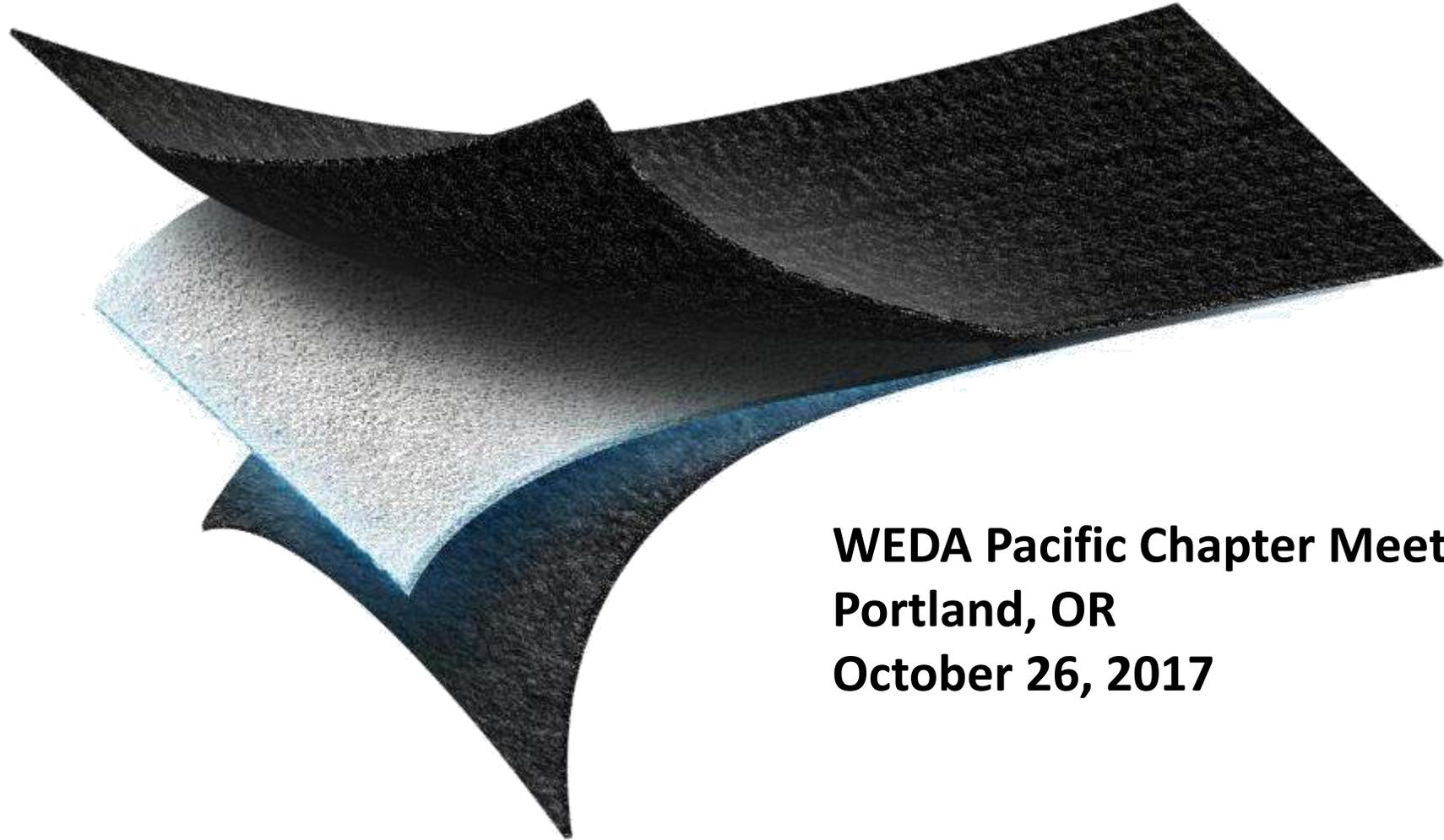


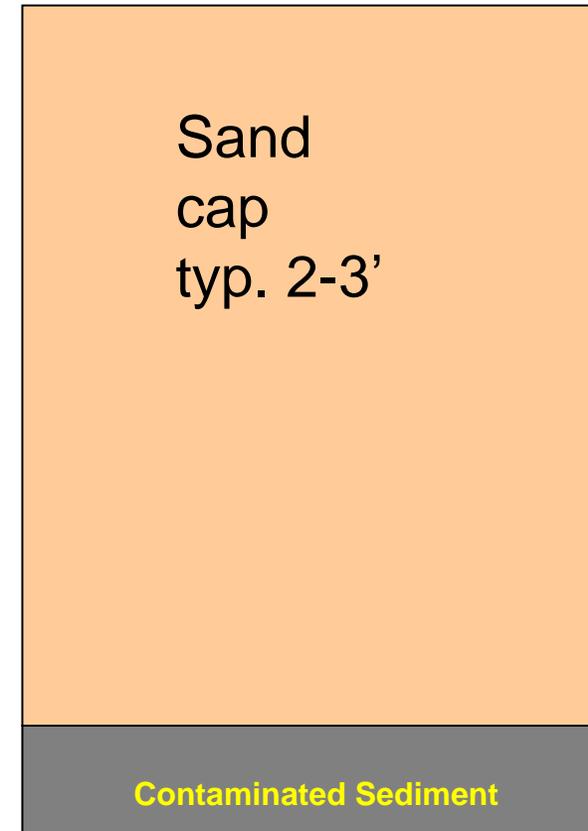
Capping Amendment Test Methods



