Reactive Barriers for the Passive Remediation of Chlorinated Solvents in Sediments and Groundwater Discharge

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In cooperation with
DoD, Aberdeen Proving Ground
USEPA, Region III
NIEHS, Superfund Research Program

Conceptual model for chlorinated solvent contamination in wetland
(modified from Lorah et al., 2005)

Chlorinated VOCs at West Branch Canal Creek and their anaerobic degradation pathways

Parent VOCs in orange
- Chlorinated ethanes: HCA= hexachloroethane
  - PCE= pentachloroethene
  - 112TCA= 1,1,2,2-tetrachloroethane
- Chlorinated ethenes: TCE= trichloroethene
- Chlorinated methanes: CT= carbon tetrachloride
  - CF= chloroform

Site Characterization

Chloroform
Tetrachloroethene

West Branch Canal Creek, APG

WBC-2 Dechlorinating Culture

Relative Abundances above 1%

Reactive Barrier Design and Monitoring

Re-amendment System

Single-hole multilevel diffusion samplers and multilevel wells
Passive diffusion bags

Sand, Peat, Compost, Chitin, WBC2

Geotextile

Hydraulic Gradient (Artesian)

Wetland Sediment (10-15 ft thick)

Seep Area

Aquifer (~40 ft thick)
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Microcosms: Wetland Sediment-Compost Mixtures
- Different composts tested for support of WBC-2 activity and VOC degradation
- Variable results with different composts for degradation of both parent and daughter compounds

APG Reactive Barrier: Upward Flow Columns

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>k (day⁻¹)</th>
<th>t₁/₂ (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1122TeCA</td>
<td>3.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Chloroform</td>
<td>2.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>1.4</td>
<td>12</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>3.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Salinity microcosms

Biodegradation Pathways
- Aerobic (reductive dechlorination)
  - CB serves as terminal electron acceptor
  - Separate e- donor required
  - Rate decreases with decreasing number of Cl
- Aerobic (oxidation)
  - O₂ required as electron acceptor
  - CBs utilized as C and e- donor
  - Rate increases with decreasing number of Cl
  - Short-lived intermediates

Chemical plant 1966-2002; EPA Superfund 2002
- 1981-5,000 gal CB
- 1985 storage tanks: 579,000 gal 14DCB and TCBs
- Abuts Red Lion Creek, part of Delaware River watershed
- Treatment in uplands, but not in wetlands
- Half of water flow to Red Lion Creek is from Columbia Aquifer

Standard Chlorine of Delaware, DNAPL Extent

Drinking Water MCL: µg/L
- Trichlorobenzenes: 135TCB, 124TCB, 123TCB
- Dichlorobenzenes: 14DCB, 13DCB, 12DCB
- Chlorobenzene
- Benzene
- CO₂, CH₄

* Parent contaminant
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Wetland Study Area, SCD
- Upward flow at all sites
- Seepage measured on wetland surface and creek bottom

Conceptual model for contamination and dual-biofilm reactive barrier in wetland

Approach to evaluate natural and enhanced biodegradation
- In situ microcosms with Bio-Traps (Microbial Insights)
  - Stable isotope probing (13C-labeled 14CDB, CB, B)
  - Microbial species and functional genes for biodegradation
- Evaluate biodegradation processes in flow-through bioreactors
  - Upflow fixed film bioreactors
  - Mimic growth in subsurface
  - Allows changing conditions
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QuantArray Microbial Analysis - Aerobic

<table>
<thead>
<tr>
<th>Gene</th>
<th>15B</th>
<th>WBC-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pMMO</td>
<td>4,000</td>
<td>6,000</td>
</tr>
<tr>
<td>sMMO</td>
<td>8,000</td>
<td></td>
</tr>
<tr>
<td>TCBD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RDEG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALKB</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SCD Bioreactors

Aerobic Native Culture (15B)

GAC with WBC-2: Classes >1% Abundance

GAC with 15B: Proteobacteria, Order

<table>
<thead>
<tr>
<th>Order</th>
<th>Relative Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burkholderiales</td>
<td>15B.1 60</td>
</tr>
<tr>
<td>Rhizobiales</td>
<td>15B.2 40</td>
</tr>
<tr>
<td>Caulobacters</td>
<td>GAC.1 10</td>
</tr>
<tr>
<td>Dehalococci</td>
<td>GAC.2 10</td>
</tr>
</tbody>
</table>

Significant increase in the Betaproteobacteria group Burkholderiales on GAC.
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**Microcosm Results:**

**Anaerobic WBC-2 Biofilm on GAC**
- Slight decrease in CBs with culture in mineral media compared to DIW
- Rapid sorption to GAC with and without anaerobic biofilm
- Distinctly faster overall CB removal in biofilm-GAC

**Aerobic 15B Seeded on GAC**
- Delay in removal

**Column Testing**
- Sand Columns: Medium Sand+ 5 % GAC + 3 % Chitin
- Sediment Columns: in progress; no data yet

**Sand Columns:**
- Outflow VOC concentrations very low in both columns
- Greater CB removal column with both the anaerobic and aerobic culture

**Sediment methanol extract analysis**
- Generally, less VOCs remaining in the columns that contained both the WBC-2 and 15B cultures

**lab testing ongoing but also started small-scale field pilot tests**
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**GM**
- GAC-chitin-sand mixed into top 10”
- GAC seeded with WBC-2 and 15B aerobes

**GC**
- GAC-chitin-sand placed as 3” cap
- (remove top root mat)
- GAC seeded with WBC-2 and 15B aerobes

**C**
- Site 135 test area with 3 plots and pre-installation sampling.

**TOTAL Sand Chitin GAC pounds**
- 783 30 43

**C**
- Sand placed as 3” control cap
- (remove top root mat)

**15B aerobes grown in lab in 5 days**
- WBC-2 in anaerobic cylinder from Sirem Lab (20L mixed with DI-H2O for GAC seeding)

Bucket of pre-measured sand-chitin-seeded GAC dumped in plot and mixed into sediment to depth of 10 inches with small auger or “egg-beater” attachments on drill.

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