Sustainable Remediation of Contaminated Sediment Using Indigenous Natural Materials

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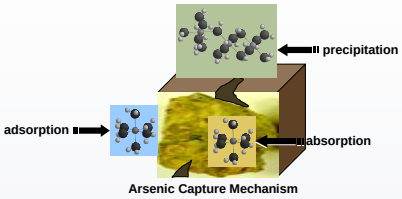
Introduction

There are various types of natural materials available that can sorb COCs physically or chemically.

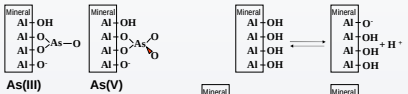
The sorption can be site-specific, depending on

- The aquatic chemistry of the site
- Physical and chemical properties of the sorbent materials
- The properties of the COCs

Reactive natural cap provides a sustainable solution by limiting the chemical flux (leaching from sediment) through a relatively thin layer of application.



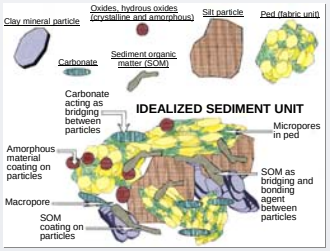
Arsenic Capture Mechanism



As(III) and As(V) form inner-sphere surface complexes

Surface Acidity and Surface Complexation Reactions

Conceptual Diagram



Sediment structure showing effectiveness of natural materials sequestering various contaminants

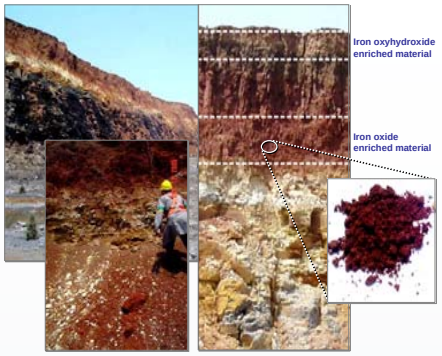
Objectives

Before designing any sediment cap, one should consider the physical, chemical, and toxicological properties of the cap materials.

A sustainable reactive cap will be

- Able to sequester chemical and biological materials to stabilize a broad range of contaminants in different types of sediments
- Environmentally friendly and cost effective
- Able to resist physical disturbance
- Predictable using conceptual and mathematical models to estimate cap life (long term performance) for contaminant attenuation
- Amenable to combination and deployment of chemical and biological amendments for constructing reactive sediment caps
- Effective on reducing contaminant mobility, toxicity, and bioavailability under field conditions

Natural Cap Materials



Iron-rich natural minerals have shown no toxicity to benthic organisms, and significant attenuation of arsenic (As)

Mineral-rich Native Material

This mineral-rich rock and sedimentary deposits from southeast U.S. have appropriate surface functional group to attenuate mercury (Hg).

Anthropogenic Organoclay

Quaternary ammonium compounds in clay can promote sorption of multiple contaminants. However, their effects on benthic communities need to be evaluated.

A site-specific sorptive cap can be a sustainable solution as it reduces bioavailable COCs, does not leach any other COCs, and is environmentally friendly to benthic organisms.

Natural Sorptive Caps

Sorbent/Potential Cap Material	Sorption Parameters for DDT and DDx
Pulverized Wood Charcoal	Kd (Log) = 220.3; sorption capacity = 4.41 mg/g
Zero Valent Iron (ZVI)	DDT half-lives @ 5 °C 36 weeks and @ 22 °C 6 weeks
Granular ZVI	DDT reduction occurred at 89% with Fe at 150 hrs and 96% with FeS at 150 hrs. A 1:1 mixture of Fe and FeS resulted in 80% DDT reduction in 4 days.
ZVI and by-products	Removed DDT at >95% within 30 days
Biofilm	Kd (Log) = 806 – 19 for p,p-DDT and Sorption rate constant: 8 – 19 L/min
Pine Bark	Kd = 843.96; Kd = 922.48; Kd = 1119.62
Sediment	varies (half-life 3 to 6 years)
Sediment	Mean log Koc, DOT: 4.54–0.19, DDE: 4.59–0.16, DDD: 4.56–0.13
Taichung Soil	Kp of p,p-DDT 8640 mL/g and Koc 479500 mL/g. Kp of p,p-DDD 2350 mL/g and Koc 130600 mL/g. Kp of 470 mL/g for p,p-DDE and Koc of 26300 mL/g.
Humic Materials	Koc 67,800 - 544,000
Soils	K (Montcalm Sandy Loam): 1.37 (Sims Clay): 10.63 (Houghton muck)
Sewage	7.9 – 10³ mL/g for sewage (84% organic); 2.1 – 10³ for sewage (100% organic)