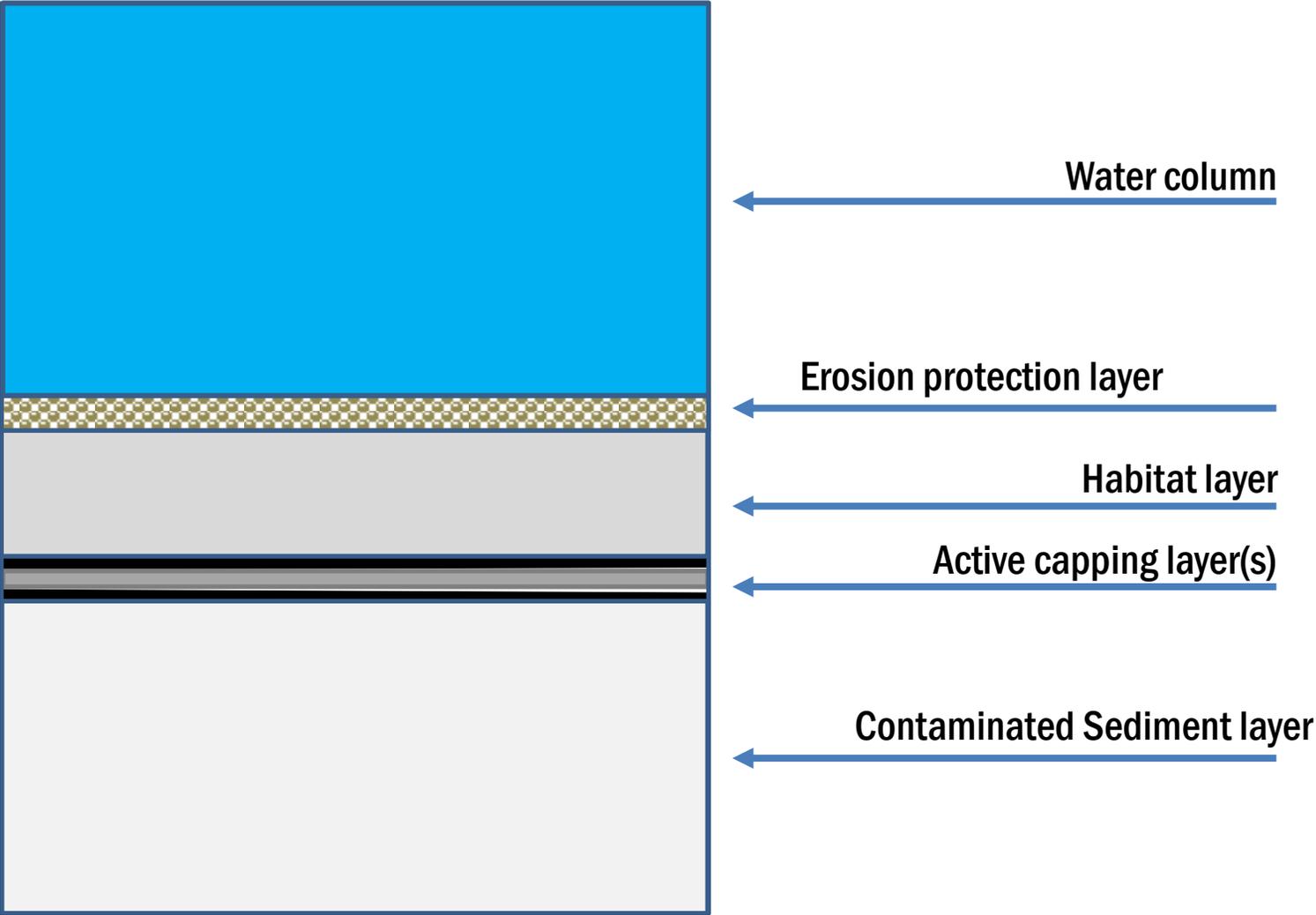
**WEDA Pacific Chapter Meeting
Portland, OR
October 26, 2017**

