TETRA TECH

PROJECT NOTE 2: MIDDLE RIVER COMPLEX SEDIMENT REMEDIATION

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DATE: 03/13/2013

SUBJECT: *In Situ* Treatment at PCB Contaminated Sediment Sites

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This Project Note provides additional information on processes included in the recommend alternative for sediments adjacent to Lockheed Martin's Middle River Complex (MRC) with a focus on the *in situ* treatment component.

The feasibility study project team recommends the application of *in situ* treatment technology as part of the remedial alternative to manage contaminated sediments in Dark Head Cove. Recommended remedial actions in Dark Head Cove include a combination of removal of higher concentration areas adjacent to the bulkhead, *in situ* treatment, and MNR following the application of *in situ* treatment in limited areas.

Under the recommended alternative, site-wide human health remedial action objectives (RAOs) will be met after the remedial construction is completed. Benthic RAOs are estimated to be achieved over 93% of the area of concern at the end of the construction. This estimate is based on the conservative assumptions for the effectiveness of *in situ* treatment. In the Feasibility Study (FS), we have assumed the effectiveness of *in situ* treatment is a 50% reduction in bioavailability of total PCBs, benzo(a)pyrene equivalents (BaPEq), and mercury concentrations, and a 20% reduction in total metal concentrations. The most recent research and pilot studies regarding *in situ* treatment by activated carbon (AC) application and its effectiveness in reducing the bioavailability of PCBs, PAHs, and metals in sediments show that *situ* treatment is 75% to 95% effective for reducing PCBs and PAHs bioavailability. At the MRC site, the effectiveness of *in situ* treatment and the need for monitored natural recovery following *in situ* treatment will be refined during design based on the results of bench scale treatability testing of *in situ* treatment effectiveness using MRC sediments. The treatability testing is scheduled for spring 2013.

This Project Note presents a general description of *in situ* treatment, brief review of ongoing research, and the projects and pilot studies where *in situ* treatment has been applied.

***In situ* Treatment of Contaminated Sediments by Sediment Amendments:**

In situ management of contaminated sediments is being increasingly utilized due to the cost and potential complications of approaches involving excavation and dredging. In general, *in situ* approaches can be implemented rapidly with little disruption of the benthic environment and substantially less short-term exposure and risk compared to excavation and dredging.

In situ treatment through contaminant immobilization is an innovative sediment remediation approach that involves introducing sorbent amendments such as AC into contaminated sediments to alter sediment geochemistry, increase contaminant binding, and therefore decrease bioavailability. Ongoing academic research (e.g., bench-scale and treatability studies) suggests that porewater concentrations and bio-uptake of hydrophobic contaminants can be reduced between 70% and 98% at AC doses similar to the native organic carbon content of sediment (Patmont et al., 2013).

An overview of the technology was presented by Dr. Upal Ghosh at an EPA Region 10 Sponsored Technical workshop: *Use of Activated Carbon Amendment as an In-situ Sediment Remedy at the Lower Duwamish Waterway* on Feb 14 and 15, 2012 (Ghosh, 2012). (Note each of the pdf files indicated by icons are attached to the end of this document).

Ghosh-LDW-talk1-overview_of_technolog

Another overview of the technology and assessment of field-scale applications was recently presented at the Battelle Sediment Conference on Feb 4-7, 2013 (Patmont et al., 2013).

Battelle 2013_patmont abstra

Additional information about the field applications of *in situ* treatment where the researchers collaborate with the consultants and stakeholders for remediation of contaminated sediment and a brief overview of ongoing academic research are provided below.

***In situ* Treatment by Activated Carbon Field-Scale Applications:**

Currently more than ten field-scale demonstration projects spanning a range of environmental conditions have either been completed or are currently underway in the United States and Norway. Some of these sites are shown in Figure 1 and briefly summarized below.

The list of few sites and brief descriptions are summarized in Figure 1.

