Comparative Validation of Innovative Capping Technologies
Anacostia River, Washington DC

Presented by

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19 February 2003

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Hazardous Substance Research Center

South and Southwest

- **Established under CERCLA (Recompeted 2001)**

LSU

Rice Texas A&M Georgia Tech

- **Mission**
  - Research and Technology Transfer
    - Engineering management of contaminated sediments
    - Primarily focused on in situ processes and risk management
    - Unique regional (4&6) hazardous substance problems
  - Outreach
    - Primarily regional in scope
    - Driven by community interests and problems

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Selecting Remedial Options

- NAS Committee On PCB Contaminated Sediments
  - Recommended framework of Presidential and Congressional Commission on Risk Assessment and Management
- Key points
  - Manage the risks not simply surrogates of risk like concentration or mass
  - Engage stakeholders early and often

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Sediment Management

- Risk controlled by relatively small well defined areas (hot spots) in dynamic sediment environment with defined on-shore disposal options?
  - Encourages removal options
- Risk defined by diffuse contamination in stable sediment environment?
  - Encourages in situ management options
- What about other sites?
  - Requires site specific assessment and conceptual model development
  - There are no default options; site specific assessment necessary!

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In Situ Capping - Advantages

- Armors sediment for containment
  - Can be designed to be stable in high flow conditions
  - High confidence in describing dynamics of noncohesive, granular media
  - Eliminates uncertainty of existing sediment dynamics
- Separates contaminants from benthic organisms
  - Eliminates bioturbation (primary source of exposure and risk in stable sediments)
  - Typical flux reduction at steady state by factor of 1000
- Reduces diffusive/advective flux
  - Increased transport path and sorption-related retardation
  - Time to achieve steady state may be thousands of years
- Provides opportunities for habitat development

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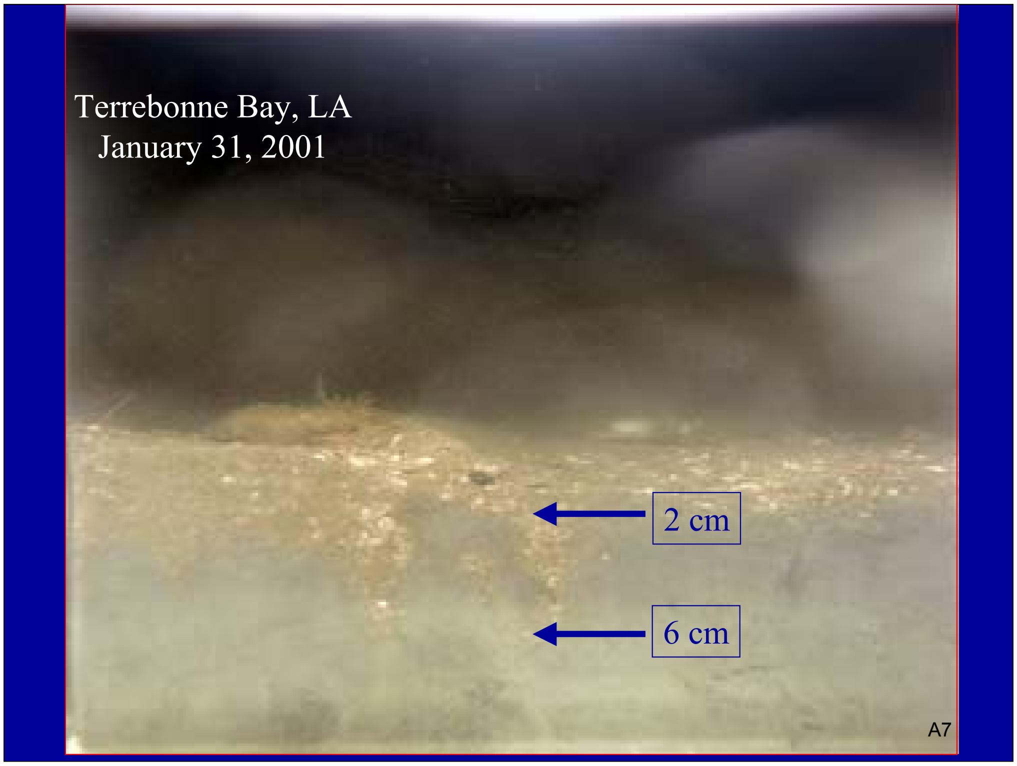
Cap Effectiveness

- Replaces particle transport processes with porewater processes
  - Elimination of erosion and bioturbation as transport processes
  - Diffusion (always present)
  - Advection if seepage significant (highly variable)
- Reduces steady state contaminant flux
- Additional reduction in transient in flux
  - Reduces migration during transient consolidation of sediment and cap materials
  - Reduces transient migration through cap
  - Partition coefficient, K_{sw} (Organics- $K_{sw} \sim f_{oc}Koc$)
  - $R_f = \varepsilon + \rho_b K_{sw}$

