Development and In Situ Application of Sorbent/reagent-amended “Active” Sediment Caps for Managing HOC-contaminated Sediments

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Outline

• Technology Description
• Development and Application
• Observations/lessons learned
• Future Directions
Concept

River Water

Degradable Products

Bioturbation Layer
Active Layer(s)
- Degradation
- Sequestration
- Treating pore water

\[
\left(1 + \frac{\rho_b K_d}{n}\right) \frac{\partial C}{\partial t} = -u_z \frac{\partial C}{\partial z} + D_e \frac{\partial^2 C}{\partial z^2} - kC
\]
Proposed Placement Method

Anacostia River Sediment Profile
Proposed Placement Method

RCM = Reactive Core Mat

RCM unrolled and placed by divers

Anacostia River Sediment Profile
Proposed Placement Method

1. Provides Containment
2. Protects Benthic organisms
3. Reduces PCB flux
4. Eliminates exposure pathway

15-25 cm clean sand placed over RCM
Development and Application

Data Gaps Addressed

• Suitable “Active” Materials
  – Degrade or sequester PCBs

• Placement Techniques
  – Clam shell, geotextiles

• Demonstration of technology (ongoing)
  – Effectiveness of placement method and risk reduction
  – Performance evaluation
Identifying Suitable Sorbents

• Treatability Study Goals
  – Determine reactivity of PCBs with Fe$^0$
  – Compare performance of different sorbents
  – Provide design criteria for demonstration
Rationale for Fe$^0$ and Sorbents

- Fe$^0$
  - Proven dechlorination potential
  - Removes meta and para chlorines
    - Potential to decrease toxicity of PCB mixtures
- Sorbents (Coke, AC, soil, sand)
  - Sequester PCBs and decreases bioavailability
  - Coke is inexpensive (~$100/ton)
  - Soil (OC) is inexpensive and previously tested
  - Sand is standard cap material
Approach: Fe₀

- Batch experiments monitoring PCB loss and byproduct formation
  - Commercial Fe(0), Pd/Fe(0), Nano-Fe(0)
  - Individual PCB congeners
  - Rate constants (k) based on byproduct formation
Fe\(^0\) Media

- **Nano Fe(0)**
  - Size: \(~50\) nm

- **Fisher Fe(0)**
  - Size: \(150\) \(\mu\)m

- **0.05% Pd/Peerless Fe(0)**
  - Size: \(0.4 - 2.4\) mm

- **Peerless Fe(0)**
  - Size: \(0.4 - 2.4\) mm
Pd/Fe\textsuperscript{0}-0.05\% \quad k \sim 21 \text{ yr}^{-1}
2,2',3,5'-Nano Fe$^0$
PCB Dechlorination Patterns

\[
\begin{align*}
\text{Parent Congeners} & : 22' \quad 34' \quad 234 \quad 22'35' \quad 22'45' \\
\text{Cl Cl} & : \text{ortho} \\
\text{Cl Cl Cl} & : \text{meta} \\
\text{Cl Cl Cl Cl} & : \text{para}
\end{align*}
\]
# Fe\(^0\) Reactivity Summary

<table>
<thead>
<tr>
<th>MEDIA</th>
<th>RESULTS</th>
<th>(k) (yr (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Fe(0)</td>
<td>No Observable Reaction (6 months)</td>
<td>0</td>
</tr>
<tr>
<td>Pd/Fe(0) (500 ppmw Pd)</td>
<td>Rapid dechlorination not sustainable</td>
<td>21</td>
</tr>
<tr>
<td>Nano Fe(0)</td>
<td>Dechlorination rates variable Meta and Para chlorine dechlorination favored</td>
<td>0.01-6</td>
</tr>
</tbody>
</table>
Approach: Sorbents

- Isotherms/column breakthrough with 1,2-DCB
- Estimate $K_d$ for PCBs
- Assess coke toxicity
  - Leaching tests-Heavy metals, PAHs, VOCs

<table>
<thead>
<tr>
<th>Material</th>
<th>K_d (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment (low)</td>
<td>180</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>14,000</td>
</tr>
<tr>
<td>Sediment (high)</td>
<td>1.9E+6</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>5.6E+9</td>
</tr>
</tbody>
</table>

Krauss et al. 2001
Jonker et al. 2002
## Properties of Sorbents

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Soil</th>
<th>Coke</th>
<th>AC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon (%)</strong></td>
<td>~0</td>
<td>3.8%</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td><strong>Porosity (eff)</strong></td>
<td>0.29</td>
<td>0.47</td>
<td>0.48</td>
<td>0.53</td>
</tr>
<tr>
<td><strong>Size (mm)</strong></td>
<td>~0.3</td>
<td>0.4-2.0</td>
<td>0.4-2.0</td>
<td>0.3-2.0</td>
</tr>
<tr>
<td><strong>Particle Density (g/cm³)</strong></td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>BET SA (m²/g)</strong></td>
<td>&lt;1</td>
<td>6.6</td>
<td>2-12</td>
<td>919</td>
</tr>
<tr>
<td><strong>R (retardation)</strong></td>
<td>6 x 10²</td>
<td>1.6 x 10⁵</td>
<td>2.3 x 10⁵</td>
<td>1.8 x 10⁷</td>
</tr>
</tbody>
</table>
Isotherms with 1,2 Dichlorobenzene