Summary of activated carbon demonstration projects

SITE LOCATION	Type of application	Funding	Application date	Contaminants	Points of Contact
Hunters Point, CA Site 1: tidal mudflat Site 2: tidal mudflat	 AC-mixed AC-mixed	 US Navy NAVFAC	 Aug 2004 Jan 2006	 PCBs PCBs	luthy@stanford.edu
Grasse River, NY: River sediments	AC-mixed/ unmixed	Alcoa, EPA, DoD	Sep, 2006	PCBs	Larry.McShea@alcoa.com ughosh@umbc.edu
Trondheim Harbor, Norway: Ocean harbor	AC-slurry unmixed	Norwegian Res. Council	May, 2007	PCBs, PAHs, PBDEs, DDT	Gerard.Cornelissen@ngi.no Gijs.Breedveld@ngi.no
US Army Installation in VA: Tidal creek & marsh	AC as SediMite	SRP, NIEHS	Aug 4-5, 2009	PCBs	ughosh@umbc.edu camenzie@exponent.com
Grenlandsfjords, Norway: Ocean harbor	Slurry of native clean clay and AC	Norwegian Res. Council, industry, Norwegian EPA	Sep, 2009	dioxins/furans	Gerard.Cornelissen@ngi.no Espen.eek@ngi.no Morten.schaanning@niva.no
Aberdeen Proving Ground, MD: Tidal creek & marsh	AC as SediMite	DoD-ESTCP	Dec 2010	Hg, Me-Hg, PCBs, DDT	camenzie@exponent.com ughosh@umbc.edu

a) Application of activated carbon in a tidal mud-flat at Hunters Point Navy Shipyard, San Francisco Bay, CA using two application devices (2004 and 2006). The Aquamog (top) using a floating platform approached the site from water and used a rototiller arm while the slurry injection system (bottom) was land based and applied a carbon slurry directly into sediment.

b) Application of activated carbon under 15 feet of water at Grasse River, NY, USA (2006). The site was enclosed with a silt curtain and application was performed using a barge mounted crane. Placement and mixing of the AC was achieved using two devices: 1) a 7-by-12-foot rototiller-type mixing unit; and 2) a 7-by-10-foot tine sled device.

c) Application of activated carbon slurry directly onto sediments at Trondheim Harbor, Norway (2007). AC-salt water slurries with/without powdered bentonite clay were pumped 3-5 ft above the sediment bed under 20 ft of water. Part of the AC-only field was successfully covered with 5 mm sand to protect from erosion.

d) Application of activated carbon in a pelletized form (SediMite™) using an air blown dispersal device over a vegetated wetland impacted with PCBs near James River, VA, USA (2009). Picture below illustrates bioturbation induced breakdown and mixing of pelletized carbon with a fluorescent tag in a laboratory aquarium.

e) Application of AC-clay mixture at 100 and 300 ft depth, Grenlandsfjords, Norway (2009). A hopper dredger was used to pick up clean clay from an adjacent site. After AC-clay mixing, the trim pipe was deployed in reverse to place an AC-clay mixture on the sea floor. Sediment-profile imaging and sediment coring (bottom figure) showed that placement of an even active cap was successful.

Descriptions of pilot-scale demonstrations of activated carbon amendment into sediment at five field sites.

Figure 1. Pilot-scale demonstrations of activated carbon amendment

Source: Ghosh et al. 2011. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3037809/

Hunters Point, CA. In 2006, a field pilot-study for *in situ* treatment of PCB contaminated sediments at Hunters Point Shipyard, California was performed. Bulk granular AC was mixed with tidal mud-flat sediment using a Rototiller and slurry injection. Hunters Point is a net depositional site, with an average sedimentation rate of 1 cm/year. Ongoing monitoring at this site showed 60% reduction in PCBs 18 months post AC-amendment and 80% reduction in PCBs 30 months post AC-amendment in top 15 cm of sediments (Oen et al., 2012).

http://nordrocs.org/wp-content/uploads/2012/09/Session-I-3-Amy-Oen-Presentation.pdf

Grasse River, NY. A field pilot-study at the Grasse River in Massena, New York, also conducted in 2006, mixed bulk granular AC with sediments at a water depth of 15 feet, using a Rototiller and tine sled to achieve a reported reduction of up to 95% in PCB uptake in benthic invertebrates (e.g., clams and worms) (Greenberg, 2012).