A6

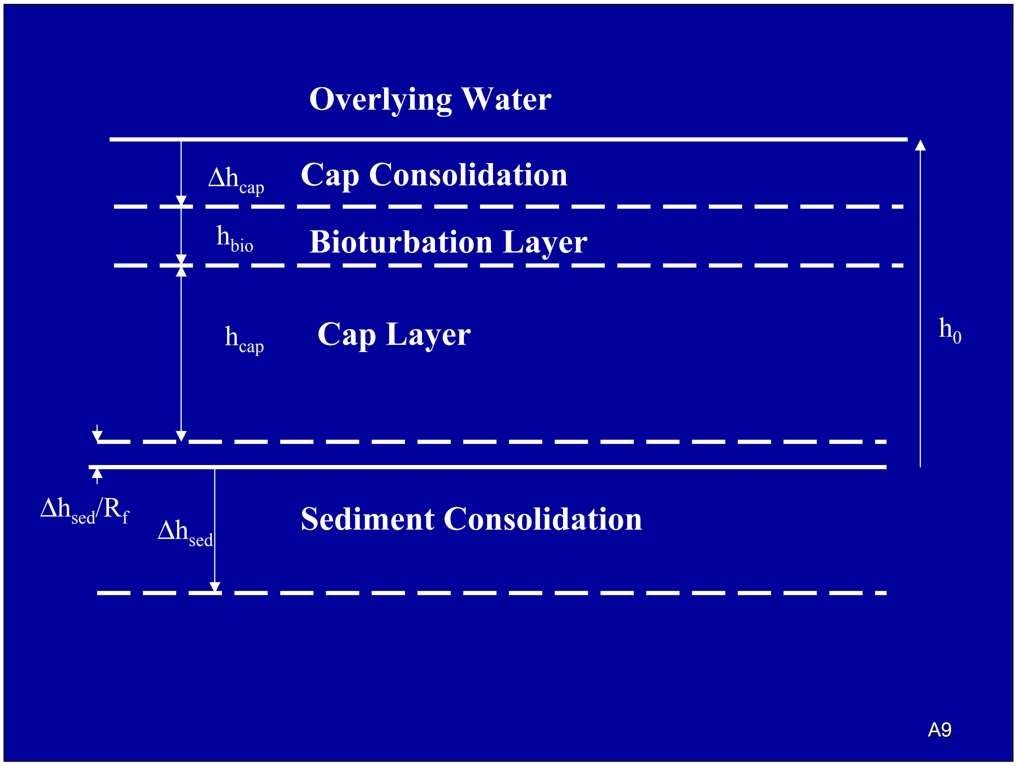


Sandy shell in thin layer – significant organism activity limited to upper6 cm – event horizon only 2 cm for relatively large hurricane on the stronger east side of the hurricane

Steady State Cap Performance

- Diffusion dominated system
  - Flux prior to capping
    - $N_A/\rho_b W_s \sim 1$ cm/yr (without erosion)
  - Flux after capping
    - $N_A/\ \rho_b W_s \sim D_{cap}/L_{eff}\ R_f$
    - For pyrene, 1 ft cap - .001 cm/yr ($R_f \sim O[10^3]$)
- Advection dominated system
  - Typically only small portions of sediment bed
  - Flux after capping ultimately approaches prior flux
  - Sediment concentrations are dependent upon sorptive capacity of capping material
    - Sand - low steady state concentrations near cap-water interface

A8



Overlying Water
Δh_cap
Cap Consolidation
h_bio
Bioturbation Layer
h_cap
Cap Layer
h_0
Δh_sed/R_f
Δh_sed
Sediment Consolidation
A9

Cap Design Factors - Stability

- Top layer stability
  - Design velocity or stresses (e.g. 100 year flood)
  - d_{50}(ft) = 1/4 τ_c (lb/ft^2) (Highway Research Board)
- Non-uniform size distribution
  - $d_{85}/d_{15} > 4$
- Angular shape
- Maximum particle size <2 d_{50}
- Minimum particle size > 0.05 d_{50}
- Thickness > 1.5 d_{50}
- Adjacent layers: d_{50} (layer 1) / d_{50} (layer 2) < 20
  - Especially important for armored caps or caps using coarse grained material for habitat enhancement to avoid washout of finer material
- Transition zone length: 5 times cap thickness

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Current Issues in Cap Design

- Optimal placement over very soft sediments
- Placement of fine-grained, heterogeneous materials
- Chemical containment
  - NAPL seeps
  - Gas generation and migration
  - Methyl mercury formation and migration
- Design and effectiveness with groundwater seepage
  - Assessment of seepage (and variation with time/space)
  - Control of seepage
- Stability
  - Selection of design flow, prediction of resulting stresses
  - Stability of innovative cap materials
- Active Caps – Caps as a reactive barrier

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Capping Concerns

- Contaminants are not removed or eliminated
  - Residual risk of cap loss
    - But all remedial measures leave residual risk
    - Intergenerational stewardship a “fact of life” for any contaminated sediment site of any complexity
  - Can caps be designed to ensure
    - Migrating contaminants are eliminated?
    - Residual pool of contaminants degrade over time?
- Continuing sources can recontaminate cap
  - Continuing sources a problem for any remedial approach
  - Can caps be designed to reduce recontamination?

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Comparative Evaluation Metrics

- Primary metric – Risk
- Secondary metrics
  - Link to appropriate conceptual model of system
  - Indicator species concentrations (e.g. fish)
  - Contaminant mass (dynamic environment)
  - Surficial average concentrations (stable environment)
    - When risk due to diffuse contamination (not "hot spots")
    - SWAC – surface area weighted average concentration
  - Integral measures (allows incorporation of time)

$$\int SWAC\ dt \approx Cumulative\ Exposure$$

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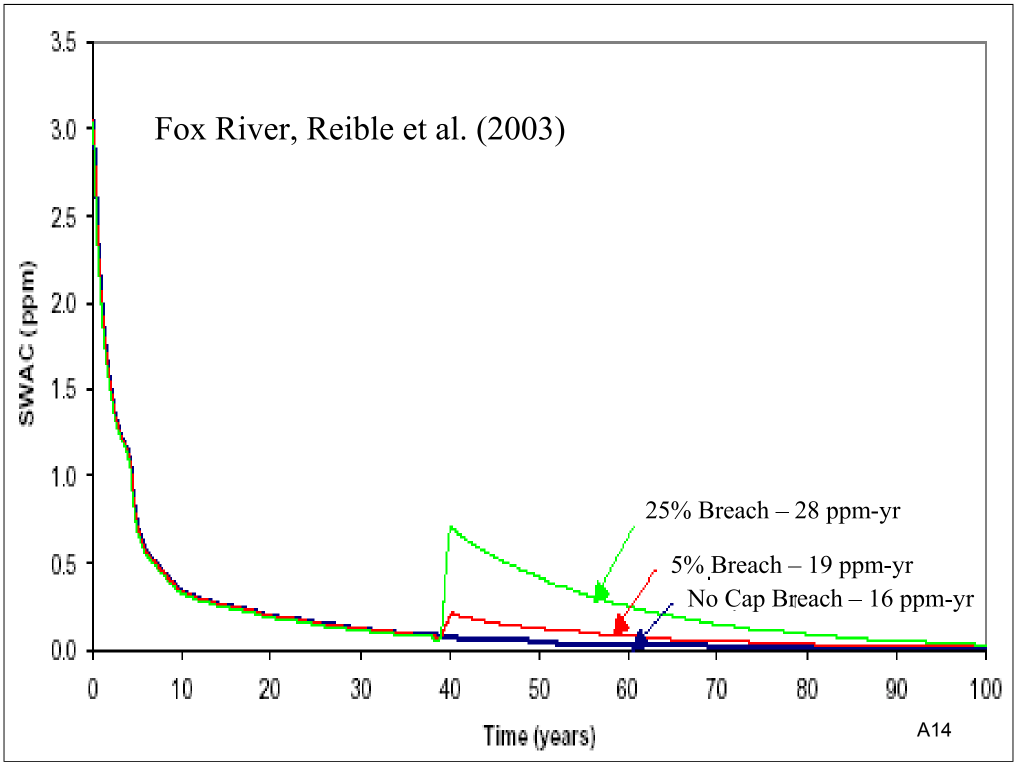