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$K_d$ (L/kg)</th>
<th>Log $K_d$ (L/kg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>62950</td>
<td>4.80</td>
<td>0.959</td>
</tr>
<tr>
<td>Coke</td>
<td>616</td>
<td>2.79</td>
<td>0.955</td>
</tr>
<tr>
<td>Anacostia Sediment</td>
<td>375</td>
<td>2.57</td>
<td>0.981</td>
</tr>
<tr>
<td>Farm Soil</td>
<td>308</td>
<td>2.49</td>
<td>0.945</td>
</tr>
</tbody>
</table>
Log $K_d = 0.9355 \log K_{ow} - 0.3792$

$R^2 = 0.9675$

Extrapolated from 1,2 DCB

<table>
<thead>
<tr>
<th>Material</th>
<th>Extrapolated</th>
<th>Jonker and Koelmans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>5.15</td>
<td>5.02</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>7.8</td>
<td>8.55</td>
</tr>
</tbody>
</table>

**Sorbent Performance and Capacity**

\[ C_0 = 35 \text{ ppm 1,2-DCB, } V_x = 1.4 \text{ m/d} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>1,2 DCB Capacity (mg DCB /g sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>0.6</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>250.8</td>
</tr>
<tr>
<td>Farm Soil</td>
<td>0.7</td>
</tr>
<tr>
<td>Sand</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

Assumptions:

- 1,2 DCB Capacity = PCB Capacity
- 1.25 cm thick cap
- 60 cm uniform contaminated sediment
Coke Toxicity Evaluation

• Solid Coke
  – 11 Heavy Metals, 16 PAHs, 33 VOCs, CN⁻, N, P

• Leachate (DI and Sediment Pore Water)
  – Heavy Metals, PAHs

• Comparison with Sediment Quality Guidelines (e.g. ERL¹) and WQ standards (e.g. CMC²)

1 Effects Range Low (NOAA)
2 Criterion Maximum Concentration (EPA)
# Heavy Metals in Solid Coke

<table>
<thead>
<tr>
<th>Metal</th>
<th>Rept. Limit (mg/kg)</th>
<th>Conc. (mg/kg)</th>
<th>ERL$^2$ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>0.033</td>
<td>0.034</td>
<td>0.15</td>
</tr>
<tr>
<td>Aluminum</td>
<td>20</td>
<td>466</td>
<td>NA</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1</td>
<td>1.7</td>
<td>8.2</td>
</tr>
<tr>
<td>Barium</td>
<td>5</td>
<td>11.4</td>
<td>NA</td>
</tr>
<tr>
<td>Chromium</td>
<td>1</td>
<td>1.5</td>
<td>81</td>
</tr>
<tr>
<td>Copper</td>
<td>2.5</td>
<td>20.2</td>
<td>34</td>
</tr>
<tr>
<td>Iron</td>
<td>10</td>
<td>2500</td>
<td>NA</td>
</tr>
<tr>
<td>Lead</td>
<td>0.3</td>
<td>0.74</td>
<td>46.7</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.5</td>
<td>10.1</td>
<td>NA</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.5</td>
<td>0.56</td>
<td>NA</td>
</tr>
<tr>
<td>Zinc</td>
<td>2</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>PAH</td>
<td>Result (µg/kg)</td>
<td>ERL (µg/kg)</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>31</td>
<td>85.3</td>
<td></td>
</tr>
<tr>
<td>Benzo (a) anthracene</td>
<td>81</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>Benzo (a) pyrene</td>
<td>83</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>Benzo (b) fluoranthene</td>
<td>70</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Benzo (ghi) pyrene</td>
<td>68</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Benzo (k) fluoranthene</td>
<td>68</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>110</td>
<td>384</td>
<td></td>
</tr>
<tr>
<td>Dibenz (a,h) anthracene</td>
<td>32</td>
<td>63.4</td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>110</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>Indeno (1,2,3-cd) pyrene</td>
<td>42</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>48</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td><strong>Phenanthrene</strong></td>
<td><strong>120</strong></td>
<td><strong>240</strong></td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>100</td>
<td>665</td>
<td></td>
</tr>
</tbody>
</table>
# Metals Detected in Leachate

<table>
<thead>
<tr>
<th>Metal</th>
<th>Leachate DI (µg/L)</th>
<th>Leachate PW (µg/L)</th>
<th>Anacostia Porewater (µg/L)</th>
<th>Rept. Limit (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>228</td>
<td>279</td>
<td>249</td>
<td>200</td>
</tr>
<tr>
<td>Ba</td>
<td>53.7</td>
<td>58.4</td>
<td>76.1</td>
<td>6</td>
</tr>
<tr>
<td>Fe</td>
<td>419</td>
<td>368</td>
<td>481</td>
<td>40</td>
</tr>
<tr>
<td>Se</td>
<td>7.6</td>
<td>10.6</td>
<td>ND</td>
<td>5</td>
</tr>
</tbody>
</table>
# PAHs in Leachate