- **Background**
- **Types of Amendments**
 - **Activated Carbon**
 - **Organophilic Clay**
 - **Calcium Phosphate (Apatite)**
- **ASTM Test Methods**
- **Summary**

- Can be effective for highly immobile contaminants, such as PCBs and metals.
- Not effective w/ DNAPL.
- May require a thick layer to be effective due to low organic content (1-5%).
- Test sand for contaminants (USEPA Sw-846 methods 8260/8270) and TOC (USEPA SW-846 method 9060).



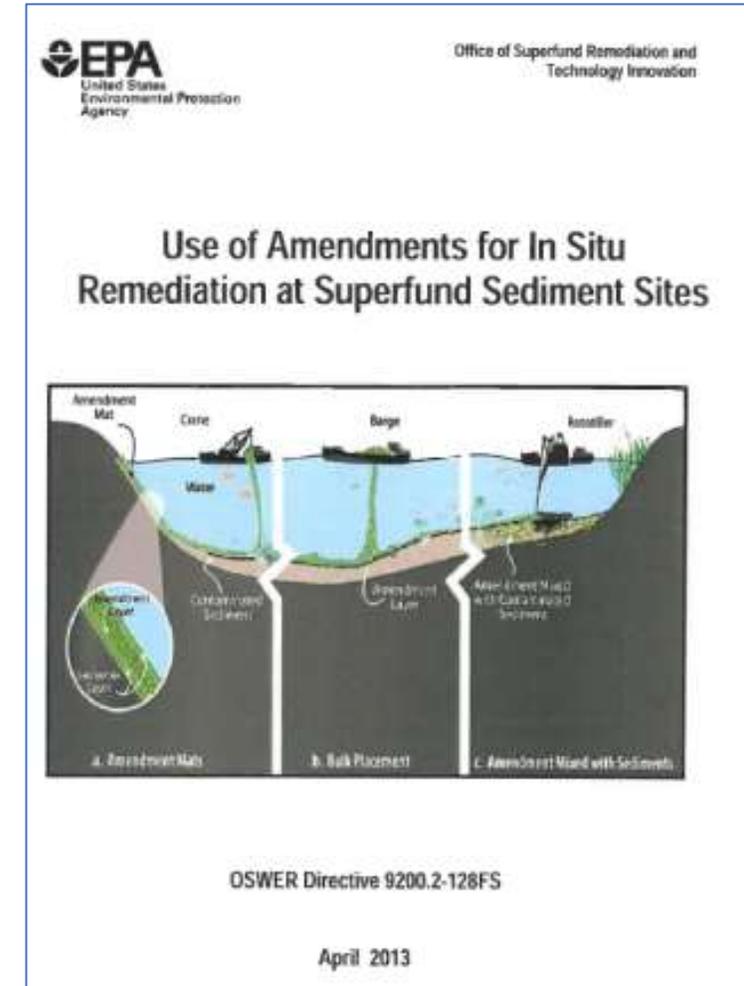
Capping Cross Section



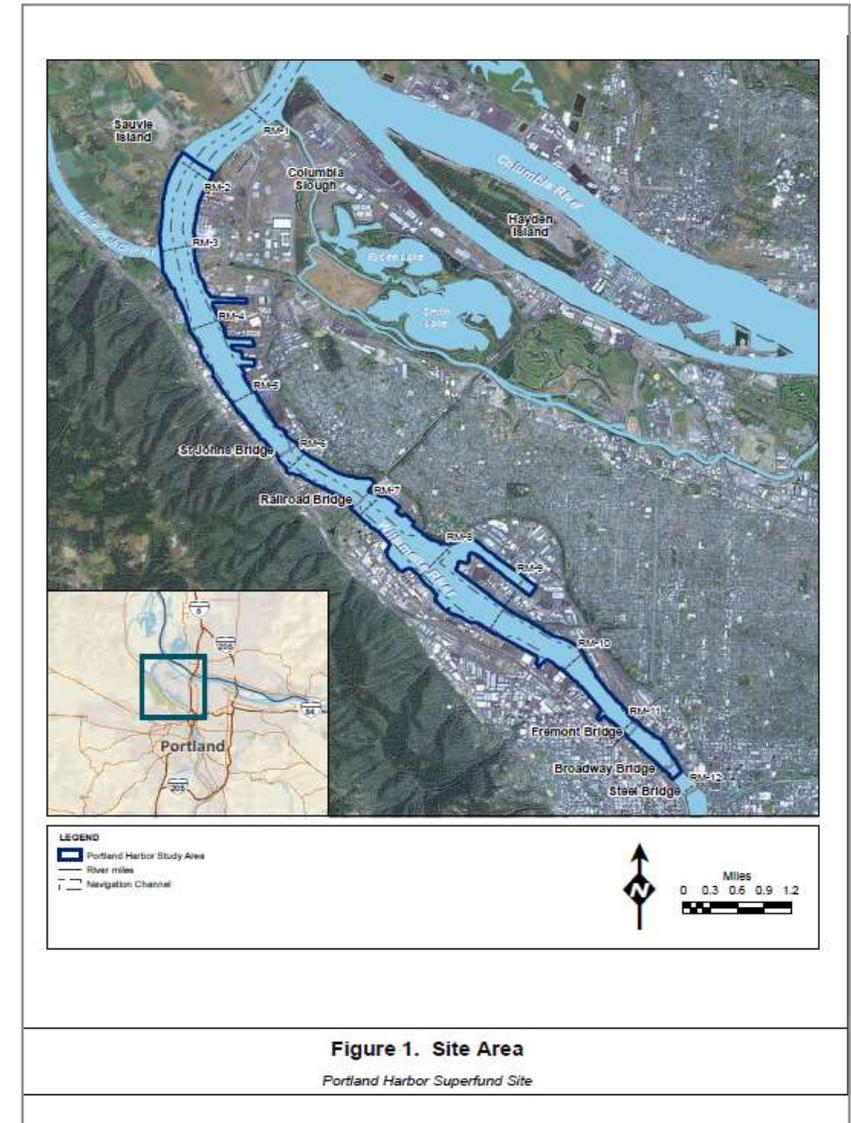
- # Typically, in waterways first dredge then cap to retain water depth for navigation and/or flood control.
- # Capping delivery methods:
 - # Bulk (sometimes w/ sand)
 - # Pelletized w/ substrate
 - # Geotextile mat
 - # Lined gabion baskets



- Recently, more sites are considering combination remedies where dredging, capping, and MNR are being concurrently selected
- The large thickness of traditional sand caps can reduce the hydraulic capacity, flood storage, and depth of the water body
- Use of amendments, such as active mats, have the potential to reduce the thickness of caps and also to improve their resistance to erosional events and advective transport of COCs by gas ebullition and NAPL flow



- # Portland Harbor Superfund Site Record of Decision, January 2017.
- # Over 130 acres of active capping.