Fox River, Reible et al. (2003)
SWAC (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
25% Breach – 28 ppm-yr
5% Breach – 19 ppm-yr
No Cap Breach – 16 ppm-yr
0
10
20
30
40
50
60
70
80
90
100
Time (years)
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Summary – Conventional Capping

- Conventional sand caps easy to place and effective
  - Contain sediment
  - Retard contaminant migration
  - Physically separate organisms from contamination
- Methods are available for key design needs
  - Cap erosion and washout
  - Cap and sediment consolidation
  - Chemical containment
  - Assessment of exposure and risk

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Active Capping

Can you Teach an Old Dog New Tricks?

Danny D. Reible
Hazardous Substance Research Center/S&SW
Louisiana State University

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Center Focused on Engineering Management of Contaminated Sedimentsf – my role is as the dog trainer!

Potential of Active Caps

- Sand caps easy to place and effective
  - Contain sediment
  - Retard contaminant migration
  - Physically separate organisms from contamination
- Greater effectiveness possible with "active" caps
  - Encourage fate processes such as sequestration or degradation of contaminants beneath cap
  - Discourage recontamination of cap
  - Encourage degradation to eliminate negative consequences of subsequent cap loss

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Active Capping Demonstration Project

- The comparative effectiveness of traditional and innovative capping methods relative to control areas needs to be demonstrated and validated under realistic, well documented, in-situ, conditions at contaminated sediment sites
  - Better technical understanding of controlling parameters
  - Technical guidance for proper remedy selection and approaches
  - Broader scientific, regulatory and public acceptance of innovative approaches

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Overall Project Scope

A grid of capping cells will be established at a well characterized contaminated sediment site:

- Contaminant behavior before capping will be assessed
- Various capping types will be deployed within the grid evaluating placement approaches and implementation effectiveness
- Caps will be monitored for chemical isolation, fate processes and physical stability
- Cap types and controls will be compared for effectiveness at achieving goals

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Demonstration Site – Anacostia River

- Anacostia River has documented areas of sediment contamination
- Anacostia Watershed Toxics Alliance (AWTA) offers unique opportunities
- Ultimate rehabilitation approaches uncertain
- Much of current focus on reducing contribution of sources
- Areas adjacent to Navy Yard are good candidate sites based on review of existing data

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Demonstration Participants

- Lead
  - Danny Reible, Hazardous Substance Research Center
  - Louisiana State University
- Prime Contractor
  - Horne Engineering, Fairfax, VA
  - Yue Wei Zhu, Lead Engineer
- SITE program evaluation of Aquablok
  - Vincente Gallardo, EPA Cincinnati
- Advisory Groups
  - Anacostia Watershed Toxics Alliance
  - Remediation Technology Development Forum

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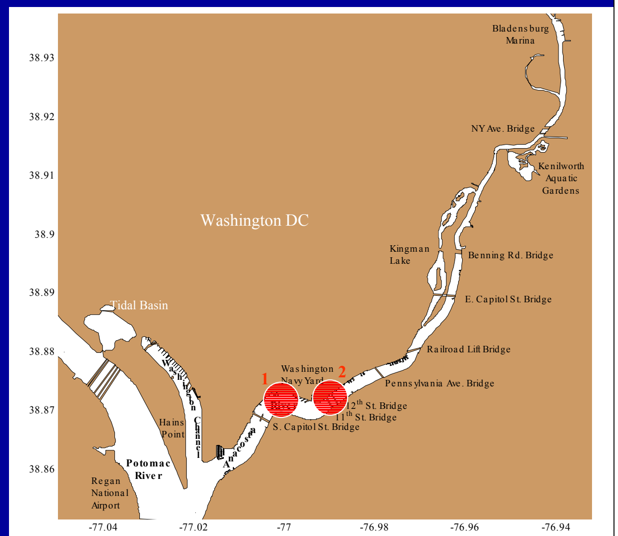
Demonstration Site – Anacostia River

- Two potential study areas identified adjacent to Navy Yard
  - First site has elevated PCBs and metals [1]
  - Second site is primarily PAHs [2]
  - Some seepage, free phase at depth at second site



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Demonstration Sites

Proposed Demonstration Area

- The proposed demonstration areas are approximately 200 ft by 500 ft (approximately 2 acres) adjacent the shoreline upstream and downstream of the Navy Yard
- Each proposed pilot study cell is approximately 100 ft by 100 ft in size and two or three study cells per area will be implemented.

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Demonstration Sites

- First Site – old CSO outfall
  - South end of Navy Yard
  - PCBs: 6-12 ppm
  - PAHs: 30 ppm
  - Metals
    - Cd: 3-6 ppm
    - Cr: 120-155 ppm
    - Cu: 127-207 ppm
    - Pb: 351-409 ppm
    - Hg: 1.2-1.4 ppm
    - Zn: 512-587 ppm
- Second site – near old manufactured gas plant
  - North end of Navy Yard
  - PAHs up to 210 ppm

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Potential Cap Technologies

- Six technologies undergoing bench scale testing and evaluation
- Bench scale testing objectives
  - Problems with physical placement?
  - Problems with contaminant or nutrient release during placement?
  - Problems with effectiveness with Anacostia contaminants?
  - What is appropriate cap design, homogeneous or layered composite?
  - What are key physical or chemical indicators of performance?
- Placement approaches also under evaluation
  - Gravity tremie placement
  - Layered placement
  - Needlepunched mats (CETCO)

