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Sediment Cap and In-Situ Treatment Performance Modeling of PCBs at Manistique Harbor

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Outline

- Introduction to site and conditions
- Sorption Study Results
  - Evaluation of amended capping and in-situ treatment for input into design of a demonstration
- Remedy Design Considerations
  - What do the sorption characteristics tell us about the performance of in-situ treatment and various cap configurations?
- Conclusions

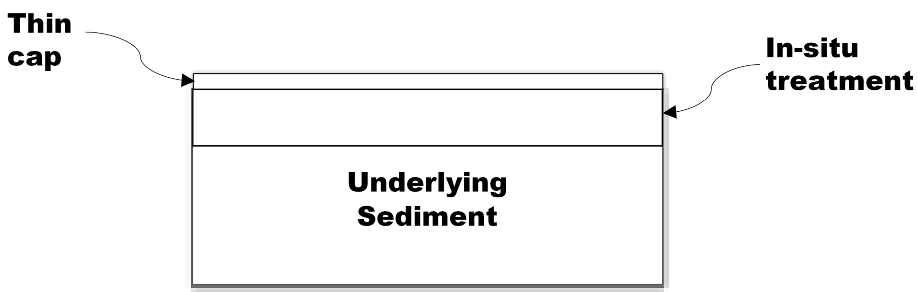
Contaminated Sediment Sites

- EPA notes 66 Superfund Sites with “Substantial Sediment Contamination”
  - Remedy includes removal of 10,000+ cubic yards of sediment or capping/MNR of 5+ acres
- Common Remediation Techniques
  - Monitored Natural Recovery
  - In-situ containment (Capping)
  - In-situ treatment
  - Removal (Dredging) and subsequent containment or removal

- southern shore of Michigan’s Upper Peninsula

In-situ Sediment Treatment

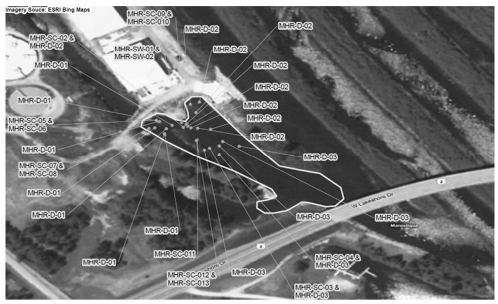
- Reduction of Risk and Exposure by Capping and In-Situ Treatment
  - Stabilization of sediments
  - Isolation from benthic community
  - Reduction of flux to surface



- southern shore of Michigan’s Upper Peninsula

Introduction to Site

- Manistique Harbor and River Superfund site located in Manistique, Michigan.
- Drains into Lake Michigan.
- Listed as a Great Lakes Area of Concern.



- southern shore of Michigan’s Upper Peninsula

Introduction to Site

- Contaminated due to historical industrial and paper milling operations.
- Contaminant of Concern: Polychlorinated Biphenyls (PCBs)
- US EPA started dredging operations in 1995.
- Additional remediation in the form of active caps or in-situ treatment is being evaluated.
- Expected to hold demonstration of suggested remedies.

- PCBs are toxins that are carcinogenic in nature and can bioaccumulate across the food web and ecosystem.

Sorption Study

- Calgon granular activated carbon and CETCO organoclay PM-199 used as sorbents.
- Batch isotherm tests done using site porewater as well as laboratory water.
- PCB congeners chosen
  - exhibited a range of hydrophobicities and planarities
  - included tri-chloro to penta-chloro PCBs

Activated Carbon Sorption

$$q_e = K_f C_w{}^{1/n}$$

- Freundlich model used with the following linearization:

$$\log(q_e) = \log(K_f) + (1/n).\log(C_w)$$

Where;

- q_e is the mass of the PCB sorbed per mass of GAC (μg/kg)
- C_w is the concentration of the PCBs dissolved in water (μg/L)
- K_f is the Freundlich constant with units of mass contaminant times $(\text{volume})^{1/n}$ per mass sorbent times $(\text{mass contaminant})^{1/n}$ i.e. $(\mu g/kg)(L/\mu g)^{1/n}$
- 1/n is a dimensionless constant.

