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

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Civil and Environmental Engineering

Technology Benchmarking Workshop
for Sediment and Floodplain Remediation
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Outline

- Technology Description
- Development and Application
- Observations/lessons learned
- Future Directions

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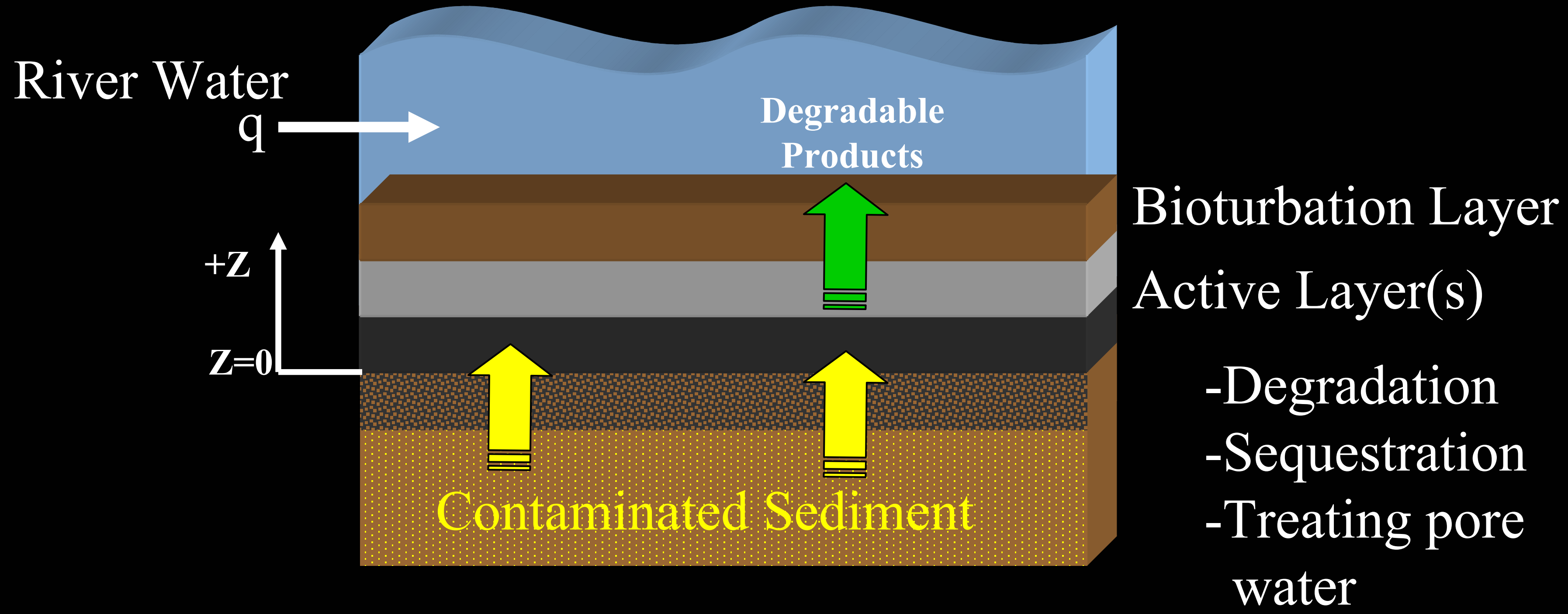
Concept



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

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Proposed Placement Method

Anacostia River Sediment Profile

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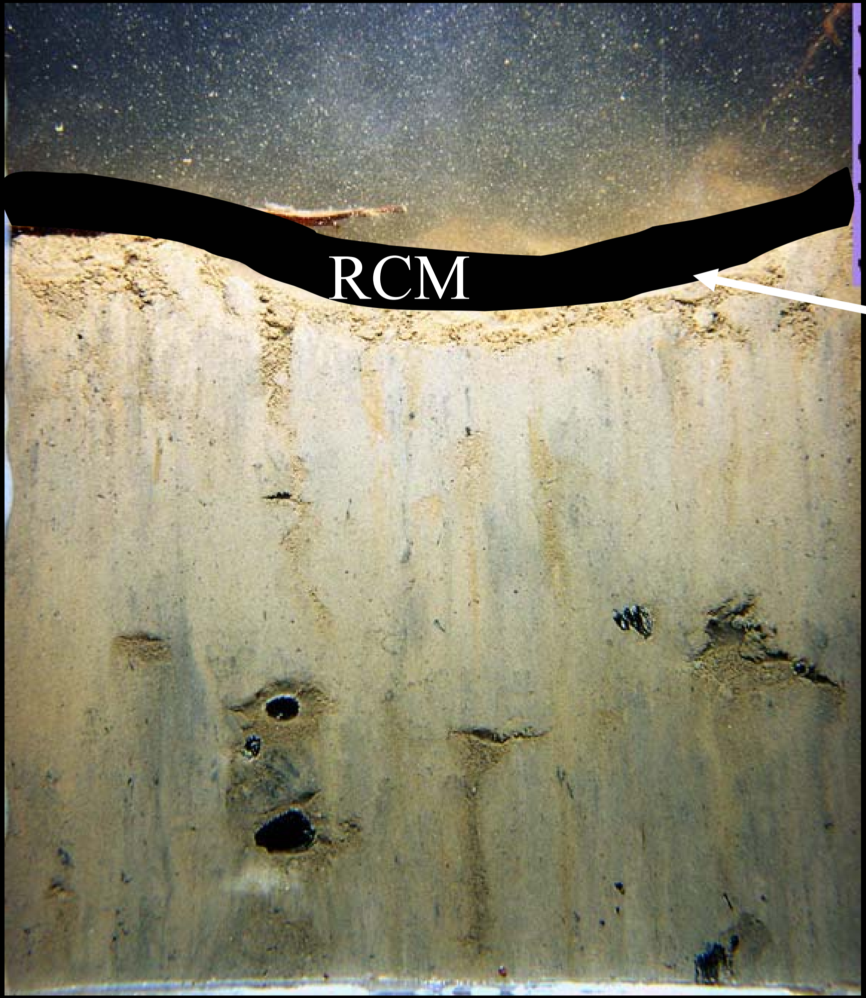
Proposed Placement Method