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Potential Cap Technologies

- Aquablok
  - Control of seepage and advective contaminant transport
  - Focus of EPA SITE Assessment
- Zero-valent iron
  - Encourages dechlorination and metal reduction
  - With or without sequestering amendments to retard migration
- Phosphate mineral (Apatite)
  - Encourages sorption and reaction of metals
- Coke
  - Encourages sorption-related retardation
- BionSoil
  - Encourage degradation of organic contaminants
- Natural organic sorbent
  - Encourages sorption-related retardation

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AquaBlok™

- Gravel/rock core covered by clay layer
- Expands in water decreasing permeability
- Applicable to seep locations (Site 2)
- May be useful as funnel in “funnel and gate” reactive barrier design
- Semi-commercial technology
- Treatability evaluation underway Hull & Assoc

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Zero-Valent Iron

- Fe(0), Fe-S, Pd/Fe(0) under consideration
  - Subject to cathodic reactions that yield hydrogen
    - Hydrogen can drive reductive biotic transformations
    - Reductive dechlorination
    - Metal reduction
  - Directly provide electrons for abiotic reduction
- Chlorinated Organic Compounds (PCBs)
  - Evaluation underway by Carnegie Mellon University
- Metals
  - Evaluation underway by Rice University

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Coke Sorbent

- Coke Breeze
  - 92% fixed carbon
  - 140 mm particles with 45-50% porosity
  - Particle density of 1.9-2 g/cm^3
  - TCLP leachate – contaminants below detection limit
- Treatability testing underway at Carnegie Mellon University

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Apatite Barrier

Apatites – $Ca_5(PO_4)_3OH$

- Subject to isomorphic substitution
  - $Pb_5(PO_4)_3OH$
  - $Cd_5(PO_4)_3OH$
- Reduces migration of metal species
- Employing XRF and XAS for metal species dynamics and migration
- Evaluation underway with LSU/University of New Hampshire

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BionSoil™

- Manufactured soil from composting
- Hydrogen source
  - Enhancement of reductive dechlorination
  - Enhancement of anaerobic degradation of PAHs
- High organic content
  - Encourages sorption and retardation of transport
- Evaluation underway at LSU

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OrganoClay Sorbent

- Candidate - Biomin EC-100 organo-modified clay
  - Low permeability
  - High organic content
  - Encourages retention of both non-aqueous and dissolved constituents
  - Evaluated for control of active hydrocarbon seeps in Thea Foss Waterway, WA
- Treatability testing underway with Hart-Crowser

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Other Potential Cap Materials

- Ambersorb commercial sorbent
  - Effective sorbent but high cost
- Activated carbon sorbents
  - Effective sorbent intermediate in cost
  - Primary focus on coke as cheaper (but less effective carbon-based adsorbent)

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Capping Demonstration Schedule

- Technology Evaluations (Initial Phase) – Jun/Dec 2002
  - Studies currently ongoing at LSU and collaborating institutions
- Site Characterization – Jan-Apr 2003
  - Phase 1 Geophysical Investigation (Jan 2003)
  - Phase 2 Geotechnical and Chemical Assessment (Feb 2003)
  - Phase 3 Biological Assessment (Apr 2003)
- Cap Design – Jan/Jun 2003
- Cap Placement (Site 1) – Jul/Aug 2003
- Cap Evaluation – Aug 2003/Sept 2004

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Site Characterization Objectives

- Establish the contamination baseline at demonstration areas
  - Define contaminant variability
  - Identify and confirm appropriate areas for cap demonstration
- Determine the geotechnical characteristics of the sediment
- Provide necessary baseline data for future evaluation of effectiveness of capping placement and capping technologies

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Site Characterization

- Preliminary physical assessment (Ocean Survey & R. Diaz)
  - Bathymetry measurement
  - Side scan and sub-bottom profiling
  - Sediment profiling camera
- Surficial sediment sample collection
- Sediment coring sample collection
- Sediment radionuclide characterization
  - Historical deposition
  - Average rate and extent of bioturbation
- Geotechnical data for the cap design
- Historical Data Collection (groundwater seepage, flow velocity, and etc.)
- Biological Assessment (type and density)