Activated Carbon Sorption

PCB	Chlorine Atoms	Planarity	Site Water		Lab Water	
			log K_F $(\mu g/kg)(L/\mu g)^{1/n}$	1/n	log K_F $(\mu g/kg)(L/\mu g)^{1/n}$	1/n
18	3	Non Planar	6.953	0.556	7.324	0.514
52	4	Non Planar	6.230	0.306	6.913	0.416
77	4	Non-Ortho Planar	6.453	0.298	7.817	0.666
101	5	Non Planar	6.204	0.399	6.886	0.478
118	5	Mono-Ortho Planar	6.286	0.374	7.265	0.542

- Effective sorption increases with increase in molecular weight.
- Planar PCBs more strongly sorbing than non-planar PCBs as seen by other studies (Jonker & Koelmans, 2002).

Organoclay PM-199 Sorption

- The following linear model was used to obtain organoclay isotherms:

$$q_e = K_d C_w$$

Where;

- q_e is the mass of the PCB sorbed per mass of organoclay(μg/kg)
- C_w is the concentration of the PCBs dissolved in water (μg/L)
- K_d is a linear constant with units of volume per mass of sorbent (L/kg)

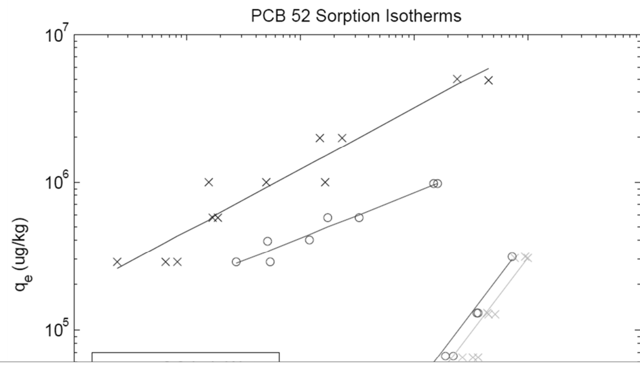
Organoclay PM-199 Sorption

PCB	Chlorine Atoms	Planarity	Site Water K_d (L/kg)	Lab Water K_d (L/kg)
18	3	Non Planar	2.09E+05	1.56E+05
52	4	Non Planar	4.02E+05	3.00E+05
77	4	Non-Ortho Planar	4.66E+06	5.14E+06
101	5	Non Planar	1.21E+06	1.12E+06
118	5	Mono-Ortho Planar	1.05E+06	1.36E+06

- Effective sorption coefficients less than those for activated carbon
  - Linear and not influenced by competitive adsorption or fouling with natural organic matter
- Similar trends of increase with increase in molecular weight of PCBs and planar PCBs showing greater sorptive capacity.

Behavior we have seen before many times! OC linear and not site specific, in generaL

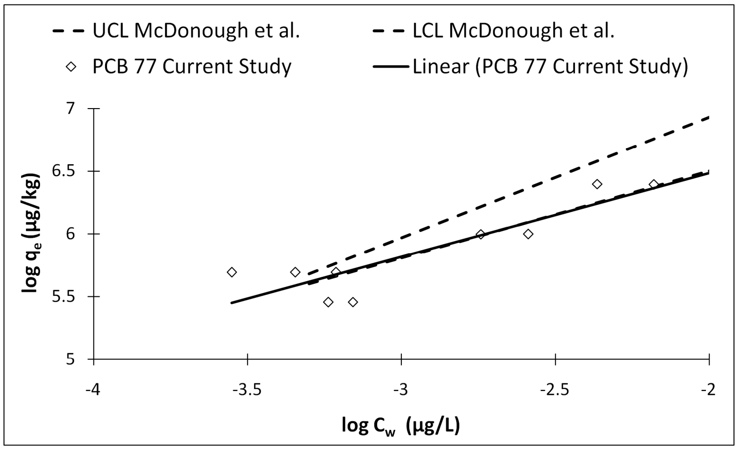
Competitive Adsorption due to NOM



- Site porewater 3 to 10 times less sorbing than laboratory water for AC.
- K_d about the same order of magnitude as K_{ow} for OC.

- As per Hawker and Connell

Comparison with McDonough et al. study (2008)



- PCB 18, 52 and 77 all comparable to McDonough,Fairey and Lowry, 2008 data.

Study showed similar findings for stronger sorption of planar PCBs.

Sorption coefficients similar to current study.