Dr. Reible, Texas Tech University

- **Activated Carbon or other carbon sequestration agent**
- **Organophilic clay for NAPL control & some dissolved organic contaminant control**
- **Phosphate additives for metals**
 - **Calcium phosphate (i.e. apatite) demonstrated**
- **Siderite (FeCO₃) for pH control**

- **Iron Sulfide for Hg and MeHg control**
- **Zeolites and surfactant modified zeolites for sorption**
- **Zero valent iron to encourage reactivity**
- **Oxygen or hydrogen release compounds/technologies**
- **Biopolymers**
- **Electrochemical controls on redox conditions**

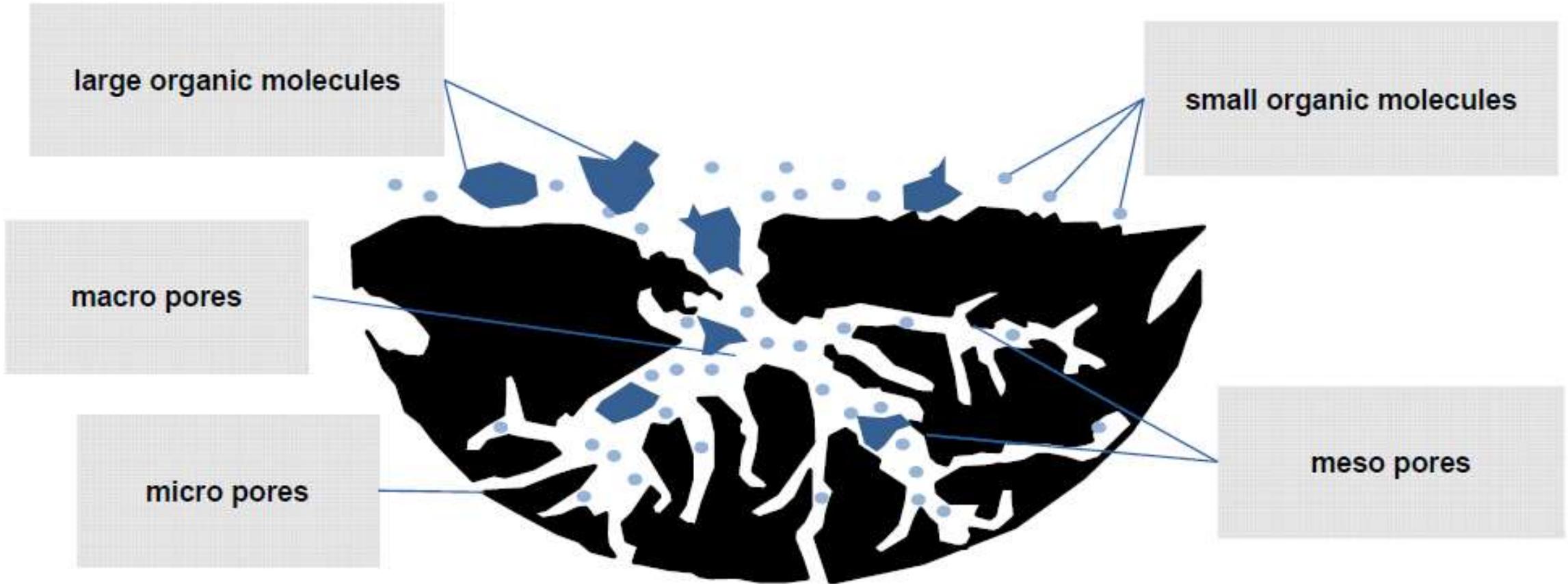
Demonstrated



Research and Development

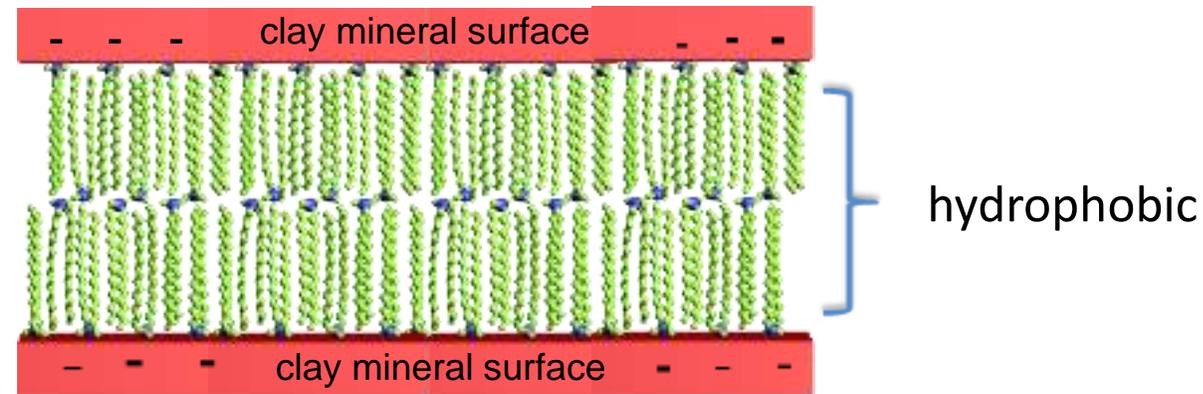
- # Activated carbon, made by the heating and activation of different raw materials (e.g., coal, coconut shells, lignite, wood), is highly porous.
- # Activated carbon has entrained air that can cause it to float. This buoyancy can be offset several ways; wetting, compressing w/ other materials, or placing in a polyester geotextile mat.







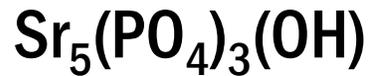
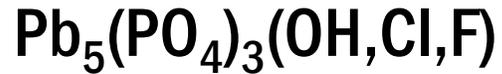
- A bentonite clay that has been treated with a quaternary amine (QAC) to replace sodium cations in the clay