RCM=Reactive Core Mat



RCM unrolled and placed by divers

Anacostia River Sediment Profile

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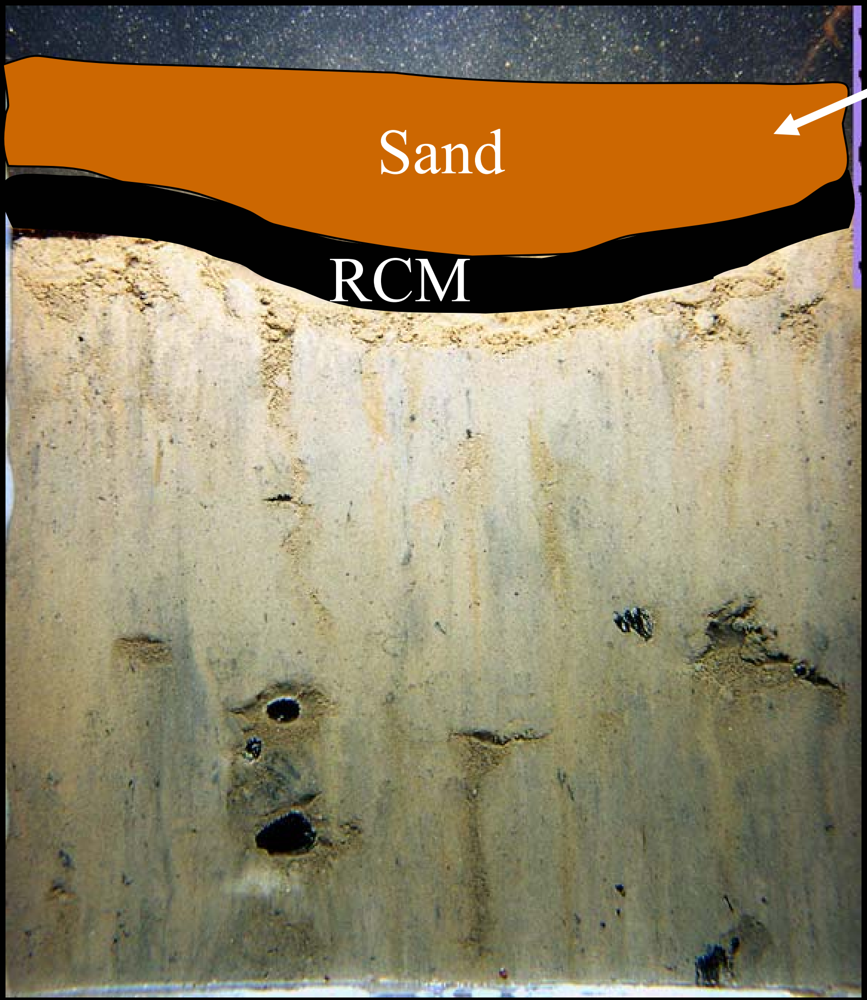

15-25 cm clean sand placed over RCM

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

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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

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Identifying Suitable Sorbents

- Treatability Study Goals
  - Determine reactivity of PCBs with Fe^0
  - Compare performance of different sorbents
  - Provide design criteria for demonstration

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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

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Approach: Fe^0

- 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

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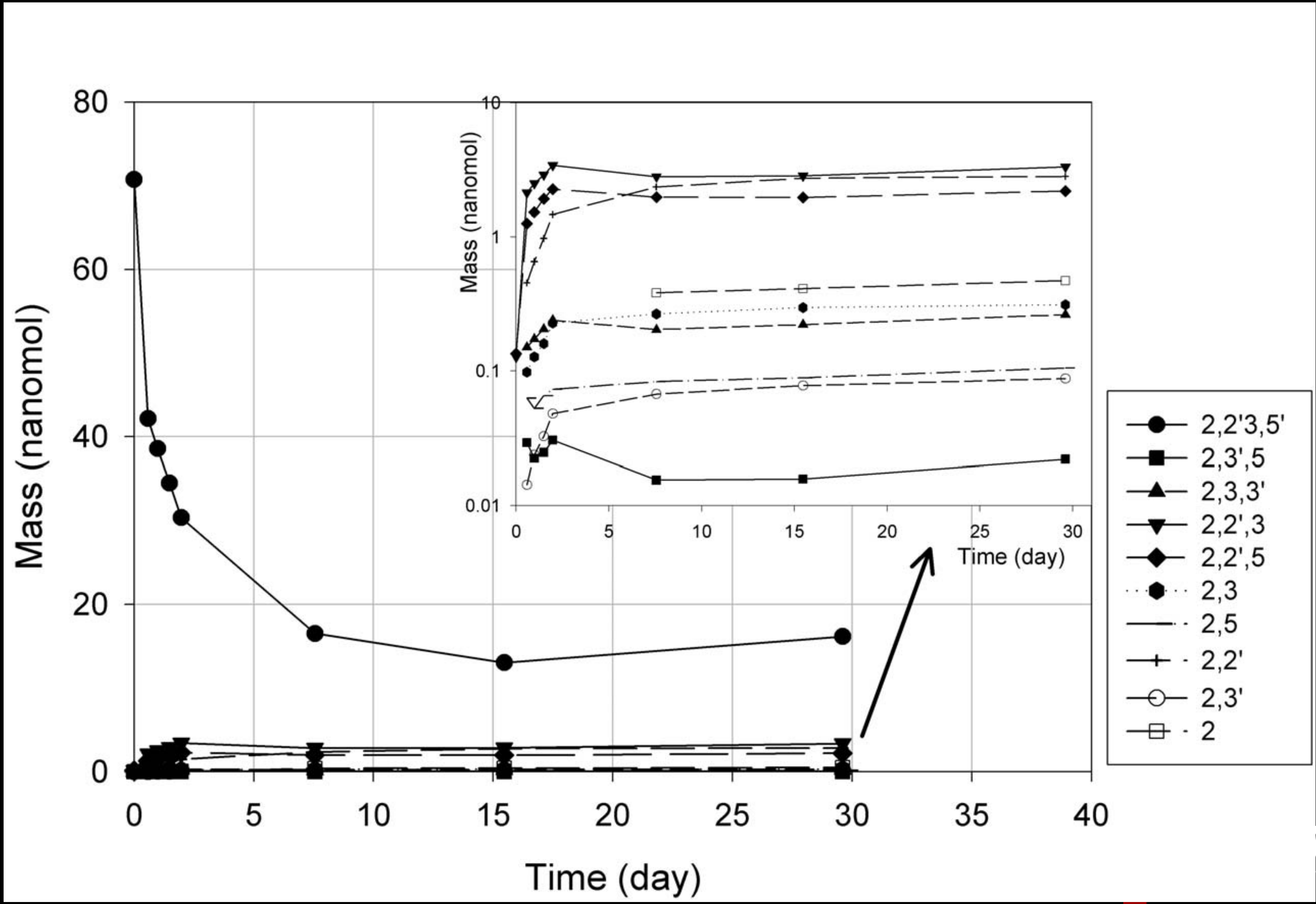
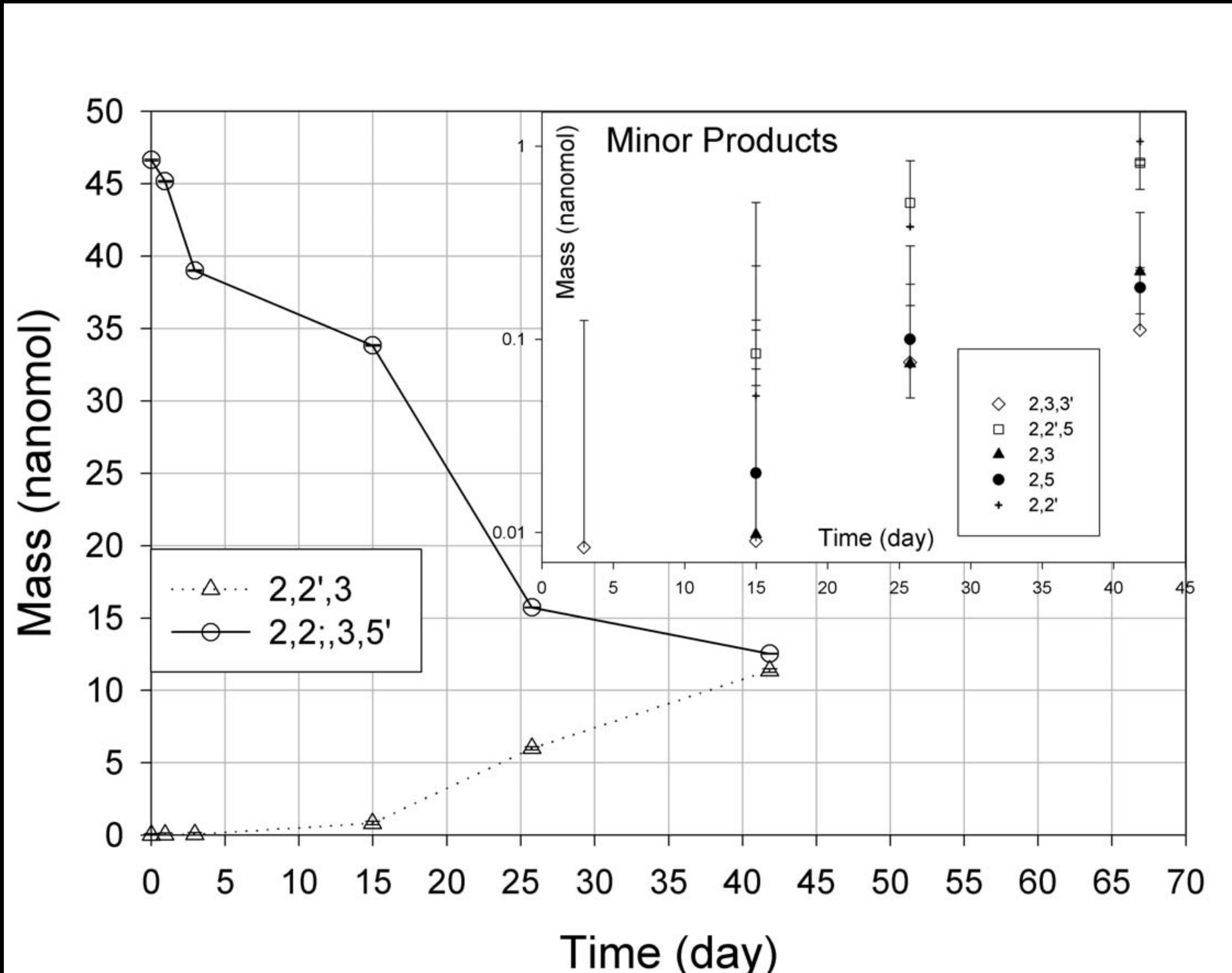
Pd/Fe^0-0.05%   k~21 yr^{-1}