Greenberg_Grasse_ACPS_review_dist.pd

James River, VA. Broadcasting of pelletized powdered AC (SediMite™) was applied to PCB contaminated sediments in James River, Virginia. PCB uptake in freshwater oligochaete was reduced by 90% (Ghosh, 2012).

Aberdeen Proving Ground, MD. Application of SediMite™ at the pilot-test area has shown that amending freshwater sediment with SediMite™ reduced mercury bioaccumulation in a freshwater oligochaete by 84%, and reduced methyl-mercury bioaccumulation by 90% (Ghosh, 2012).

Trondheim Harbor, Drammen, Grenlandfjords, Fiskerstrand, Norway. In Norway, several *in situ* treatment and thin layer amended capping pilot studies have been performed. The target contamination is PCBs, PAHs, TBTs, dioxins and furans. The results of field scale application have been reported in a number of publications. At these sites, the bioavailability of contaminants was reduced by 50 – 95 % by *in situ* AC treatment or thin layer placement of sediments with or without AC amendment (Oen et al, 2010).

6CornelissenOenHavKyst.pdf

At PAH contaminated sites in Norway, the sediment-to-water PAH flux was reduced for all AC treatments and the greatest reduction (factor of 10) was observed for the AC+clay. Porewater PAH concentrations were reduced up to 50 % in the biologically active 0-5 cm deep sediment layer which contained AC. Bioaccumulation of PAHs to worms and benthic mussels decreased 80-90% for the AC+clay placement. At Drammen, powdered and granular (PAC and GAC) AC were added to a soil. Freely dissolved aqueous PAH concentrations in drainage water and soil pore water were monitored with passive samplers. More than one year after amendment, the free aqueous concentrations in the drainage water were reduced by 93 % and 55 % for the PAC and GAC, respectively, and the free aqueous PAH concentration in the soil pore water itself, as measured by innovative dug-in passive samplers, was reduced by 93 and 70 % for PAC and 84 and 61 % for the GAC (Hale, 2011).

S.Hale
abstract_SETAC 2011

In situ Treatment Sediment Amendment Delivery Mechanisms:

At the MRC site, surface broadcasting of bulk activated carbon (AC) pellets, without additional capping material, is assumed as the *in situ* treatment technology used to reduce the bioavailability of MRC COCs. Currently, two such products are available in the market: AquaGate and SediMite™. Both of these products are agglomerates comprised of a treatment agent (usually AC), a weighting agent to make it sink and resist resuspension, and an inert binder. They are designed to cause minimal environmental impact, and can thus be used whenever a primary goal is to limit destruction of existing habitat. The most viable remedial applications for AC include depositional environments that are hydrodynamically stable and have low erosion potential, and sensitive environments where minimizing habitat disruption is a goal (e.g., contaminated sediments in aquatic or marine grass beds and wetlands).

SediMite™ is an agglomerate comprised of a treatment agent (typically activated carbon), a weighting agent (to enable it to sink and resist resuspension), and an inert binder.

http://sedimite.com/

Menzie_Presentation
_on_SediMite_to_Reg

AquaGate™ is a family of permeable, treatment or adsorptive materials that are intended to remove contamination from pore water and/or reduce potential of contaminant break-through. These materials can be used in a reactive cap, for *in-situ* treatment, or in a range of other applications to control contaminant migration.

http://www.aquablokinfo.com/

AquaGate+PAC.pdf

On-going *In Situ* Treatment Research:

In situ management of contaminated sediments by introducing sediment amendments is a focus of on-going research in US and Europe in the last decade. Application of contaminant sequestering agents and amendments, to reduce the bioavailability of hydrophobic organic compounds and metals is well established in the scientific literature. Of the amendments developed to date, activated carbon is the furthest along in terms of both science and field-scale applications as an adsorbent to reduce porewater concentrations and therefore bioavailability of contaminants.

The most recent workshop report on research and development needs for long-term management of contaminated sediments by U.S. Department of Defense (DOD) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) identified critical and high priority technology transfer, additional research, demonstration needs in application of *in situ* treatment in various environments to gain wide-spread acceptance. These research areas include technology transfer of state of the science for using activated carbon; demonstration of long term efficacy of *in situ* amendments or amended caps and demonstration of tools to evaluate amendment placement; improved assessment of parameters that impact long-term effectiveness of *in situ* amendments and amended caps; new approaches for implementing *in situ* amendments or amended caps.