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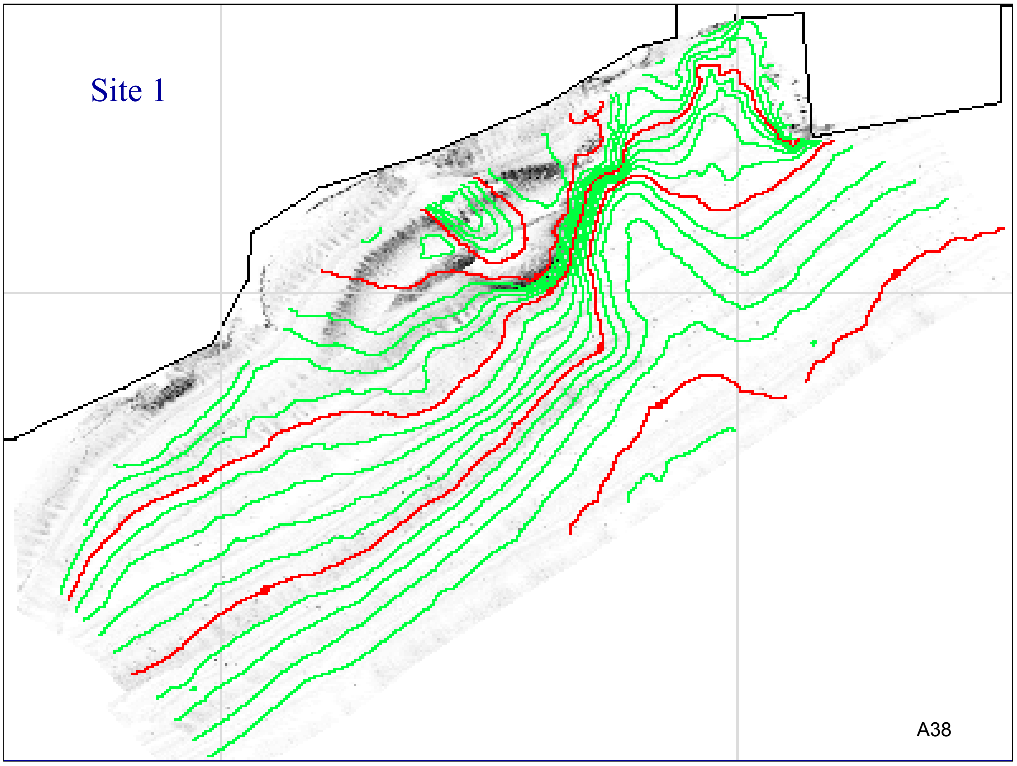
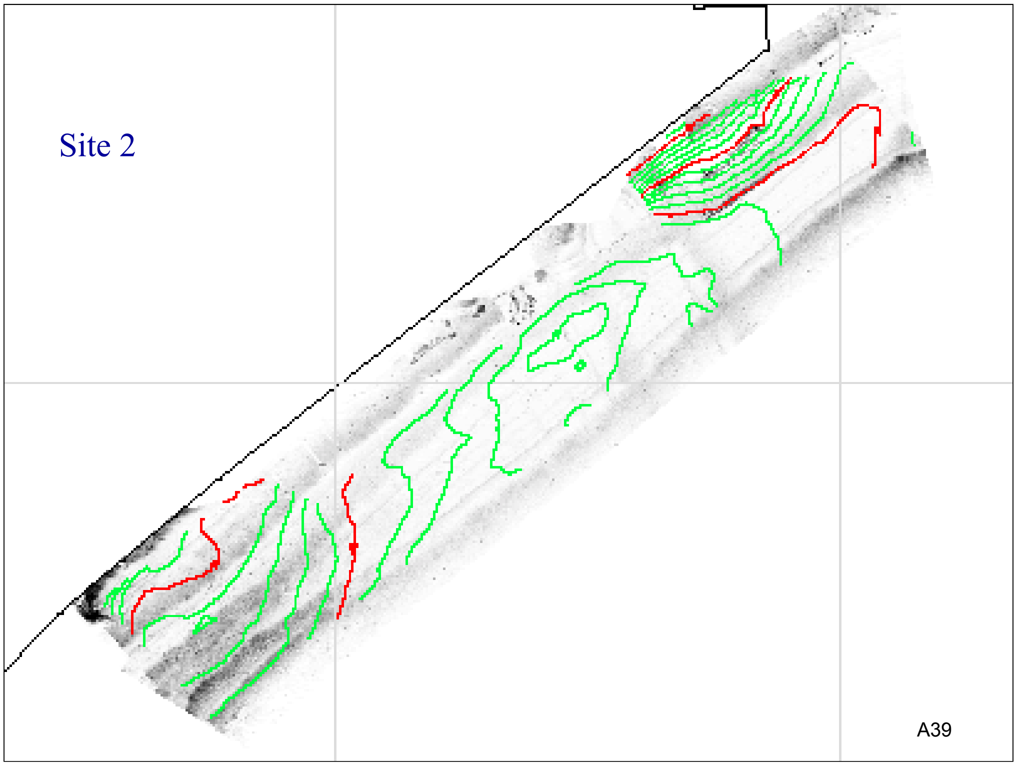

Site 1
A38


Site 2
A39


Site 1 – Typical Conditions
• Sandy, oxidized surface
• Gas voids
A40

Site 2
• Similar to Site 1in some areas
• More organic and more mobile surface layer in other areas

Site 2 – Disturbed area
- Oxidized
- Easily disturbed surface

Chemical Sampling

- Surficial sediments
  - ~40 surficial sediment samples will be collected from each site four (4) inch and up to six (6) inch thick at each grid point using a stainless steel Van Veen grab sampler or Petite Ponar grab sampler.
- Core sediments
  - 8 cores will be collected from each site to a depth of 3 ft
    - Samples collected from 0-6", 6"-12" and 12"-36"
  - Additional deeper cores will be used to assess underlying stratigraphy and provide geotechnical information for design
    - One water sample from underlying sand unit
  - Additional shallow cores (gravity corer) employed to supplement baseline sampling
- Water sampling
  - To define chemical baseline in water and potential for recontamination of caps

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Physical, Chemical, and Biological Parameters

Parameter	Surficial Sediment	Core Sediment Sample	Water Column/ Pore-water
PCBs	X	X	X
PAHs	X	X	X
8 RCRA Metal & Mercury	X	X	X
Total Organic Carbon	X	X	
Water Contents	X	X	
Total Kjeldahl Nitrogen	X	X	
pH			X
Total Suspended Solids			X
Salinity			X
DO			X
Conductivity			X
Benthic Macroinvertebrate	X		
SAV Survey	X		

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Analytical Methods

Analytical Parameter	Aqueous Methodology	Solid Methodology*
	Chemical	
PAHs	SW-846 5030B/8270C	SW-846 8270C
TCL Pesticides/PCBs	SW-846 5030B/8180A	SW-846 8180A
PCBs	SW-846 5030B/8082	SW-846 8082
8 RCRA Metals	7060A/7421/7740/7061/ 7131A/7191	7060A/7421/7740/7061/ 7131A/7191
Total Suspended Solids- (TSS)	EPA 160.2	Not Applicable
Total Kjeldahl Nitrogen	EPA 351.3	EPA 351 modified
Phosphorus	EPA 365	EPA 365 modified
Total Organic Carbon	EPA 415, SW-846 9060	EPA 415 modified
	Biological	
Benthic Macroinvertebrate		EPA/600/4-90/030
SAV Survey		General Acceptable Method

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Geotechnical Parameters

Parameter	Number of Sample	Method
Grain Size Distribution	10	ASTM D421/422
Specific Gravity	4	ASTM D854
Atterberg Limits	10	ASTM D4318
Classification	10	ASTM D2487
In-Situ Vane Shear Test (Shear Test)	20	ASTM D2573
Unconsolidated, Undrained Strength	4	ASTM D 2850
Permeability*	4	ASTM D 2434
Consolidation**	4	ASTM D2435 USACE VIII
Moisture Content	40	ASTM D2216
Bearing Capacity	Calculated	
Slope Stability	Calculated	

Note:

* One value of permeability must be calculated from the self-weight consolidation test.

** Use the Modified standard consolidation test and self-weight consolidation test as described in USACE 1987 (Department of Army Laboratory Soils Manual EM 1110-2-1906 - USACE 1970).