<table>
<thead>
<tr>
<th>PAH</th>
<th>Leachate (DI)</th>
<th>Leachate (PW)</th>
<th>Reporting Limit</th>
<th>CMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>1.4</td>
<td>ND</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>1.6</td>
<td>ND</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.9</td>
<td>ND</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1.7</td>
<td>ND</td>
<td>10</td>
<td>3980</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3.2</td>
<td>1.2</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2</td>
<td>ND</td>
<td>10</td>
<td>300</td>
</tr>
</tbody>
</table>
Predicting Performance in the Anacostia River

<table>
<thead>
<tr>
<th>Depth</th>
<th>5.6 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>260 m³/min</td>
</tr>
<tr>
<td>$U_z$ (seepage)</td>
<td>-2-6 cm/d</td>
</tr>
<tr>
<td>$k$ (assumed)</td>
<td>0 yr⁻¹</td>
</tr>
<tr>
<td>RCM</td>
<td>1.25 cm</td>
</tr>
</tbody>
</table>

\[
\left(1 + \frac{\rho_b K_d}{n}\right) \frac{\partial C}{\partial t} = -u_z \frac{\partial C}{\partial z} + D_e \frac{\partial^2 C}{\partial z^2} - kC
\]
Sorbent Performance ($v=1$ cm/d)

Assumes capacity not exceeded and no attenuation
Cap Placement and Concerns

• Methods of placement
  – Particle Broadcasting
  – Reactive Core Mat (RCM)
Particle Broadcasting
Potential Problems with Particle Broadcasting for Sorbents

- Difficult to place thin layers
- Variable settling velocities
- Floating material
- Fines
Release of Fines From Coke

1.6 kg Coke
~ 6 L Water

Release of fines during placement could be an issue!
Coke Settling

$V_s \sim 12-24 \text{ cm/s}$

6 Hours after release
~13% of material does not sink
Some fines still suspended

Uneven distribution
Reactive Core Mat (RCM)
Reactive Core Mat II
Mat Properties and Costs

- **Thickness**
  - ~0.5 in. (1.25 cm)

- **Loading**
  - ~0.8-1.0 lb/ft² (3.4 kg/m²)

- Twelve 10’ x 100’ rolls produced
  - ~6.5 tons of (10 x 40 mesh coke)

- **Costs**
  - Materials ($2700)
  - Lamination ($1750)
  - Labor ($2850)
  - Coke ($950)
  - Shipping ($2900)
  - Total ($11,100) ($1.11/ft²)
Comparative Materials Costs

- Activated Carbon ($1/lb)
- Coke ($0.07/lb)

Materials Cost ($/yd³) vs. Depth of Contaminated Sediment (ft)
Factors Affecting Suitability of Approach

- Types of contaminants
- Site characteristics
- Geotextile properties
Types of Contaminants

• Hydrophobic organics
  – PCBs (log $K_{ow}$=4-8)
  – PAHs (log $K_{ow}$=3-6)
  – PCDD (log $K_{ow}$=4-8)
  – PCDF (log $K_{ow}$=4-8)

• Other contaminants
  – Metals
  – Less hydrophobic organics
Favorable Site Characteristics

- Diffuse contamination
- Low energy depositional and stable environment
- Minimal surface roughness/debris
- Minimal seepage rates

Parameters (coke)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Porosity</td>
<td>0.48</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>0.78 g/cm³</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>0.5 cm/sec</td>
</tr>
<tr>
<td>Log $K_d$</td>
<td>5.15 L/kg</td>
</tr>
</tbody>
</table>
Geotextile Properties

- **Strength**
  - Placement and integrity
- **Permeability (gas and liquid)**
  - Seepage and burping potential
- **Susceptibility to pore plugging**
  - Changes in permeability with time
- **Density**
  - Placement and stability
Observations/conclusions

• Most Promising Aspects
  – RCM technology is simple
  – **Provides ability to accurately place thin layer caps
  – Will work with AC as sorbent, less expensive sorbents may be effective if natural attenuation occurring
  – High potential for future development of reactive media
  – Technologies with modest reaction rates (<1 yr⁻¹) can be effective

• Concerns
  – Sorbents do NOT directly provide PCB mass reductions
  – Sorbent capacity
  – Fe⁰ may NOT be cost effective (lifetime unknown)
  – Further research needed to develop reactive media for RCMs
  – Effect of NOM and colloids on sorptive properties
  – Geotextile/cap integrity
Open Scientific Questions?

- What should design lifetime be?
- How will NOM affect performance?
- Cap Stability
- What geotextiles properties are needed?
- Can contaminants effectively be degraded in situ?
- Who will fund development/testing?
Ongoing Research

• Column studies-long term performance
  – Evaluating the effect of DOM and colloids in porewater on sorbent/mat performance (lower $K_d$, competition, ...)
• Anacostia River Pilot Demonstration (April 04)
  – Mat placement and performance
• Evaluate alternative geotextiles
• Develop “reactive” media for PCBs and other contaminants
Questions/Comments?