Design Parameters

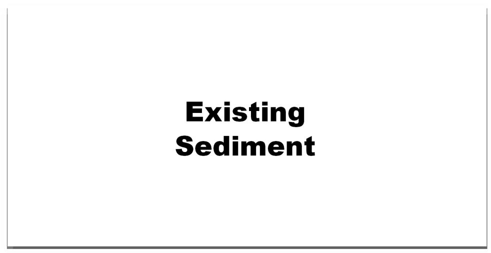
- Modeling carried out for non-planar PCBs using Capsim 2.6.
- Sorption characteristics combined with field conditions.
- 1cm/yr and 1cm/day groundwater upwelling flow rates.

Common Parameters	
Bioturbation depth	10cm
Particle biodiffusion coefficient	1.0 cm^2/yr
Pore water biodiffusion coefficient	100 cm^2/yr
Bottom boundary condition	Constant Flux

- Modeling carried out using Capsim 2.6, a fate and transport modeling software developed at University of Texas at Austin.
- Two extreme flow rates

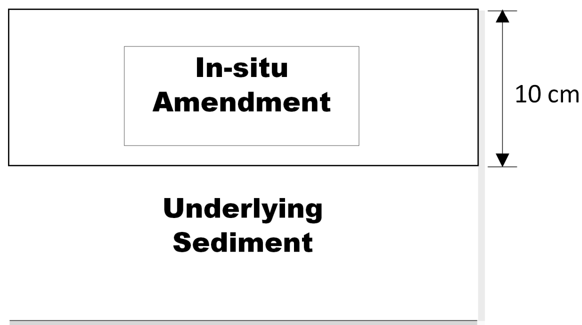
Design Scenarios

- Total 5 scenarios modeled
- Existing condition (no remedy)



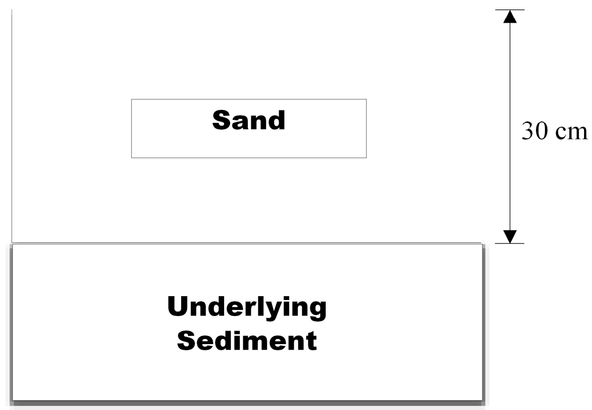
Design Scenarios

- In-situ sediment amendment (AC and OC)
- Sorbent loading equivalent to commercial reactive core mat:
  - 0.4 lb/ft^2 of AC
  - 0.8 lb/ft^2 of organoclay



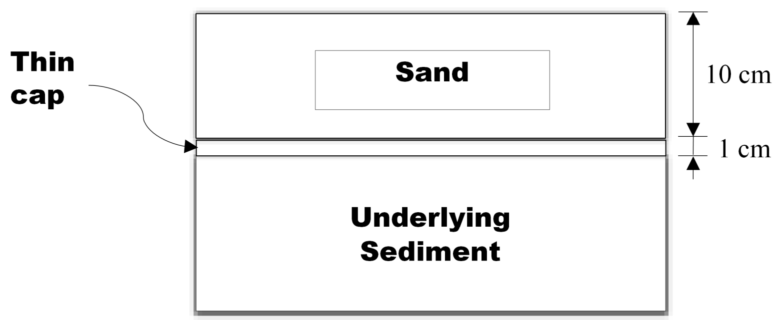
Design Scenarios

- 30 cm sand cap



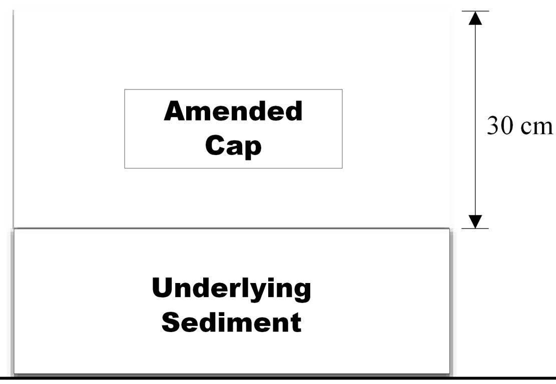
Design Scenarios

- 1cm sorbent mat (AC and OC)
- Sorbent loading:
  - 0.4 lb/ft^2 of AC
  - 0.8 lb/ft^2 of organoclay



Design Scenarios

- 30 cm sorbent amended cap (AC and OC)
- Sorbent loading:
  - 0.4 lb/ft^2 of AC
  - 0.8 lb/ft^2 of organoclay



In-situ Amendment

- In-situ AC treatment leads to reduced porewater concentrations.

