

Time (days)

Percent Removal (%)

yield rate

percent removal

www.AdventusGroup.com
Example Field Data

Initial concentrations vs. distance

Distance from upgradient end of PRB (ft)

<table>
<thead>
<tr>
<th>Conc. (ppb)</th>
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<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>10000</td>
</tr>
<tr>
<td>20000</td>
</tr>
<tr>
<td>30000</td>
</tr>
<tr>
<td>40000</td>
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PRB

- VC
- 1,1-DCE
- trans-DCE
- cis-DCE
- TCE

25 ft upgradient

<table>
<thead>
<tr>
<th>days</th>
<th>ppb</th>
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<tbody>
<tr>
<td>0</td>
<td>10000</td>
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<tr>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
</tr>
</tbody>
</table>

Within PRB

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0</td>
<td>10000</td>
</tr>
<tr>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
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</table>

38 ft downgradient

<table>
<thead>
<tr>
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<th>ppb</th>
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<tbody>
<tr>
<td>0</td>
<td>10000</td>
</tr>
<tr>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
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</table>

48 ft downgradient

<table>
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<th>ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10000</td>
</tr>
<tr>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
</tr>
</tbody>
</table>

www.AdventusGroup.com
Data collected at multiple points up and downgradient of the PRB analyzed using Buschek and Alcantar relationship (Buschek and Alcantar, 1995), as modified by Carey and Wiedemeier (2000):

\[ \lambda = \frac{v}{(4\alpha_x R)((1-2 \alpha_x m)^2 - 1)} \]

Where:
- \( \lambda \) = decay constant [1/T]
- \( v \) = average linear groundwater velocity [L/T]
- \( \alpha_x \) = hydrodynamic dispersion coefficient along flow path [L]
- \( R \) = retardation factor [1]
- \( m \) = slope of ln-linear concentration versus distance [1/L]

This approach analyses 1D, steady-state sorbed & dissolved phase biodegradation & dispersion, but results in conservative (high) estimates of half life because no daughter-production assumed. Desorption and transient effects not considered.
Analytical Assessment of Field Data vs. Distance

Half Life Along Plume Centerline

Half Life (hours) vs. Distance (ft)

- Blue line: Carbon Tetrachloride
- Green line: Chloroform

- PRB

Legend:
- Biotic: Biostimulation
- Abiotic: Indirect iron effects
- Biotic/abiotic: Greatly reduced redox
- Abiotic: Direct iron effects
Modeling Assessment of Field Data (Ethenes)

Half life (1.5 or 8 h) based on lab data

Good match at early times

Half life 8h

Good match at late times

Half life 1.5h

MW-46
- Modeled effluent
- Observed effluent

MW-48
- Modeled influent
- Observed influent

Approximate direction of groundwater flow

Consultant: www.AdventusGroup.com
Field Data vs. Time

Time-Varying Half Lives in PRB

- Carbon Tetrachloride
- Chloroform
- PCE
- TCE
- cis 1,2-DCE
- trans 1,2-DCE
- 1,1-DCE
- VC
Field Data vs. Time - Ethenes

![Graph showing field data vs. time for Ethenes contaminants: VC, Cis 1,2-DCE, TCE, and PCE. The x-axis represents time in days ranging from 0 to 800, and the y-axis represents half-life in hours ranging from 1 to 10,000. The graph includes data points for each contaminant, indicating their degradation over time.]
Lab and Field Half Lives vs. Application Rate & Method

Comparison of Laboratory and Field Half Lives in Amended Zone

**Graph Description:**
- The graph compares laboratory and field half lives of various contaminants in an amended zone.
- **Trench PRB** and **Injected PRB** are shown.
- **Column Test** and **Field Data** are represented.
- **Contaminants: PCE (3%;10%), TCE (0.5%;10%), TCE (1%;10%), cis 1,2-DCE (0.5%;10%), cis 1,2-DCE (0.5%;10%), Chloroform (30%;1%), Chloroform (0.5%;1%), Carbon Tetrachloride (0.5%;0.5%), Carbon Tetrachloride (0.5%;0.5%).**

**Half Life (hours):**
- The x-axis represents different contaminants and their concentrations.
- The y-axis represents the half life in hours, ranging from 0 to 70.