2,2',3,5'-Nano Fe^0



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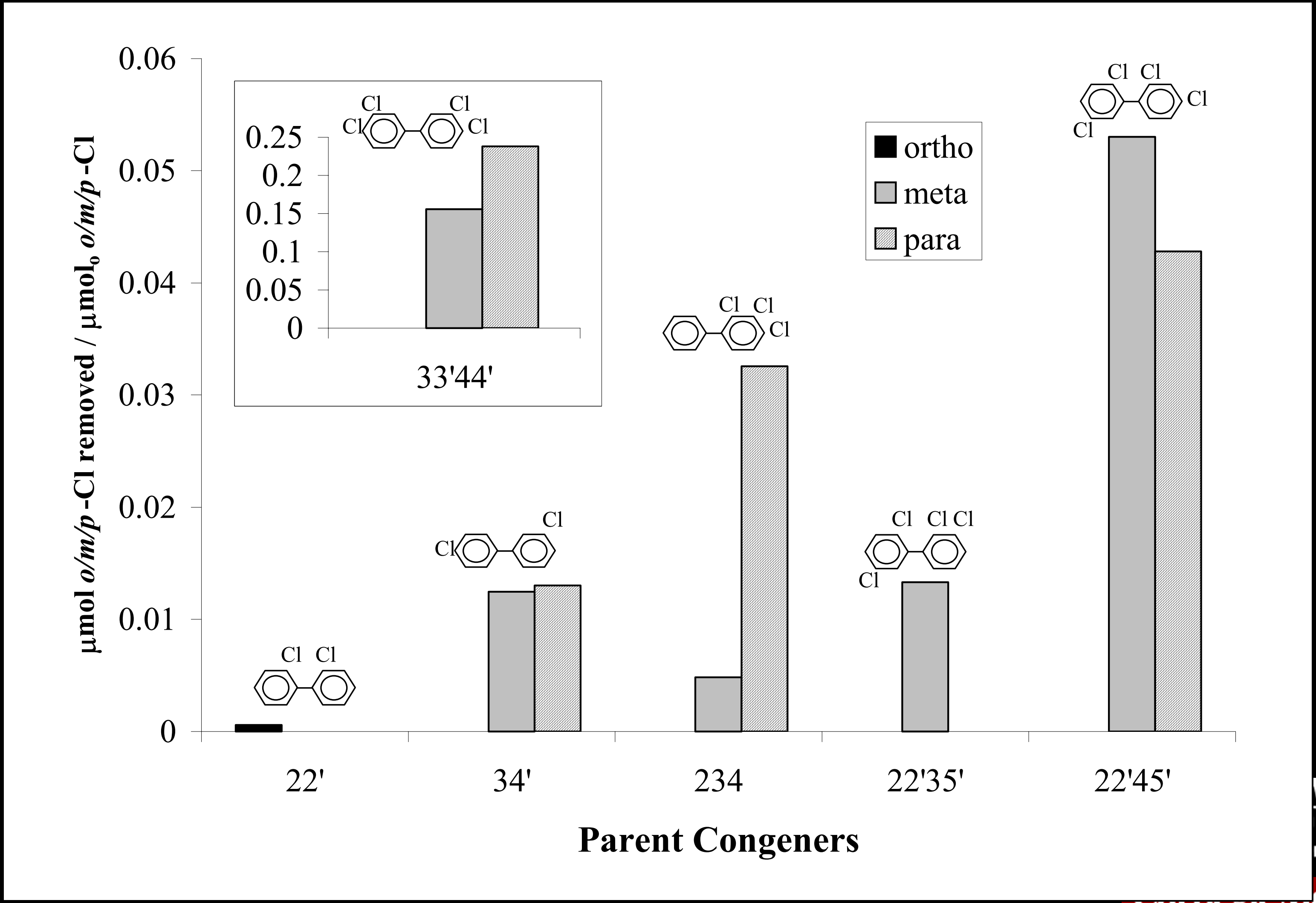
PCB Dechlorination Patterns