SERDP 2012. SERDP and ESTCP Workshop on Research and Development Needs for Long-Term Management of Contaminated Sediments

http://www.serdp.org/News-and-Events/News-Announcements/Program-News/SERDP-and-ESTCP-workshop-identifies-R-D-needs-for-long-term-management-of-contaminated-sediments

MRC Feasibility Study team is following up on the latest research, bench scale and pilot studies in this area. Some of the selected research mostly linked to the field scale applications is summarized in Table 1.

Table 1
Recent Sediment Amendment Research

Research Description	Research Description
Innovative *In-Situ* Remediation of Contaminated Sediments for Simultaneous Control of Contamination and Erosion (A. Knox, D. Reible, 2006-2010)	The objective of this project is to develop an active capping technology that contains and stabilizes a wide range of contaminants (metals, polycyclic aromatic hydrocarbons [PAH], and polychlorinated biphenyls [PCB]) in different aquatic environments (marine and freshwater) by designing *in situ* stabilization treatments that combine chemical and biological amendments. The active capping technology will consist of in situ application of phosphate materials (apatite and calcium phytate), organoclays, and biopolymer products. http://www.clu-in.net/download/contaminantfocus/sediments/Sediment-ER-1501-FR-Pt-2.pdf
Activated Carbon as Multifunctional Amendment to Treat PCBs and Mercury (R. Luthy, 2007-2011)	Investigators are attempting to impregnate activated carbon particles with nanoscale zero-valent iron to induce PCB and mercury reduction and sequestration. Further bench scale studies utilize San Francisco Bay marsh sediments. This project is part of Hunters Point pilot scale test. http://tools.niehs.nih.gov/srp/programs/Program_detail.cfm?Project_ID=R01ES16143
SERDP/ESTCP Research ER-2136: Activated Biochars with Iron for In-situ Sequestration of Organics, Metals, and Carbon. (Dr. U. Ghosh, 2010-2012)	The objective of this SERDP Exploratory Development (SEED) project is to develop specially formulated biochars that can reduce the bioavailability and leaching of PAHs, PCBs, and selected heavy metals in sediments. A range of biochars made from agricultural residue, poultry litter, wastewater sludge, and coconut shell are evaluated. Unactivated biochars were able to reduce PCB porewater concentration by 18-80%, while the activated carbons and activated biochars consistently reduced organic contaminant porewater concentration by more than 99% in a Department of Defense impacted sediment. http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-2136
SERDP/ESTCP Research ER-201131: Demonstration of *In Situ* Treatment with Reactive Amendments for Contaminated Sediments in Active DoD Harbors. (Dr. D. Bart Chadwick, 2011-2015	This project extends current pilot-scale testing of the application of activated carbon (AC) to decrease the bioavailability of PCBs in contaminated sediment to near full-scale demonstration under realistic conditions at an active Department of Defense (DoD) harbor site, Puget Sound Naval Shipyard, Bremerton, WA. This project will demonstrate an AC amendment over a relatively large-scale footprint (approximately 1,900 m2) at 10-meter depth in an active DoD harbor area using a conventional deep water capping technology (AquaGate+PAC). The AC will be combined with a clay and aggregate substrate to form a composite particle that will readily fall through the water. The construction was completed in summer 2012, no monitoring results have been reported yet. http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-201131/ER-201131