PCB Congener	Reduction in PW Concentration
18	95%
52	75%
101	30%

- Reduction is not substantial for in-situ application of organoclay.
- Reductions sensitive to:
  - sorption onto existing sediment
  - proportion carried by dissolved organic carbon

- porewater concentration which has been shown to be directly proportional to the bioaccumulation of contaminants in benthic organisms
- reductions are sensitive to the sorption of the PCB onto the existing sediment and the proportion of PCBs carried by dissolved organic carbon (14 mg/L in the Manistique sediment). The smaller reduction associated with the higher molecular weight PCB is associated with the strong sorption of that congener onto the sediment (based upon measured porewater and bulk solid concentrations)
- This is because the organoclay is only marginally more sorbing than the existing sediment (based upon measured porewater concentrations and sorption isotherm information).

Passive Cap

- 30 cm sand layer with no sorptive amendment.
- Increases time for PCBs to migrate to surface.
- Maximum flux for low upwelling rate was 500 times less than the unremediated case.

- Effect not that dramatic for 1cm/day flow rate.
- The faster 1cm/day flow rate showed similar results with breakthrough occurring sooner.

Sorbent Mat

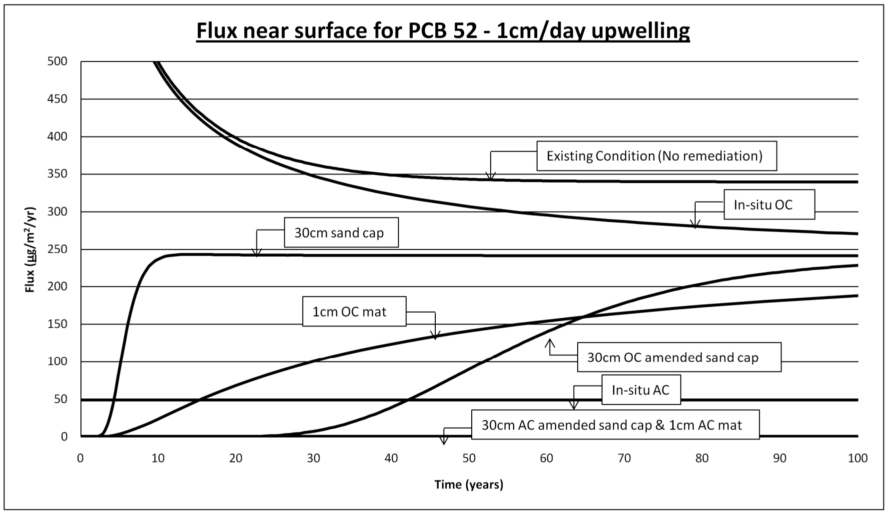
- AC mat eliminates any concentration and flux to the surface for at least 1000 years.
  - Issues with placement due to low density
- OC mat leads to longer breakthrough times compared to the passive cap.

- 1cm mat leads to longer breakthrough times compared to the 30 cm sand only cap although steady state fluxes (after several hundred years) are higher due to the thinner cap thickness in this simulation.

Amended Cap

- AC amended cap eliminates any concentration and flux to the surface for at least 1000 years.
  - Expected to perform better than mat.
- Amended cap provided the best performance for OC.
  - Low porewater concentrations and fluxes observed at the surface in slow upwelling case (up to 1000 years).
  - Concentration and fluxes began to increase after a few decades in the high upwelling case.

Model Results



Y-axis has been cut off at 500.

Conclusions – Sorption Study

- AC sorption:
  - Nonlinear
  - Less effective for site than laboratory water because of fouling effects due to natural organic matter.
- OC sorption:
  - Linear
  - Not significantly influenced by other contaminants or natural organic matter.

Conclusions - Remedy Design

- Breakthrough times for AC are much higher (several orders in most cases) than organoclay.
  - The low density of AC hinders its effective placement.
  - Organoclay is preferred at sites with NAPL.
- A mixed amendment throughout cap is more effective than sorbents as an in-situ amendment or even a sorbent mat.
  - Cap encroachments on water depth
- AC amended cap is expected to be an extremely effective remedy for this and other similar sites.

Thank you!