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Monitoring Cap Effectiveness

- Employ cores and dialysis samplers to define placement and cap effectiveness
  - Bottom of core – undisturbed sediment
  - Middle of core – cap/sediment interface
    - Examine interlayer mixing
    - Examine contaminant migration/fate processes
  - Top of core – cap/water interface
    - Examine recontamination
    - Examine recolonization
- Supplement with physical monitoring
  - Water column (flow, suspended sediment and chemical)
  - Non-invasive (sonar, bathymetry)
  - Invasive (sediment profiling camera)

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Summary

- Capping technologies undergoing bench-scale evaluation and testing
- Site characterization efforts currently underway
- Site 1 placement planned for summer 03
  - Aquablok
  - Zero valent iron/coke breeze
  - Apatite
- Additional information www.hsrc-ssw.org

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Fe(0) and Coke as "Active" Cap Media for PCB Destruction/Sequestration

Gregory V. Lowry
Kathleen M. Johnson
Paul J. Murphy
Meghan L. Smith

EPA-TIO Anacostia River Internet Seminar
March 12, 2003

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B1

Overview

- "Active" cap concept
- Potential "active" media
  - Fe(0)-based media for PCB dechlorination
  - Coke breeze to strongly sequester PCBs
- Simulated cap performance
- Media concerns
- Summary

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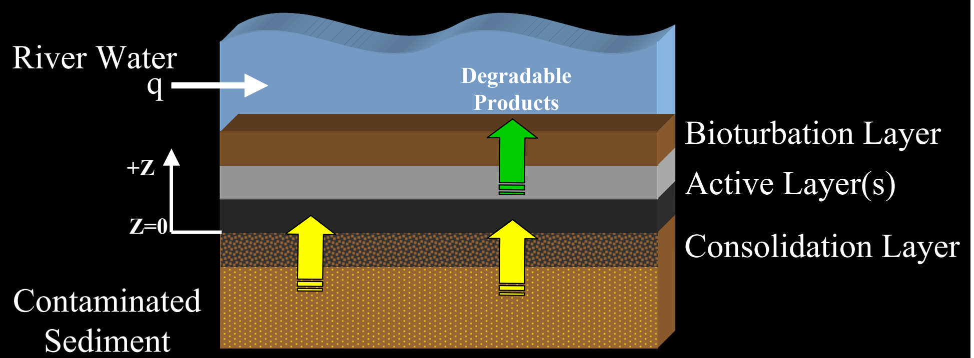
Conceptual Model



Criteria: No PCB flux through active layer after 100 years

$$\left(1+\frac{\rho_b \mathbf{K_d}}{n}\right)\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial z^2} - \mathbf{k}C$$

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Potential "Active" Media

- Study Goals
  - Evaluate suitability of Fe(0) and coke as 'active" media
    - Measure PCB destruction rates and partition coefficients
    - Determine cap composition and thickness
    - Estimate costs based on reactivity, lifetime, and materials costs

B4

Rationale for Fe(0)

- Fe(0)-based reactants are proven dechlorinators
  - Fe(0) dechlorinates halogenated hydrocarbons
    - e.g. TCE and other chlorinated solvents
    - Extensive use in PRBs
  - Pd/Fe(0) dechlorinates PCBs
    - Grittini et al. 1995, Wang et al. 1997
  - Nano-sized Fe(0) may dechlorinate PCBs
    - Wang et al. 1997
- Low levels of H_2 produced during Fe(0) corrosion
  - Potential to stimulate microbial dechlorination

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Approach Fe(0)

- Batch experiments monitoring PCB loss and product formation
  - Peerless Fe(0)
  - Pd/Fe(0)
  - Nano-size iron

- Individual PCB congeners
  - Structure/activity relationships

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Fe(0) Media

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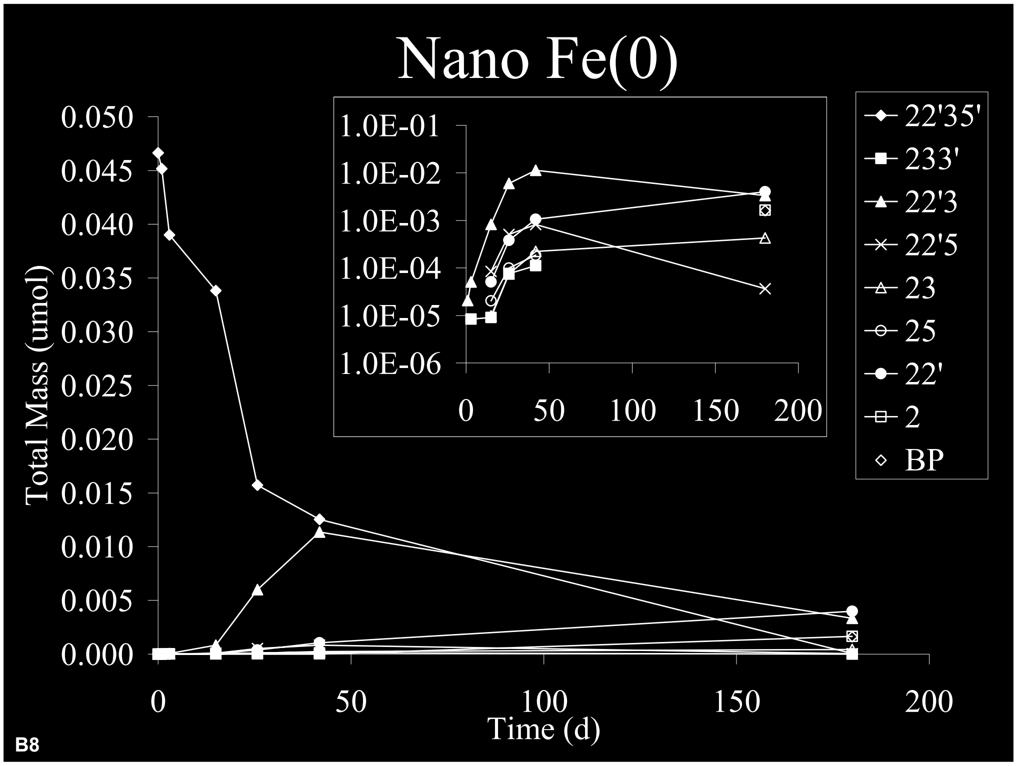
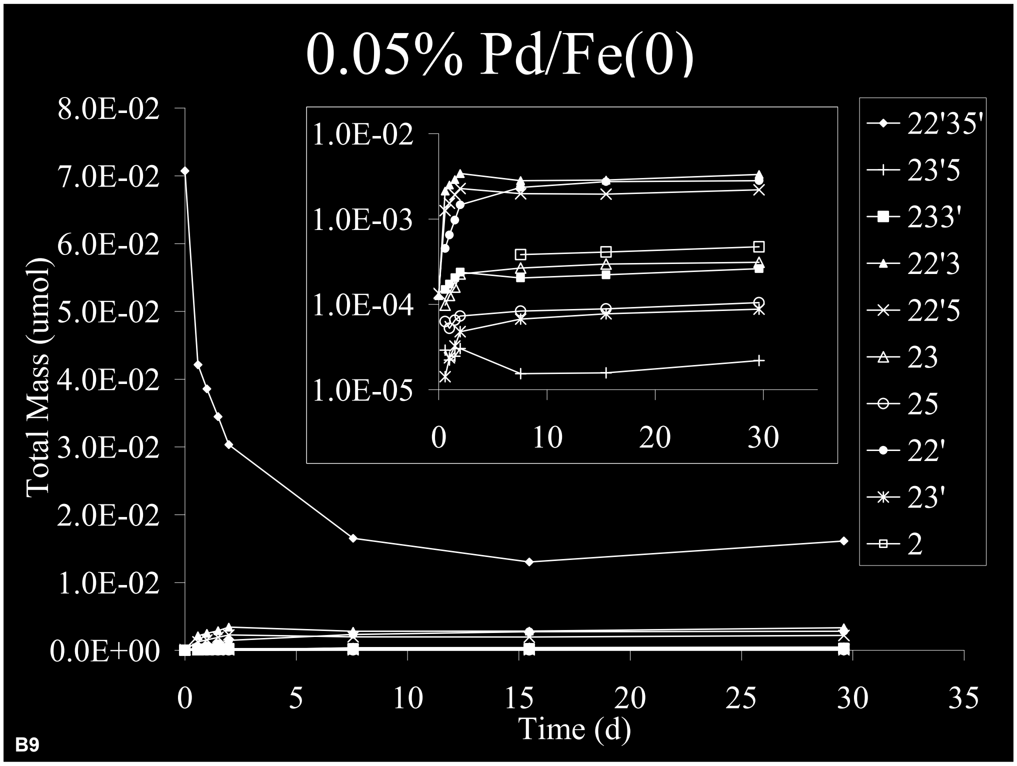