 - The sorption properties of the resulting organophilic clay depend upon the selected quaternary amine
 - HUESKER employs long-chain hydrocarbon tails on the amine



- **Creating an organophilic material with high affinity for hydrophobic compounds such as NAPL, PAHs, PCBs**

Image: <http://ms.cc.sunysb.edu/~cburger/cbsu2.html>

Formed salt crystals



Solubility constant in water

$$\log K_{\text{sp}} \ll -76.5$$

$$\log K_{\text{sp}} \sim -51.3$$

$$\log K_{\text{sp}} \sim -49.0$$

$$\log K_{\text{sp}} \sim -35.3$$

$$\log K_{\text{sp}} \sim -32.6$$

$$\log K_{\text{sp}} \sim -24.4$$

Other Common Mineral Solubility Constants

Salt (NaCl)

$$\log K_{\text{sp}} \sim 0.0$$

Quartz (SiO_2)

$$\log K_{\text{sp}} \sim -4.0$$

→ Stable and permanent binding of metals with CP > 1,000 years

- # Performance test measures directly a property that is part of design (e.g., PAH adsorption isotherm test).
- # Index test measures a property that is related to the design property (e.g., surface area).
- # Performance tests can be costly and/or time consuming. So index tests are useful in minimizing costs and turnaround in quality control.