Potential Cap Materials to Sequester DDT and DDX

Sorbent	Sorption Capacity
Iron oxyhydroxides (α- or β-FeOOH)	1.62 – 4 mg/g
Iron (Fe^{III} oxides and hydroxides (Jarosite, Ferrihydrite, Limonite)	0.9 – 1.79 mg/g
Manganite (γ-MnOOH)	variable
Sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$)	0.9 – 1.3 mg/g
Bentonite	0.9 – 1.3 mg/g
Aluminum oxides and hydroxides	0.36 – 13.64 mg/g
Granular Activated Carbon	1.05 – 20.22 mg/g

Cap Materials to Sequester As

Sorbent	Sorption Capacity
Montmorillonite	296 to 346 mmol/kg
Humic acid	2700 to 2815 mmol/kg
Ferrihydrite	501 to 577 mmol/kg
Goethite (α-FeOOH)	0.39 to 0.42 μmol/m²
gamma-alumina (γ-Al_2O_3)	0.54 to 0.13 μmol/m²
Bayerite (β-$Al(OH)_3$)	0.39 to 0.44 μmol/m²
Sorbent from Coriandrum sativum	24 to 55 mg/g (Hg^{2+}); 7 to 17 mg/g (CH_3Hg^+)
Natural zeolites (clinoptilolite)	1.21 meq/g
Activated carbon (clothe)	65 mg/g
Furfural-based carbon adsorbents	132 to 174 mg/g
Bauxite	0.8 to 5.29 L/kg (max. 2.7 mg/g)
Yellow tuff	0.18 mg/g at 3000 μg/L
Pozzolana	0.8 mg/g at 1000 μg/L
Estuarine sediments	log kd = 4.3 - 6.0 mL/g

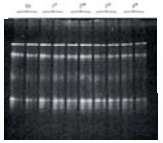
Cap Materials to Sequester Hg

Description	Total Hg (Hg_T) Concentration in Aquatic Sediment (ng/g dry wt.)		Estimated Hg(II) Surface Water Concentration (ng/L)		Calculated Benthic Sediment kd for Hg(II) (L/kg)		Calculated Benthic Sediment kd for MeHg (L/kg)	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
80 study lakes, MN	34	753	0.7	5.8	5,700	990,000	650	110,000
25 study lakes in Sweden	150	460	1.6	6.5	23,000	290,000	2600	32,000
Little Rock Lake, WI	10	170	0.3	0.6	16,000	560,000	1800	63,000
Savannah River Site, Aiken, SC	20	9450	NA	2000	4704	5725	NA	NA
Fox River, WI	970	7400	1.8 (unfiltered); 1.0 (filtered)	182 (unfiltered); 1.6 (filtered)	275422	912010	43651	151356

Intrinsic Capacity of Native Sediment to Sequester COCs (Hg)

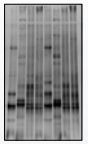
Biological Community Profiling

Amplified ribosomal DNA restriction analysis (ARDRA) and denaturing gradient gel electrophoresis (DGGE) conducted to evaluate the effects of the commercial organoclays, native and spiked sediment on bacterial community.

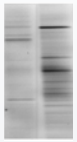


DGGE gel of bacterial community not treated with clays

ARDRA gel of bacterial community treated with montmorillonite (untreated)



Community profiling by DGGE of 16S rRNA gene fragments for unspiked Hg-contaminated sediment



DGGE profile of amplified DNA from a portion of the 16S rRNA gene for high and low-TOC Hg-spiked sediment

Substrate		Modifier Conc.	Effect on Microorganism
Commercial Organoclay	**Montmorillonite modified with quaternary ammonium salt (MT2EtOH)**	**90 meq/100g clay**	Toxic effect on ***Pseudomonas putida***
	Montmorillonite modified with quaternary ammonium salt	**NA**	Strong toxic effect on ***Pseudomonas putida*** Slight toxic effect on ***Pseudomonas monteilii***
	Montmorillonite modified with dihydroxymethyltallow quaternary	**NA**	Did not show significant **influence on sediment bacterial community**
Watershed sediment	**Sediment spiked with Hg**	**4600 mg/Kg**	Showed presence of *Clostridium*, *Anaeroarcus*, *Thermodesulfovibrio*, *Magnetobacterium*

MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

- Many bands indicating a high diversity were present in native sediment sample.
- Microbial consortium showed no change after the enrichments without clay and with montmorillonite.
- Significant change in SRB community structure did not occur during enrichment with the exception of absence of *Thermodesulfovibrio* and *Magnetobacterium* in high TOC (4600 mg/L). These dominating bands appeared at low TOC (5 mg/L) sediment.

Summary

- The antibacterial properties of quaternary ammonium compounds are known and are closely linked with the chemical properties of cationic surfactants. These positively charged functional groups are attracted to negatively charged substances (such as, bacterial proteins). Quaternary ammonium compounds denature these proteins exerting their antibacterial activity.
- Microorganisms can use the cationic surfactants in organoclay as carbon and energy sources.
- Organoclays may inhibit or stimulate the various microorganisms present in the natural (sediment-water) systems. Thus, it is important to perform microorganism toxicity studies in order to identify environmental impact.
- Natural minerals can provide sustainable solution as the microorganisms may have acclimatized by the indigenous materials.

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