Table 1 (continued)
Recent Sediment Amendment Research

Sediment Amendment/ Reactive Cap Research	Research Description
Rational Selection of Tailored Amendment Mixtures and Composites for *In Situ* Remediation of Contaminated Sediments (U. Ghosh, 2006-2008)	Research focused on comparing different sorbents either alone or in formulated combinations of new amendments, improving scientific understanding of how multiple amendments function together and reduce contaminant bioavailability, and developing efficient delivery methods for applying amendments to impacted sediments. A list of 75 potential sediment amendments was identified based on literature information. The screening yielded a list of 11 sorbents used for further sorption testing of metals and organics. Biouptake of Cd, Pb, Hg, was evaluated in sediments amended with selected sorbents. http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA512835&Location=U2&doc=GetTRDoc.pdf
Predicting and Validating Field Performance of Novel Sorbent Sediment Caps (G.Lowry, 2005-2008).	Field test of thin layer sorbent amendment cap. This study evaluated the performance of thin layer activated carbon (AC) amended sand sediment caps as a tool for *in situ* remediation of PCB contaminated sediments. This project provided new knowledge regarding the effectiveness of activated carbon-amended sediment caps under *in situ* conditions mainly on performance of AC when natural organic matter is present and at certain flow conditions. http://ciceet.unh.edu/news/releases/spring09_reports/pdf/lowry_FR.pdf
Measurement and Modeling of Ecosystem Risk and Recovery for *In Situ* Treatment of Contaminated Sediments. Richard Luthy (Stanford University), Samuel Luoma and Janet Thompson (R. Luthy 2010-2013)	The project [ER 1552] addresses strategies to assess the ecological recovery after *in situ* sediment treatment by activated carbon (AC) amendment at Hunters Point, San Francisco Bay, California. Rapid assessment tools to measure polychlorinated biphenyls (PCBs) sediment pore water concentrations were tested to correlate aqueous concentrations of PCBs with reduced bioavailability. Though PCB tissue concentrations are expected to remain slightly higher at Hunters Point than at the reference sites, the model and field measurements suggests that the expected remedial success with AC-amendment would comply with the clean-up goal for Hunters Point and sediment quality guidelines.http://www.serdp.org/Program-Areas/Environmental-Restoration/Risk-Assessment/ER-1552

REFERENCES IN THE ORDER APPEARED IN THE TEXT

New Advances in Contaminated Sediment Remediation by Controlling Bioavailability

Upal Ghosh

Department of Chemical, Biochemical, and Environmental Engineering,

University of Maryland Baltimore County, Baltimore, MD

ughosh@umbc.edu

Lower Duwamish Waterway Workshop,

February 14-15, 2012

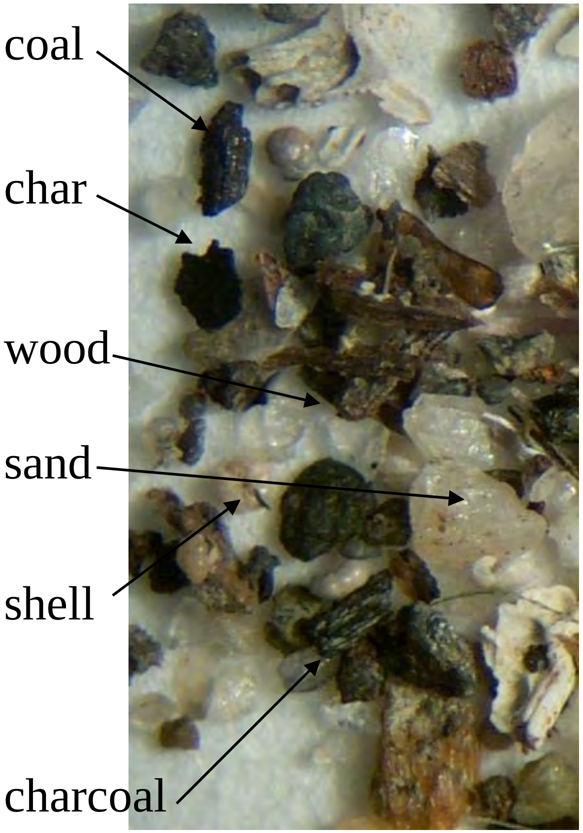
MANAGING EXPOSURE FROM HISTORIC DEPOSITS OF CONTAMINATED SEDIMENTS

- How do you clean up an ecologically sensitive site without destroying it?
- Contaminated sediment sites are large
- Current technologies are disruptive and expensive
- Need for innovative techniques that reduce risks

PCB contaminated wetland in VA

UMBC

NATURE OF SOIL/SEDIMENT PARTICLES



- Sediment contains:
  - mineral grains
  - natural organic matter (vegetative & animal origin)
  - black carbon (soot, coke, charcoal)
- PCBs bound to black carbon less bioavailable
- Black carbon naturally present in sediments reduce bioavailability
- Introducing strongly binding black carbon may reduce exposure