Fe^0 Reactivity Summary

MEDIA	RESULTS	k (yr^{-1})
Commercial Fe(0)	No Observable Reaction (6 months)	0
Pd/Fe(0) (500 ppmw Pd)	Rapid dechlorination not sustainable	21
Nano Fe(0)	Dechlorination rates variable Meta and Para chlorine dechlorination favored	**0.01-6**

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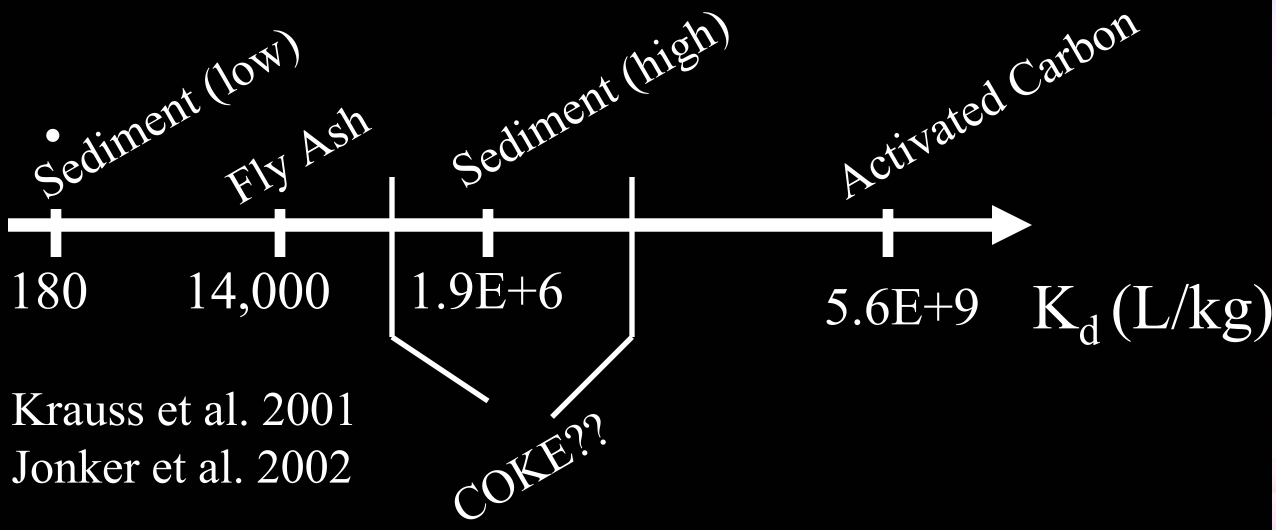
Approach: Sorbents



Krauss et al. 2001
Jonker et al. 2002

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

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Properties of Sorbents

	Sand	Soil	Coke	AC
Carbon (%)	~0	3.8%	92	90
Porosity (eff)	0.29	0.47	0.48	0.53
Size (mm)	~0.3	0.4-2.0	0.4-2.0	0.3-2.0
Particle Density (g/cm^3)	2.5	2.0	1.5	1.4
BET SA (m^2/g)	<1	6.6	2-12	919
R (retardation)	6×10^2	1.6×10^5	2.3×10^5	1.8×10^7

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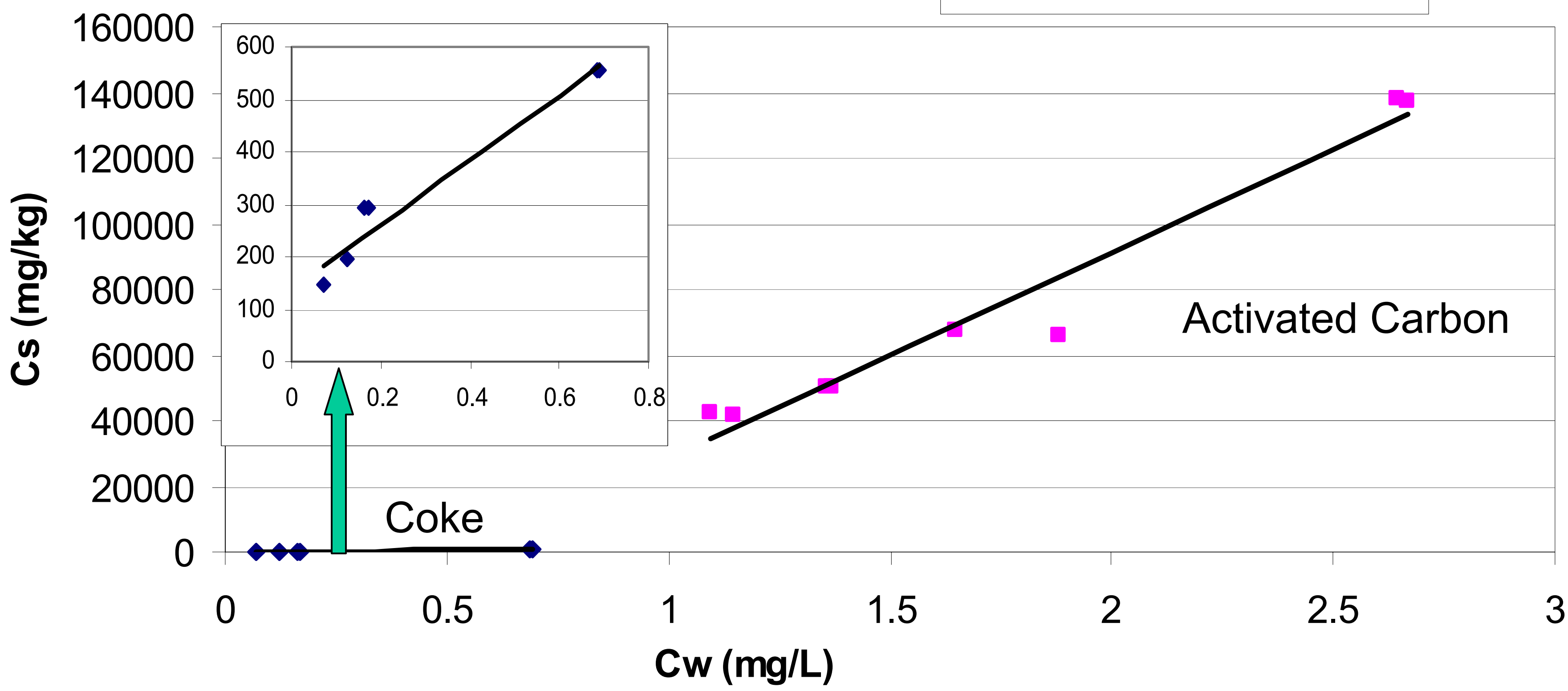
Isotherms with 1,2 Dichlorobenzene



