CURRENT STATUS OF IN-SITU CAPPING FOR SEDIMENT REMEDIATION

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Current Issues in Capping

- Biogeochemistry beneath the cap
- Active Capping - Permeable adsorptive barrier
  - Material Options
  - Management of upwelling water /gas/NAPL
  - Effectiveness of materials
  - Placement of materials
  - Capping design - modeling
- Monitoring Cap Performance
  - Definition of Cap Objectives
Metals and Capping

- Metals often effectively contained by a conventional cap
- AVS vs. SEM - Capping will enhance reducing conditions

\[
\text{AVS} > \text{SEM} \\
\text{Metals will not be toxic} \\
M^{2+} + \text{FeS}(s) \rightarrow \text{MS}(s) + \text{Fe}^{2+} \\
\text{AVS} < \text{SEM} \\
\text{Divalent metals may be toxic}
\]
Conceptual Model

Pre-Cap

Methyl mercury

Post-Cap

Methyl mercury
Organics and Capping

- Mobility and toxicity generally not redox sensitive
- Degradation is redox sensitive
  - Hydrocarbon degradation facilitated aerobically
  - Chlorinated organics reductively dechlorinate but many sediment contaminants refractory
- Dynamics controlled by sorption in cap and groundwater upwelling
Active Capping

- Potentially greater effectiveness than with sand can be achieved with “active” or amended caps
  - Encourage fate processes such as sequestration or degradation of contaminants beneath cap
  - Discourage recontamination of cap
- Feasible if high value components are placed in thin layer in a controllable manner
- Effective if time/capacity of active cap sufficient to manage finite mass of contaminants
- Significant stakeholder acceptance advantage
Goals of Capping Amendments

- **Permeability Control**
  - Discourage upwelling through contaminated sediment by diverting groundwater flow

- **Contaminant Migration Control**
  - Slow contaminant migration, typically through sorption related retardation

- **Contaminant Degradation Aid**
  - Less well developed, contaminant specific but designed to encourage contaminant fate processes
**Potential Active Cap/Treatment Materials**

- Clays for permeability control
- Activated Carbon or other carbon sequestration agent
- Organoclays for NAPL control & some dissolved control
  - Significant swelling and permeability reduction with NAPL
- Clay and sequestration agent mixtures
- Phosphate additives for metals
  - Rock phosphate (i.e. apatite) demonstrated
- Iron Sulfide for Hg and MeHg control
- Siderite (FeCO₃) for pH control
- Zero valent iron
- Oxygen or hydrogen release compounds/technologies
- Biopolymers
- Electrochemical controls on redox conditions
Impermeable Caps

- Commercially available
  - AquaBlok
  - Bentomat
  - HDPE
- Can successfully divert groundwater upwelling
  - Where will the groundwater go?
  - Plan for gas accumulation and release
  - Long term effectiveness in the face of gas/tidal dynamics?
Contaminant Migration Control

- **pH**
  - Siderite
  - Ferrous Sulfate
  - Alum
- **Metals**
  - Apatite
  - Iron Sulfide
- **Organics**
  - Organoclay
  - Activated carbon

![Graph showing pH levels and FeCO3 reacted](image)

Vlassopoulos and Serrano, 2008

Available FeCO3 ~ 2 g/cm of layer thickness/cm²
2 cm/yr upwelling = 1000 years of pH protection
Organic Retardation

- **NAPL present - Organoclay**
  - Capacity of $O(1 \text{ g NAPL/g organoclay})$
  - Placement within a laminated mat for residual NAPL or to allow replacement if capacity exceeded
  - Placement in bulk for significant NAPL volumes
  - Multiple organoclay layers or organoclay/activated carbon layer for both NAPL and dissolved contaminant control

- **Dissolved contaminants only - Activated carbon**
  - Placement in mat may be necessary to allow easy placement
  - Placement as amendment also possible
  - Activated carbon typically more subject to fouling than organoclay
**Hg sorption**

Special Hg formulations exist

Conventional formulations may be similarly effective if Hg complexed with suspended organic matter.

**Hg (PM199)**

\[ y = 6920.9x^{0.7212} \]

\[ R^2 = 0.9516 \]

**Hg (MRM)**

\[ y = 9417.7x^{0.6709} \]

\[ R^2 = 0.935 \]
AC/OMC Relative Effectiveness Matrix Effects (Naphthalene)
AC/OMC Relative Effectiveness
Linear Scale (Naphthalene)
Dense Non-Aqueous Phase Liquid, DNAPL
Sorbents for Sequestration and Bioavailability Reduction

- Expect bioavailability reduction proportional to porewater concentration (inversely proportional to partition coefficient, $K_d$)
- Equivalent sand cap thickness – diffusion/ dispersion dominated ($u << 1$ cm/day)

$$L_{eff} = L_{active} \sqrt{\frac{R_{active}}{R_{sand}}} \sim L_{active} \sqrt{\frac{K_{d_{active}}}{K_{d_{sand}}}}$$

<table>
<thead>
<tr>
<th>Material</th>
<th>$\log K_d$</th>
<th>$K_{oc}$</th>
<th>$f_{oc}K_{oc}$</th>
<th>$f_{oc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>$\sim 10^{-4}$</td>
<td>$K_{oc}$</td>
<td>$0.01K_{oc}$</td>
<td>$f_{oc}K_{oc}$</td>
</tr>
<tr>
<td>Coke</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organoclay</td>
<td></td>
<td></td>
<td>$\sim 1-10K_{oc}$</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td></td>
<td></td>
<td>$\sim 100K_{oc}$</td>
<td></td>
</tr>
</tbody>
</table>