Nano Fe(0)
Total Mass (umol)
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
50
100
150
200
Time (d)
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
22'35'
233'
22'3
22'5
23
25
22'
2
BP
B8


0.05% Pd/Fe(0)
Total Mass (umol)
Time (d)
22'35'
23'5
233'
22'3
22'5
23
25
22'
23'
2
B9

Fe(0) Reactive Media Summary

MEDIA	RESULTS	k (yr^{-1})	RELATIVE COST
Commercial Fe(0)	No Observable Reaction	0	$$
Pd/Fe(0) (500 ppmw Pd)	Rapid dechlorination of 22'35' does not appear sustainable	21	$$$
Nano Fe(0)	Dechlorination of 22'35'-CB to 22'3-CB and other congeners	6	$$$$

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Rationale for Coke Breeze

- Inexpensive
  - ~$40/ton
- Environmentally Friendly
  - TCLP good
  - Likely to meet SQVs and CCC* standards
    *EPA 822-Z-99-001
- Sequestered PCBs less bioavailable
  - Talley et al. 2002

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Furnace Coke and Coke Breeze

B12

Properties: Coal vs. Coke

	COAL	COKE
Moisture (%)	4	2
Volatile Organics (%)	30	<u>0.7</u>
Fixed Carbon (%)	60	92
Ash (%)	6	7
Porosity (%)		<u>45-50</u>
Size (mm)		<20
Particle Density (g/cm^3)		1.9-2.0

Sorptive Media

- Coke
  - Strong PCB sorption (K_d)
  - Less bioavailable (Talley et al. 2002)

Sediment (low) | Fly Ash | Sediment (high) | COKE | Activated Carbon

180 | 14,000[b] | 1.9E+6 | 5.6E+9[b]

K_d (L/kg)

SORPTION STRENGTH →

[b] Jonker et al. 2002

Modeling Diffusive Transport of Biphenyl

$$\left(1+\frac{\rho_b \mathbf{K_d}}{n}\right)\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial z^2}$$

CAP MEDIA	n (--)	K_d (L/kg)	R
Sand [a]	0.35	10	52
Peerless Fe(0) [b]	0.5	200	800
Coke	0.6	60,000	72,000

[a] f_{oc} = 0.001, [b] f_{oc} = 0.02,
$K_d = K_{oc} * f_{oc}$, log K_{oc} =4 (biphenyl)
D_e=1.9 E-5 cm^2/s for all cases. This incorporates diurnal seepage of ±5 cm/d due to tides.