Sorbent	K_d (L/kg)	Log K_d (L/kg)	R^2
Activated Carbon	62950	4.80	0.959
Coke	616	2.79	0.955
Anacostia Sediment	375	2.57	0.981
Farm Soil	308	2.49	0.945

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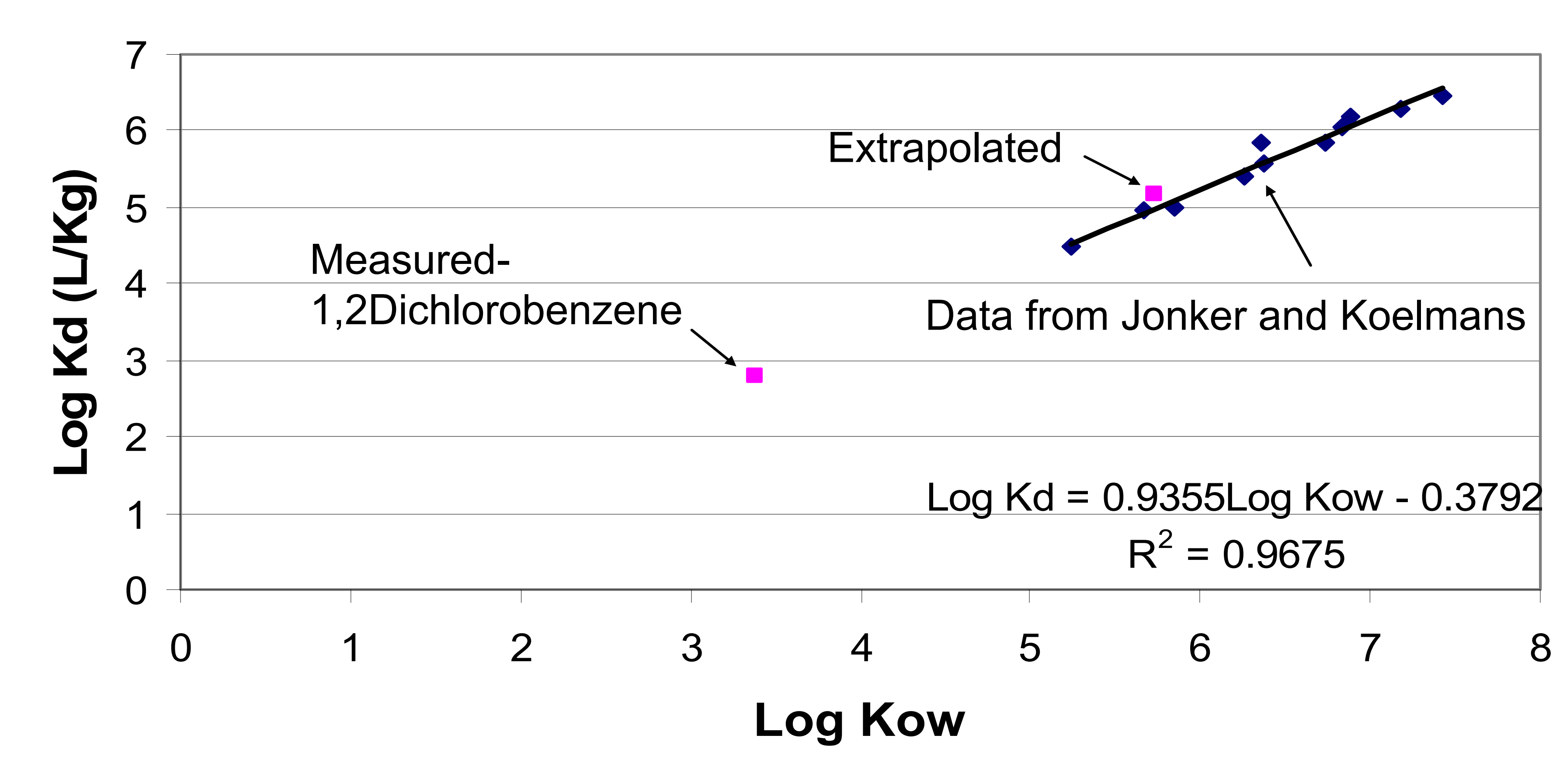

	Extrapolated from 1,2 DCB	Jonker and Koelmans
Coke	5.15	5.02
Activated Carbon	7.8	8.55

Jonker and Koelmans. Environ. Sci. Technol. 2002, 36, 3725-3734

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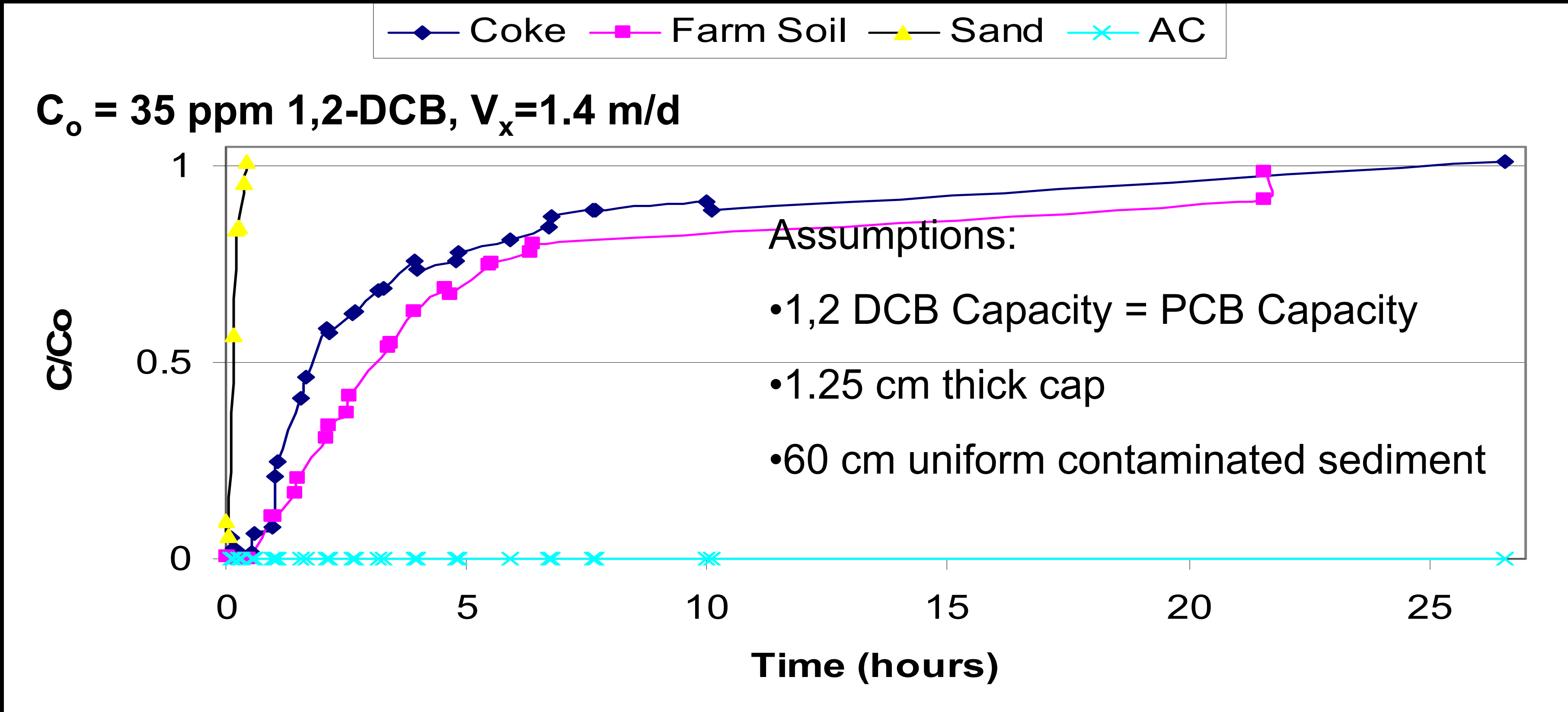
Sorbent Performance and Capacity