$f_{oc} \sim 0.01-0.05$
**ACTIVE CAP DESIGN MODEL**
including steady state design model from Lampert and Reible (2009)*
Version 3.13
2/9/2008

**Instructions:** This spreadsheet determines concentrations and fluxes in a sediment cap at steady-state worksheet 1), unsteady state (worksheet 2), assuming advection, diffusion, dispersion, bioturbation, deposition/erosion, sorption onto colloidal organic matter, and boundary layer mass transfer. An active cap layer with enhanced sorption is considered by converting to an equivalent conventional cap thickness. Depth is defined from the cap-water interface. A constant deposition rate can be entered but is not allowed to result in a net contaminant velocity <0 (relative to the changing cap-water interface). The cells in blue are input cells; these can be changed for the design of interest. DO NOT CHANGE THE CELLS IN RED (or the spreadsheet will not function properly). A second worksheet calculates the transient profiles for a semi-infinite case. The third worksheet title “array” allows the user to create an array of outputs for a given input (e.g. to study different compounds for a given site).

**Contaminant Properties**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Chlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon partition coefficient, ( \log K_{oc} )</td>
<td>2.52 log L/kg</td>
</tr>
<tr>
<td>Colloidal organic carbon partition coefficient, ( \log K_{DOC} )</td>
<td>2.15 log L/kg</td>
</tr>
<tr>
<td>Water diffusivity, ( D_w )</td>
<td>6.0E-06 cm(^2)/s</td>
</tr>
<tr>
<td>Cap decay rate (porewater basis), ( \lambda_1 )</td>
<td>0.00 yr(^{-1})</td>
</tr>
<tr>
<td>Bioturbation layer decay rate (porewater basis), ( \lambda_2 )</td>
<td>0.00 yr(^{-1})</td>
</tr>
</tbody>
</table>

**Sediment/Bioturbation Layer Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminant pore water concentration, ( C_0 )</td>
<td>1 ug/L</td>
</tr>
<tr>
<td>Biological active zone fraction organic carbon, ( (f_{oc})_{bio} )</td>
<td>0.05</td>
</tr>
<tr>
<td>Colloidal organic carbon concentration, ( \rho_{DOC} )</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>Darcy velocity, ( V )</td>
<td>2 cm/yr</td>
</tr>
<tr>
<td>Depositional velocity, ( V_{dep} )</td>
<td>0 cm/yr</td>
</tr>
<tr>
<td>Bioturbation layer thickness, ( h_{bio} )</td>
<td>10 cm</td>
</tr>
</tbody>
</table>

**Transient Concentration Profiles**

![Transient Concentration Profiles Diagram](Image)
Design Models

- Spreadsheet model
  - Transient model until penetration of chemical isolation layer
  - Steady state model (bioturbation & isolation layer)
  - Variant for additional active cap layer - transient and ss

- Numerical model
  - Matlab version
  - Multiple layers, nonlinear sorption, finite source

- Available at http://www.caee.utexas.edu/reiblegroup/
Performance Measures

Managing Contamination

- Isolation of contaminated sediment - Cap stability?
- Elimination of sediment resuspension - Cap stability?
- Reduction in contaminant flux to water - Flux?
- Reduction in contaminant accumulation in benthic organisms - Flux? Contaminant isolation? Bioaccumulation?

Thin Layer Capping

Thick Layer Capping
Effectiveness from Bulk Solids?

Percent Sediment and Phen C/C₀ versus Depth

- Clean Sand Cap
- Cap-sediment Intermixing Zone
- Sediment

C/C₀ and Percent Passing

Depth (cm)
In. Situ Porewater Measurement

- Bulk sediment concentration is less useful as indicator of exposure-risk
- **Porewater concentration** is better indicator *(even for active benthic uptake by ingestion)*
- Porewater is difficult to measure, but possible with solid phase micro extraction (SPME)

Field deployable SPME, capable of measuring porewater with vertical resolution
SPME and Body Burden
San Diego Bay

PAHs – B(b)F, B(k)F, BaP in *Muscalista*

Single correlation with porewater concentrations works well for all three compounds
Thin Layer Capping

Day 28

4-cm Sand Cap
Laboratory Studies of Thin Layer Capping

Day 28

4-cm Sand Cap
Capping Performance

B[a]A Pore Water Concentrations

Pore Water Concentration (ng/L)

Overlying Water

Depth (cm)

ACS
- 0cm
- 2cm
- 4cm
- 6cm
Thin Layer Capping to Manage Residuals

Pyrene Concentrations in Worm Tissue

<table>
<thead>
<tr>
<th>Depth of Cap</th>
<th>C (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Contaminated Sediment</td>
<td>~11000</td>
</tr>
<tr>
<td>0cm</td>
<td>~12000</td>
</tr>
<tr>
<td>2cm</td>
<td>~11000</td>
</tr>
<tr>
<td>4cm</td>
<td>~9000</td>
</tr>
<tr>
<td>6cm</td>
<td>~1500</td>
</tr>
<tr>
<td>10cm</td>
<td>~2000</td>
</tr>
</tbody>
</table>
Correlation of Bioaccumulation with Porewater Concentration

Unit slope is BSF estimated by $K_{ow}$
Capping Summary

- Conventional sand caps easy to place and effective
  - Contain sediment
  - Retard contaminant migration
  - Physically separate organisms from contamination
- There are existing and developing alternatives when a conventional cap is not sufficiently protective
  - Permeability Control
  - Adsorptive Caps
- Porewater concentrations/profiles can be an effective tool for defining contaminant migration, exposure and risk