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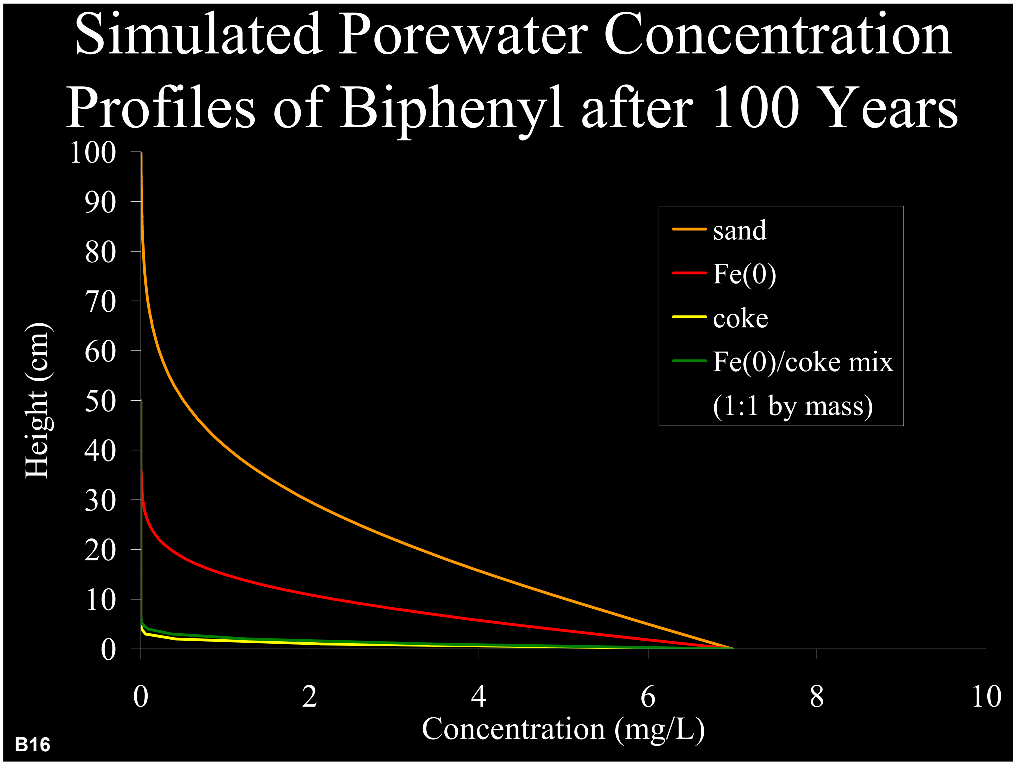
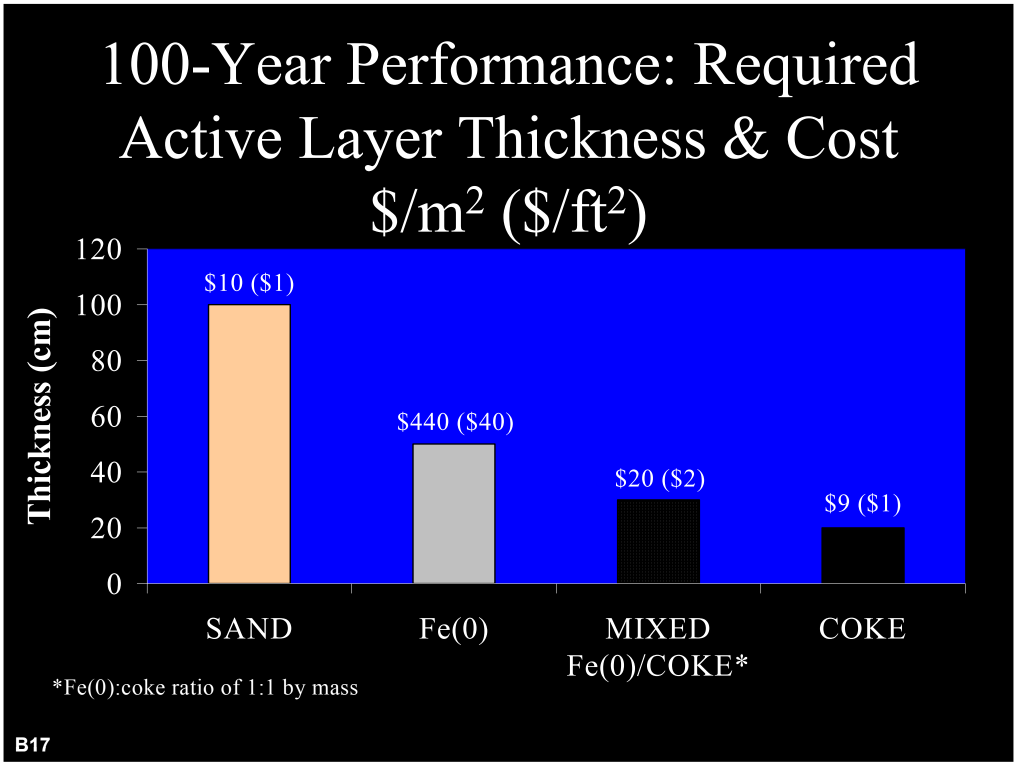


Simulated Porewater Concentration Profiles of Biphenyl after 100 Years
Height (cm)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
Concentration (mg/L)
sand
Fe(0)
coke
Fe(0)/coke mix (1:1 by mass)
B16


100-Year Performance: Required Active Layer Thickness & Cost $/m² ($/ft²)
Thickness (cm)
120
100
80
60
40
20
0
$10 ($1)
$440 ($40)
$20 ($2)
$9 ($1)
SAND
Fe(0)
MIXED Fe(0)/COKE*
COKE
*Fe(0):coke ratio of 1:1 by mass
B17

Media Concerns

- Toxicity
  - Fe(0)
    - Peerless Fe(0) contains heavy metals (% range)
    - Metals should remain sequestered (not demonstrated)
  - Coke
    - Little or no concern
    - TCLP test OK
    - CCC should be met (under investigation)
    - SQVs should be met (under investigation)

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Coke: TCLP and CCC Criteria

Metal	Coke (mg/kg)	Leachate (mg/L)	TCLP Limit (mg/L)	CCC Limit (mg/L)
Arsenic	<10	<0.1	5.0	0.15
Barium	22	0.5	100	N/A
Cadmium	<10	<0.1	1	**0.0043**
Chromium	<10	<0.1	5	0.59
Lead	<10	<0.1	5	**0.065**
Selenium	<10	<0.1	1	N/A
Mercury	<0.033	<0.0002	0.2	0.0014
Silver	<10	<0.1	5	**0.0034**

TCLP=Toxic Characteristics Leaching Procedure
CCC=Criterion Continuous Concentration

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Active Capping Summary

- Coke
  - Inexpensive and promising PCB sequestration media
  - Thinnest caps possible
  - Provides NO PCB dechlorination
- Fe(0)
  - Cost-effective abiotic PCB destruction NOT currently possible
  - Fe(0)-enhanced biodegradation possible, but not yet explored
- Mixed Fe(0)/coke cap
  - Provides sequestration
  - PCB dechlorination *possible* but not proven

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Ongoing Research

- PCB sorption isotherms for coke breeze
- Fe(0)-sediment-coke microcosms to assess potential for enhanced PCB biodegradation
- Column studies to assess long term performance of each media
- Methods for Evaluating Cap Performance

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