Material	1,2 DCB Capacity (mg DCB /g sorbent)
Coke	0.6
Activated Carbon	250.8
Farm Soil	0.7
Sand	Neglible

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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. ERL[1]) and WQ standards (e.g. CMC[2])

1 Effects Range Low (NOAA)
2 Criterion Maximum Concentration (EPA)

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Heavy Metals in Solid Coke

Metal	Rept. Limit (mg/kg)	Conc. (mg/kg)	ERL[2] (mg/kg)
Mercury	0.033	0.034	0.15
Aluminum	20	**466**	NA
Arsenic	1	1.7	8.2
Barium	5	11.4	NA
Chromium	1	1.5	81
Copper	2.5	**20.2**	34
Iron	10	2500	NA
Lead	0.3	0.74	46.7
Manganese	1.5	10.1	NA
Selenium	0.5	0.56	NA
Zinc	2	5.8	150

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PAHs in Solid Coke

PAH	Result (µg/kg)	ERL (µg/kg)
Anthracene	31	85.3
Benzo (a) anthracene	81	261
Benzo (a) pyrene	83	430
Benzo (b) fluoranthene	70	N/A
Benzo (ghi) pyrene	68	N/A
Benzo (k) fluoranthene	68	N/A
Chrysene	110	384
Dibenz (a,h) anthracene	32	63.4
Fluoranthene	110	600
Indeno (1,2,3-cd) pyrene	42	N/A
Naphthalene	48	160
Phenanthrene	**120**	**240**
Pyrene	100	665

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Metals Detected in Leachate

Metal	Leachate DI (μg/L)	Leachate PW (μg/L)	Anacostia Porewater (μg/L)	Rept. Limit (μg/L)
B	228	279	249	200
Ba	53.7	58.4	76.1	6
Fe	419	368	481	40
Se	**7.6**	**10.6**	**ND**	**5**

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PAHs in Leachate

PAH	Leachate (DI)	Leachate (PW)	Reporting Limit	CMC
	μg/L	μg/L	μg/L	μg/L
Benzo(a)anthracene	**1.4**	ND	10	300
Benzo(a)pyrene	**1.6**	ND	10	300
Chrysene	**1.9**	ND	10	300
Fluoranthene	**1.7**	ND	10	3980
Phenanthrene	**3.2**	**1.2**	10	30
Pyrene	**2**	ND	10	300

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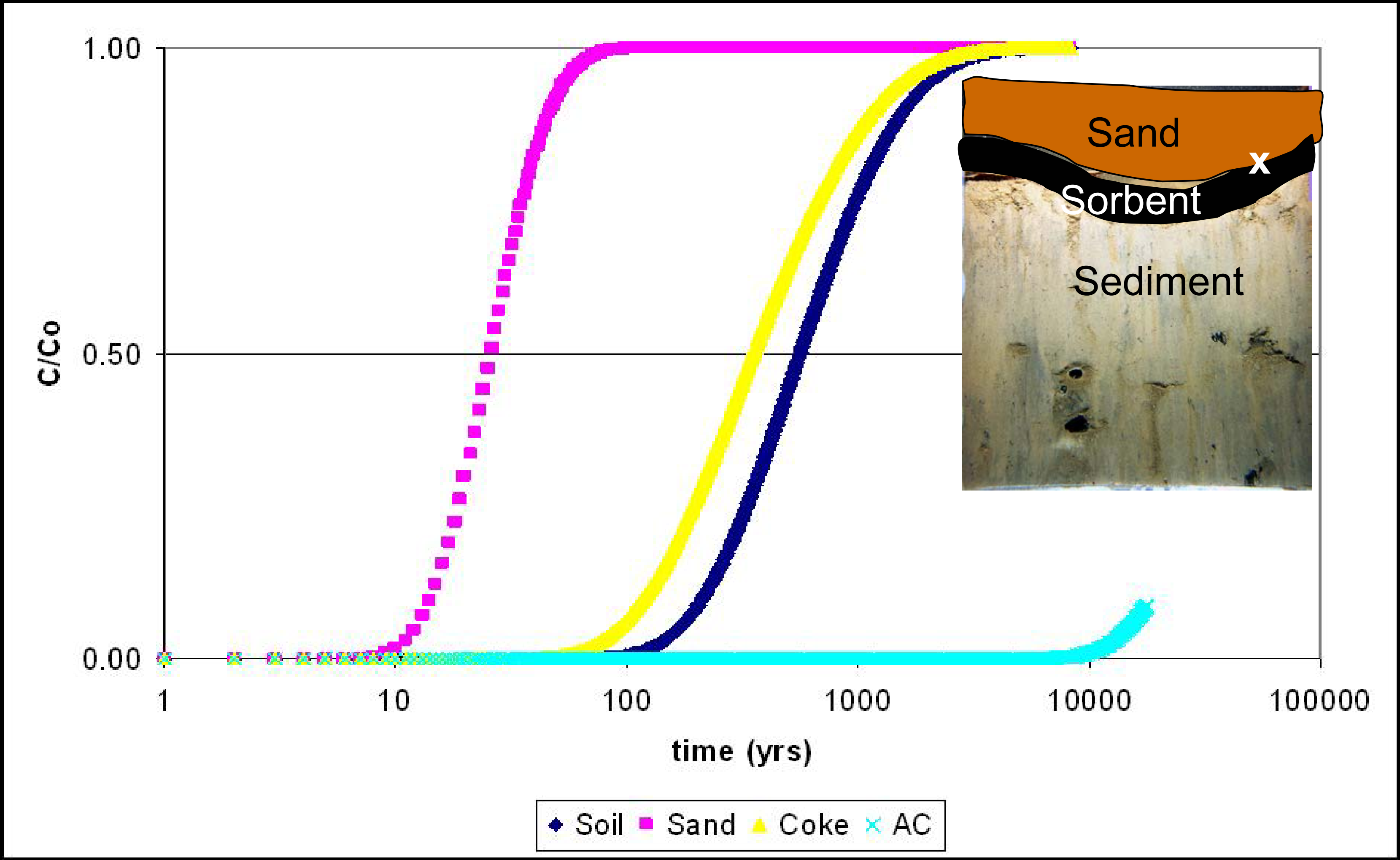
Predicting Performance in the Anacostia River