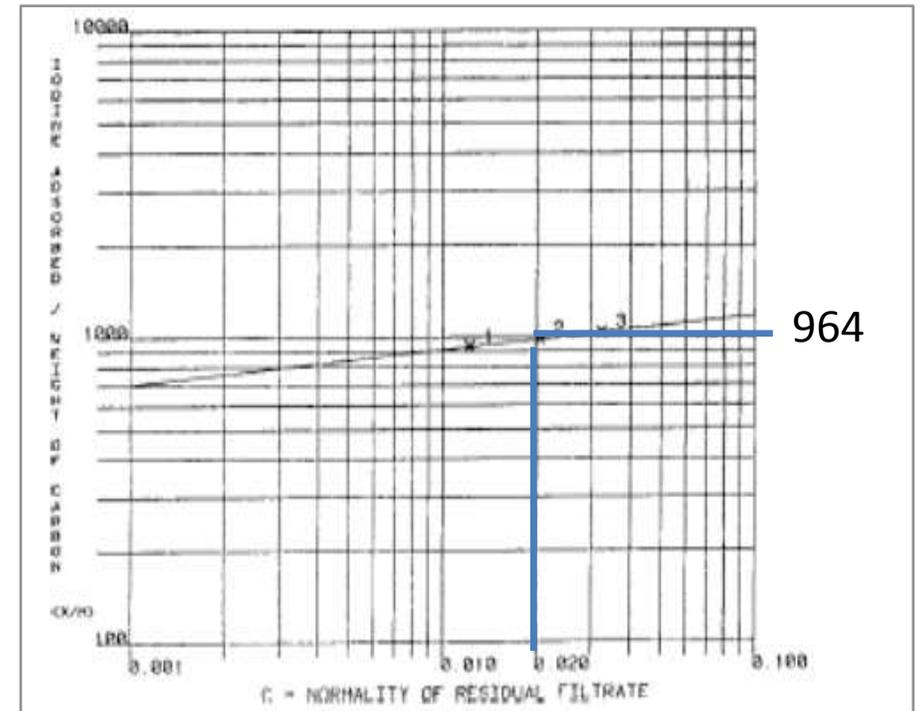
- # An international standards body.
- # Open to all: consultants, contractors, laboratories, manufacturers, regulators, industry.
- # Consensus based standards are drafted, discussed and balloted within committees.
- # Committees:
 - # D18, D28, D35
- # www.astm.org



- ASTM D2854 – Apparent Density. Tapped cylinder.
- ASTM D2862 – Particle Size Distribution. Sieve analysis. Sieves conforming to E11.
- ASTM D2866 – Total Ash Content. Muffle furnace @ 650 °C for 3 hours.
- ASTM D4607 – Determination of Iodine Number. Relative activation level by adsorption of iodine from aqueous solution.

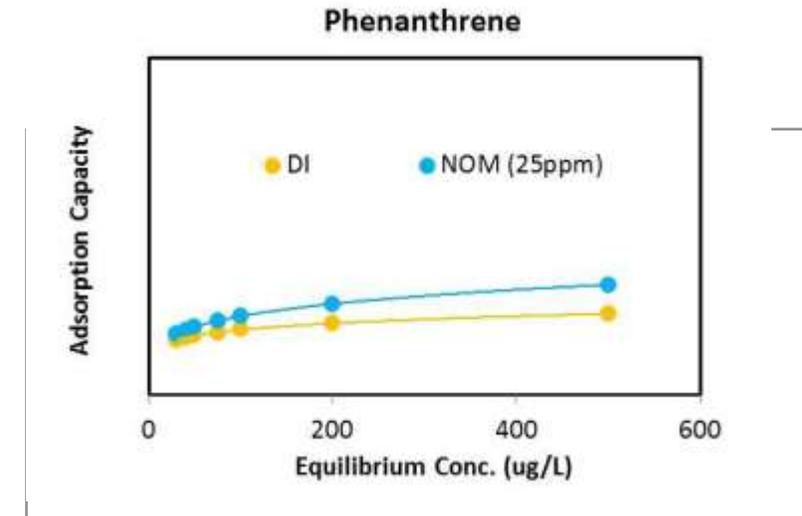


- # ASTM D4607.
- # A standard iodine solution is treated with 3 different weights of AC under specified conditions. The solution is filtered and iodine remaining in solution is measured by titration.
- # The iodine number is defined as the milligrams of iodine adsorbed by one gram of material when the iodine residual concentration of the filtrate is 0.02N based on a three-point isotherm.