**Legend:**
- **Dark line** represents Column Test.
- **Blue line** represents Field Data.

**Note:**
- The graph illustrates the decreasing field application rate, indicated by the arrow pointing downward.
Comparison of Amended and Unamended Half Lives

Amended and Unamended Field Half Lives

- PCE (10%): 5,736 hours
- PCE (0.5%): 5,736 hours
- TCE (10%): 6,648 hours
- TCE (1%): 6,648 hours
- TCE (0.5%): 6,648 hours
- Vinyl Chloride (10%): 2,112 hours
- Vinyl Chloride (1%): 2,112 hours
- Vinyl Chloride (0.5%): 2,112 hours
- Carbon Tetrachloride (0.5%): 456 hours
- Chloroform (0.5%): 552 hours

**Effect of carbon & finer iron**

- Anaerobic Natural Attenuation Rates (Alvarez & Ilman, 2006)
- Injected PRB Field Half Life
- Trench PRB Field Half Life
- Granular ZVI (Abiotic)
PRB Design Based on Half Lives - Residence Time Requirement

- Residence requirements - ca 5.5 days
- Linear groundwater velocity - 4 ft/day
- Treatment zone width - 5.5 days * 4 ft/day = 22 ft
Extrapolation of Field Data to Calculate Time to Reach Remedial Goal (NAPL Affected Source Area)

- Treatment Goal Projected to be Achieved: About 1.5 years
- Baseline: 20,000 ug/L
- Considering source feed and degradation
- Net half life ~ 160 days
Model Prediction of Plume Cleanup (Carbon Tetrachloride and Daughters)

- Plume extends 800 m from grain elevators.
- Discharges into small creek.
- Bedrock rises to an elevation of ~3 m above present day water table at presumed source area.
- PRB installed down-gradient of suspected source area.
- PRB installed as a line of injection points spaced ~3 m apart.
- PRB extends across width of the plume and measures ~90 m long.
Model Prediction of Plume Cleanup (Carbon Tetrachloride and Daughters)

Calibrated half lives:
carbon tetrachloride: 7 hours
chloroform: 20 hours

calculated half lives:
carbon tetrachloride: 13 hours
18 hours
148 hours

Model calibrated ½ life
Feb 07

Analytical half lives

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feb 07</th>
<th></th>
<th>Aug 07</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS (µg/L)</td>
<td>105.7</td>
<td>99.2</td>
<td>94.45</td>
<td></td>
</tr>
<tr>
<td>NRMS (%)</td>
<td>17.35%</td>
<td>16.28%</td>
<td>15.5%</td>
<td>21.4%</td>
</tr>
<tr>
<td>Correlation</td>
<td>0.858</td>
<td>0.859</td>
<td>0.873</td>
<td>0.765</td>
</tr>
<tr>
<td>Residual mean (µg/L)</td>
<td>+23</td>
<td>-5.32</td>
<td>2.03</td>
<td>-33.56</td>
</tr>
</tbody>
</table>

Calibrated half lives:
carbon tetrachloride: 18 hours
18 hours
148 hours
Model Prediction of Plume Cleanup (Carbon Tetrachloride and Daughters)

Calibrated half lives:
carbon tetrachloride: 7 hours
chloroform: 20 hours

March 2005
February 2007
August 2007
March 2010

Calibration
Prediction
Conclusions - Factors Affecting Field Decay rates (Using EHC)

- Decay observed 100s of ft downgradient from PRB (multiple decay mechanisms)
- Half lives decrease with time
- Parents decay faster than daughters (but minimal daughter production)
- Half lives decrease with uniformity of application
- Half lives decrease with application rate (to a point)
- Carbon + iron more effective than carbon alone or iron alone
- Database of half lives can be used in design, extrapolation, prediction
Conclusions - Factors Affecting Field Decay rates (other amendments)

- Decay observed 100s of ft downgradient from PRB (multiple decay mechanisms)
- Half lives decrease with time
- Parents decay faster than daughters (but minimal daughter production)
- Half lives decrease with uniformity of application
- Half lives decrease with application rate (to a point)
- Carbon + iron more effective than carbon alone or iron alone
- Database of half lives can be used in design, extrapolation, prediction
Future Work

- Effect of the following on effective degradation rates:
  - Desorption and back diffusion
  - pH
  - Eh