Depth	5.6 m
Flow rate	260 m^3/min
$U_{z\ (seepage)}$	-2-6 cm/d
k (assumed)	0 yr^{-1}
RCM	1.25cm

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

Sorbent Performance (v=1 cm/d)



Assumes capacity not exceeded and no attenuation

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Cap Placement and Concerns

- Methods of placement
  - Particle Broadcasting
  - Reactive Core Mat (RCM)

Particle Broadcasting

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Potential Problems with Particle Broadcasting for Sorbents

- Difficult to place thin layers
- Variable settling velocities
- Floating material
- Fines

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Release of Fines From Coke

1.6 kg Coke
~ 6 L Water

Release of fines during placement could be an issue!

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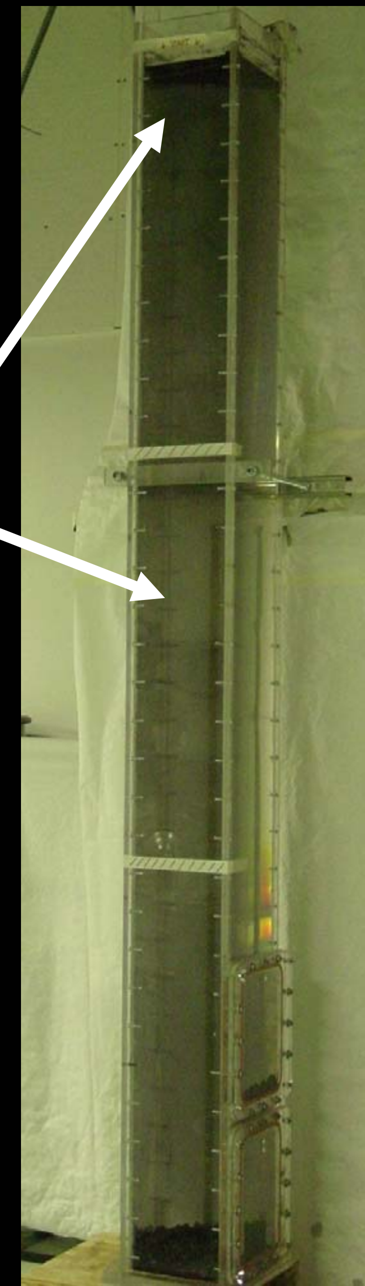
Coke Settling

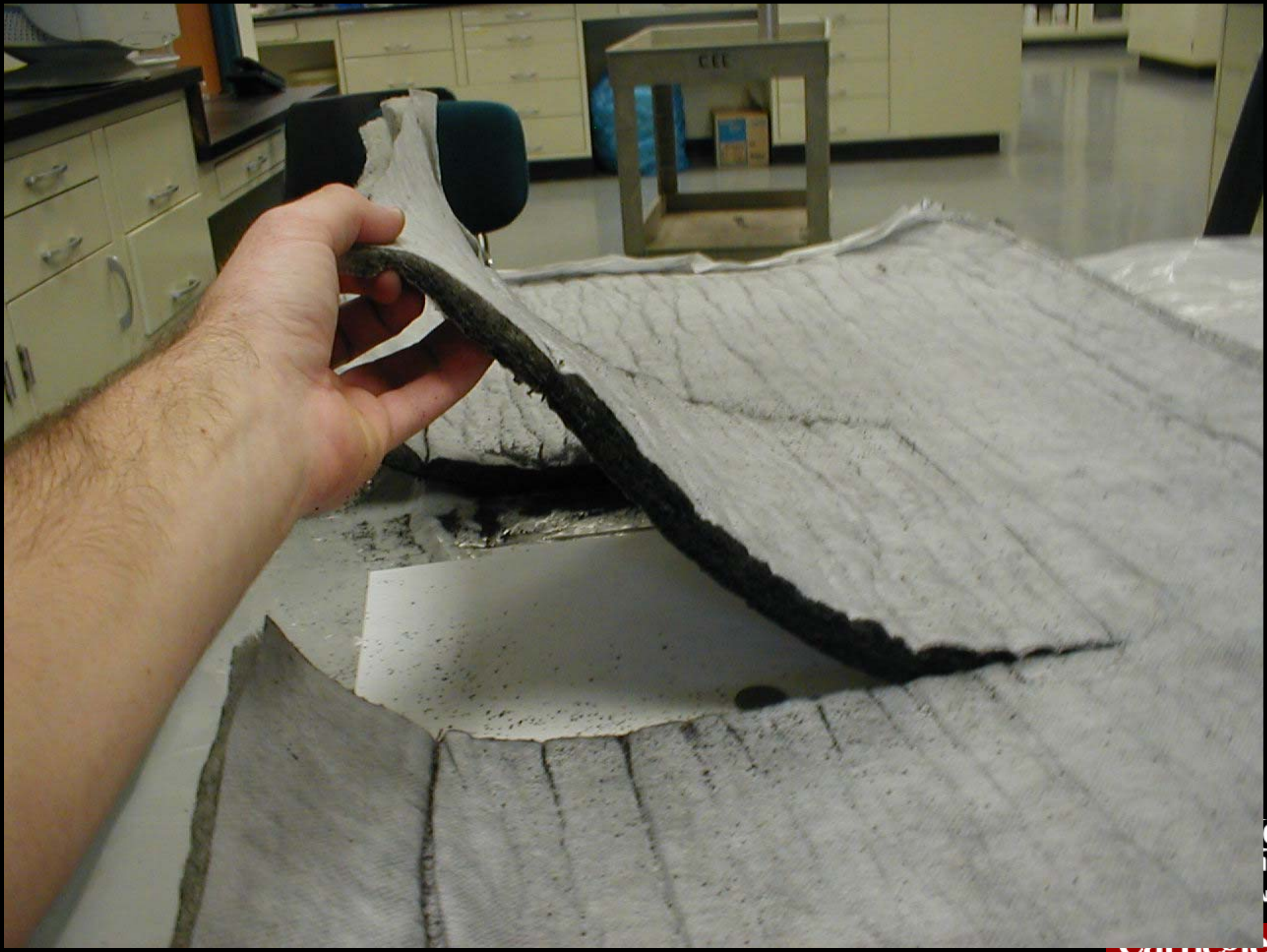
V_s~12-24 cm/s

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



Uneven distribution

Reactive Core Mat (RCM)