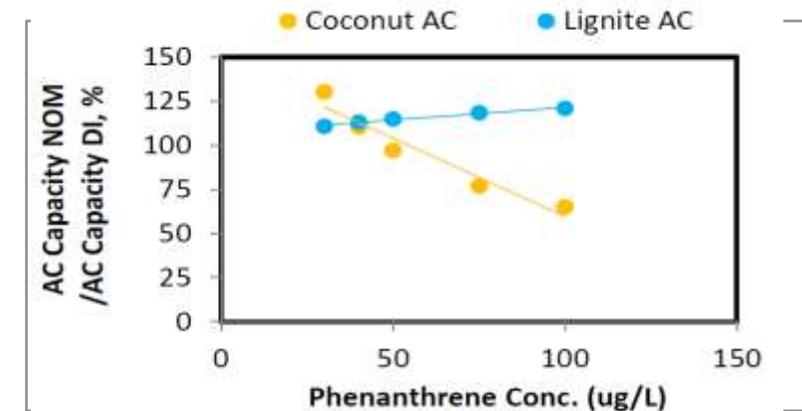


Graph of three iodine adsorption tests

- # Xin (Cabot Carbon) et al. “Evaluation of Impact of Natural Organic Matter on Activated Carbon Performance”. This study involved bench-scale tests of adsorption kinetics and equilibrium capacities of ACs on PCB congeners and PAHs in water with and without NOM. Activated carbons included granular and powdered forms produced from various sources.
- # At low flow 1 cm/day, PAC and GAC adsorb same amount of PAHs. PAC outperforms GAC at high flow \geq 3cm/day.
- # Lignite AC is resilient to NOM of 25 ppm. NOM reduced coconut carbon sorption by up to 5 fold.
- # European AC manufacturer – double activated AC.



Lignite AC with and without NOM (25 ppm)



Relative Capacity w/ NOM of 25 ppm

- # ASTM D7626 – Determining the Organic Treat Loading of Organophilic Clay. Two different procedures have been developed. In one method, a 50 mg sample is heated in a thermal gravimetric analyzer (TGA) in stages up to a minimum 750 °C. The mass of material remaining during heating is tracked continuously. Since many laboratories do not have TGA equipment, a second method allows for a more readily available muffle furnace. In this procedure, a 10-50 g sample is heated in a muffle furnace in two stages, first at 160°C for 16 hours, and then at 750 °C until there is a constant weight. In both procedures, the loss on ignition is adjusted for the ash content of the base bentonite clay.



Thermal Gravimetric Analyzer



Muffle Furnace

ASTM D8106 - Oil Sorption Capacity of Organophilic Clay. This is an index test that uses an additive-free oil, such as SAE 30 API SA grade motor oil. There are two procedures, one for granular form and another for powdered form. In the granular form procedure, 250 ml of organophilic clay is mixed with the specified oil and allowed to absorb the oil for 24 hours. The mixture is then placed on a 70-mesh screen and allowed to drain freely for another 24 hours. The mass of organophilic clay and absorbed oil is then weighed and the oil sorption calculated. In the powdered form procedure, 10 ml of the organophilic clay is mixed with the specified oil in a container and allowed to absorb the oil for 2 hours. In the second step the container is placed and spun in a centrifuge for 30 minutes at 3000g. The free phase oil is decanted and the mass of organophilic clay and absorbed oil is weighed.



Contaminant of Concern	Activated Carbon	Organophilic-clay
Non-aqueous phase liquids (NAPL)	NAPL causes fouling	Organophilic-clay can adsorb NAPL
Dissolved organic compounds	Can adsorb all dissolved organic compounds	Adsorbs low soluble dissolved organics (e.g., PAHs, PCBs)

Note: Can use as a treatment train: OC to capture NAPL and AC to adsorb dissolved organics

Active Cap Modeling

- # **Dr. Danny Reible, Texas Tech University, has developed a capping model, CapSim, for predicting contaminant transport through sand and amended caps.**
- # **The latest version, CapSim 3.5, is available for download.**
- # **A free one-day short course that includes cap design by Dr. Reible will be held November 14th in Portland, OR.**

- # **Characterizing the capping media using test methods is critical for:**
 - Design Testing**
 - Specification Writing**
 - Construction Quality Control Testing**
- # **ASTM International has a number of standard test methods that are used by manufacturers for quality control.**
- # **Performance tests can be costly and time consuming.**
- # **ASTM standard index test methods that correlate to performance can be substituted.**