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Reactive Core Mat II

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Mat Properties and Costs

- Thickness
  - ~0.5 in. (1.25cm)
- Loading
  - ~0.8-1.0 lb/ft^2 (3.4 kg/m^2)
- 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 <u>($11,100)</u> ($1.11/ft^2)

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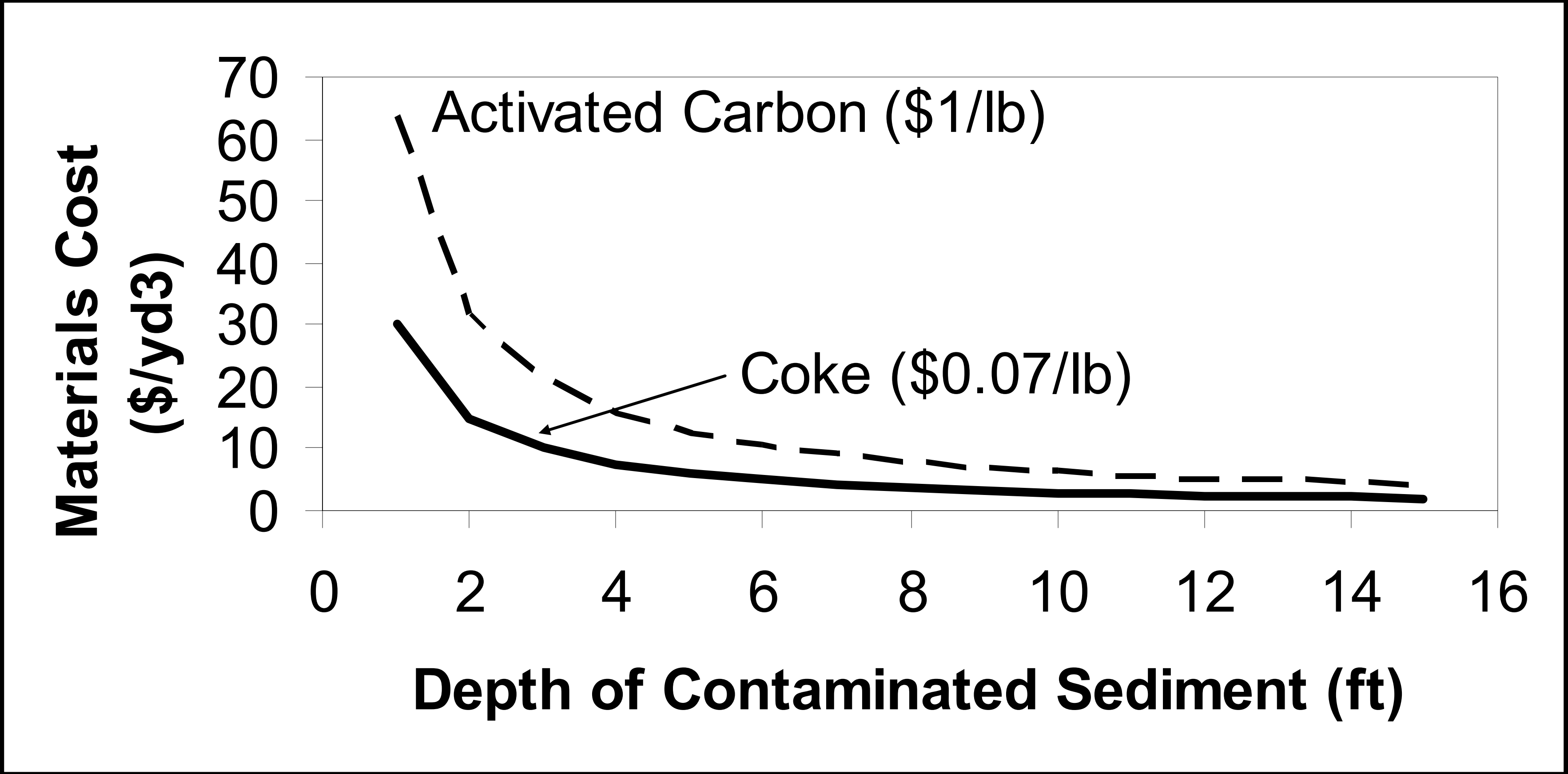
Comparative Materials Costs



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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

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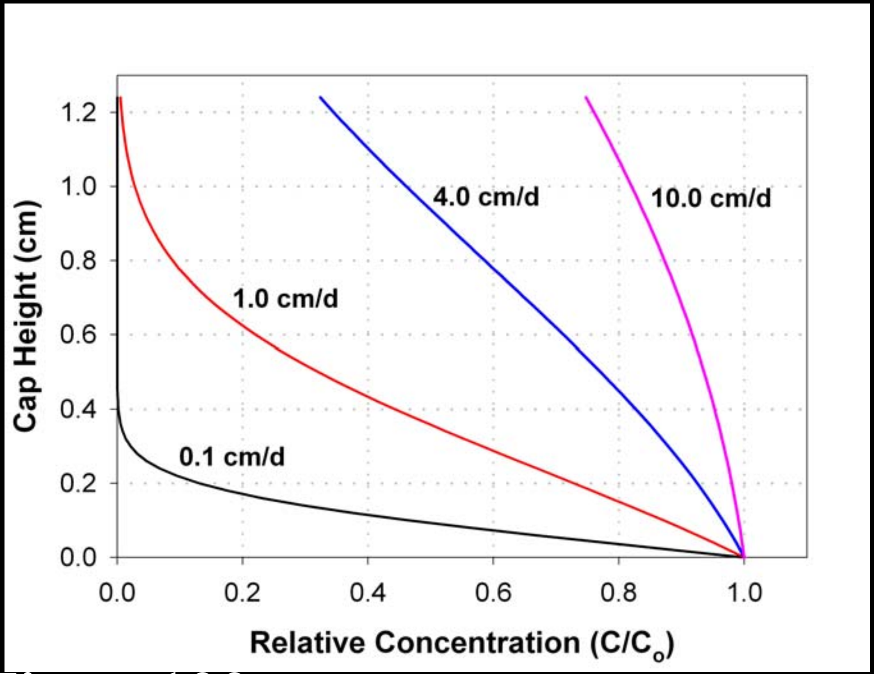
Favorable Site Characteristics



Time=100 yrs

Parameters (coke)		
Effective Porosity	0.48	
Bulk Density	0.78	g/cm^3
Dispersivity	0.5	cm/sec
Log K_d	5.15	L/kg

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

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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

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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
  - Fe^0 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

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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?

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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

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Questions/Comments?

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