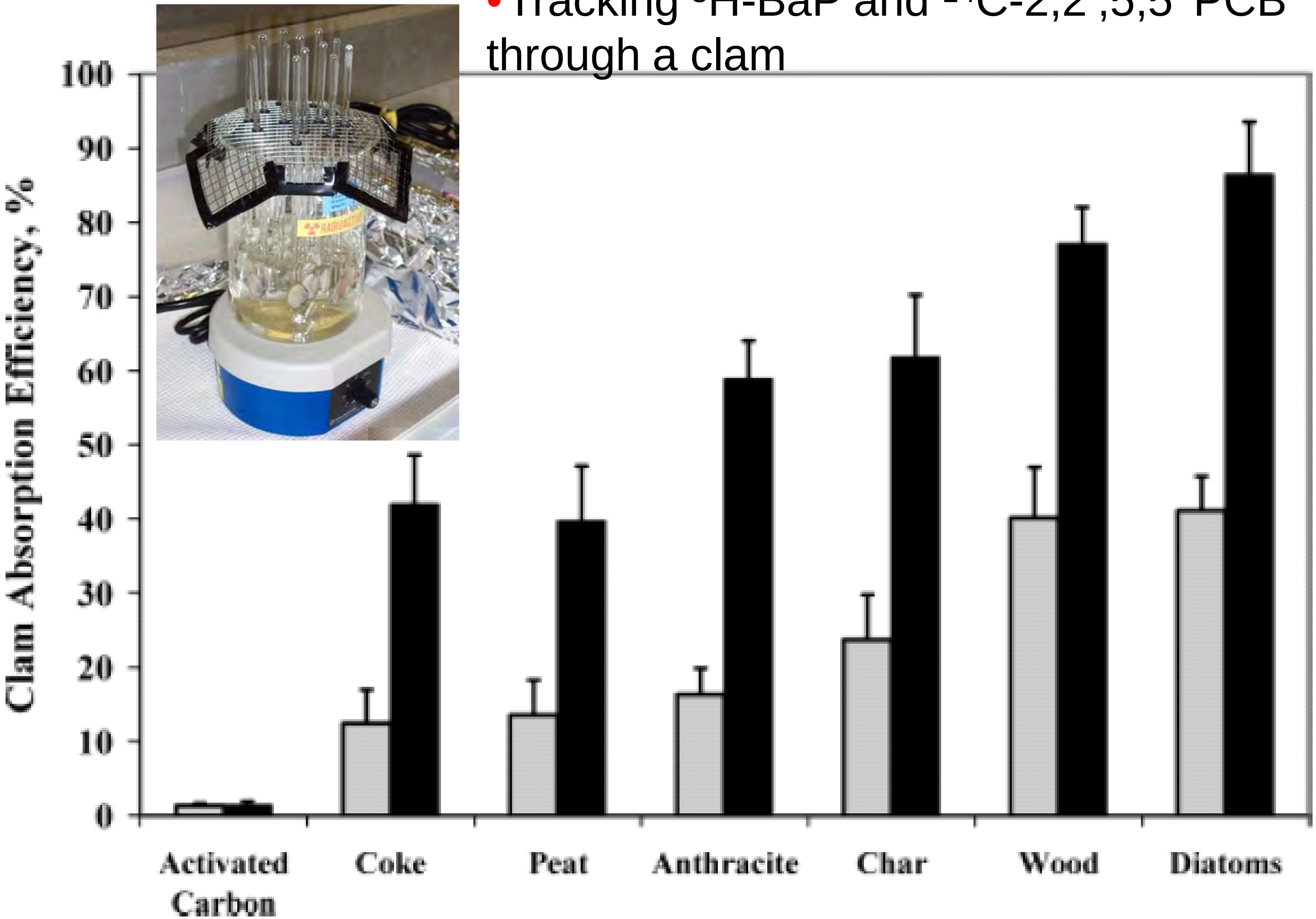
Petrography images

coal charcoal coke

From: Ghosh et al. Environ. Sci. Technol. 2003

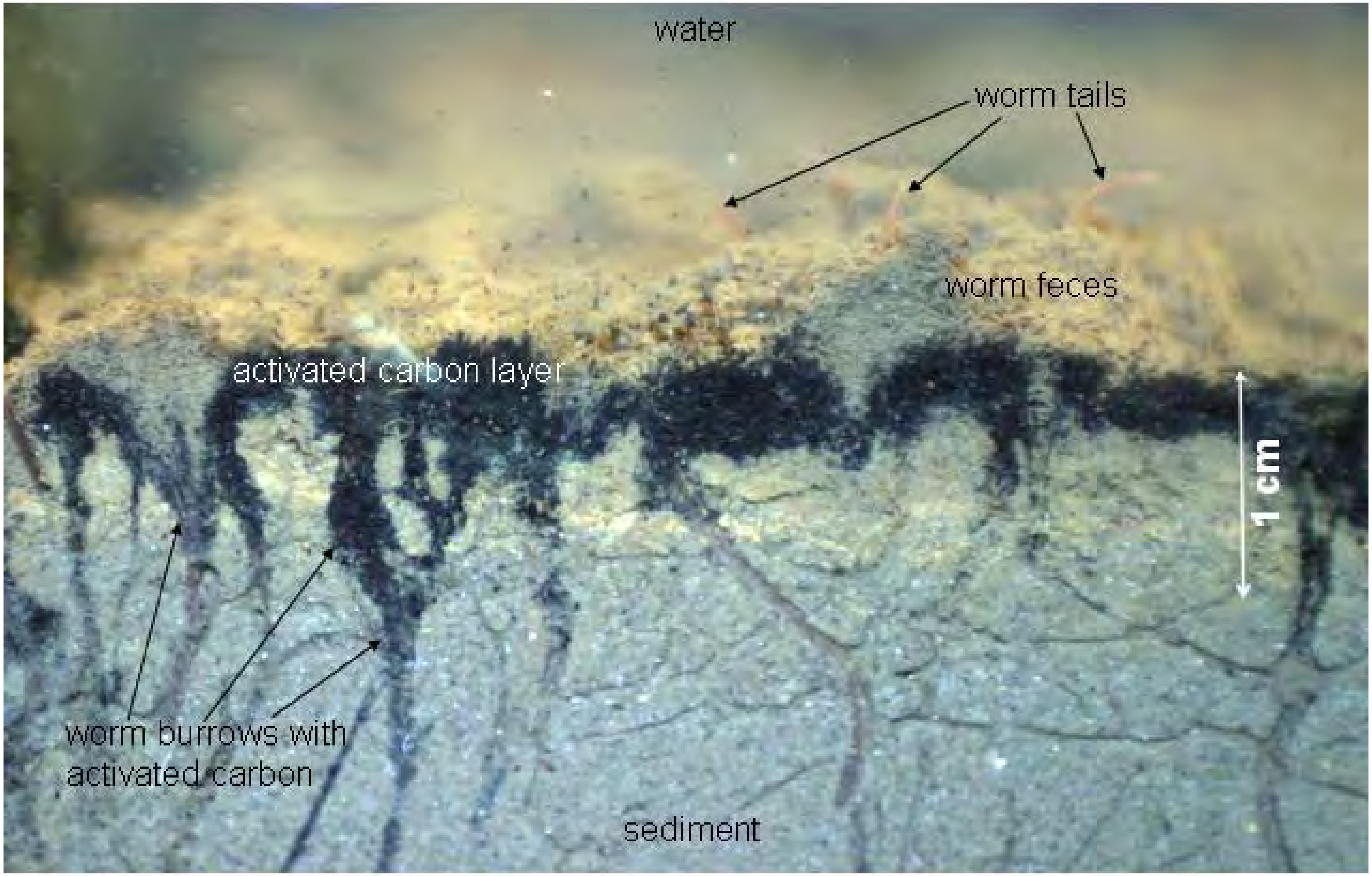
PAH AND PCB ABSORPTION EFFICIENCY IN CLAMS

- Tracking ^{3}H-BaP and ^{14}C-2,2’,5,5’ PCB through a clam



From: McLeod et al. Environ. Sci. Technol. 2004

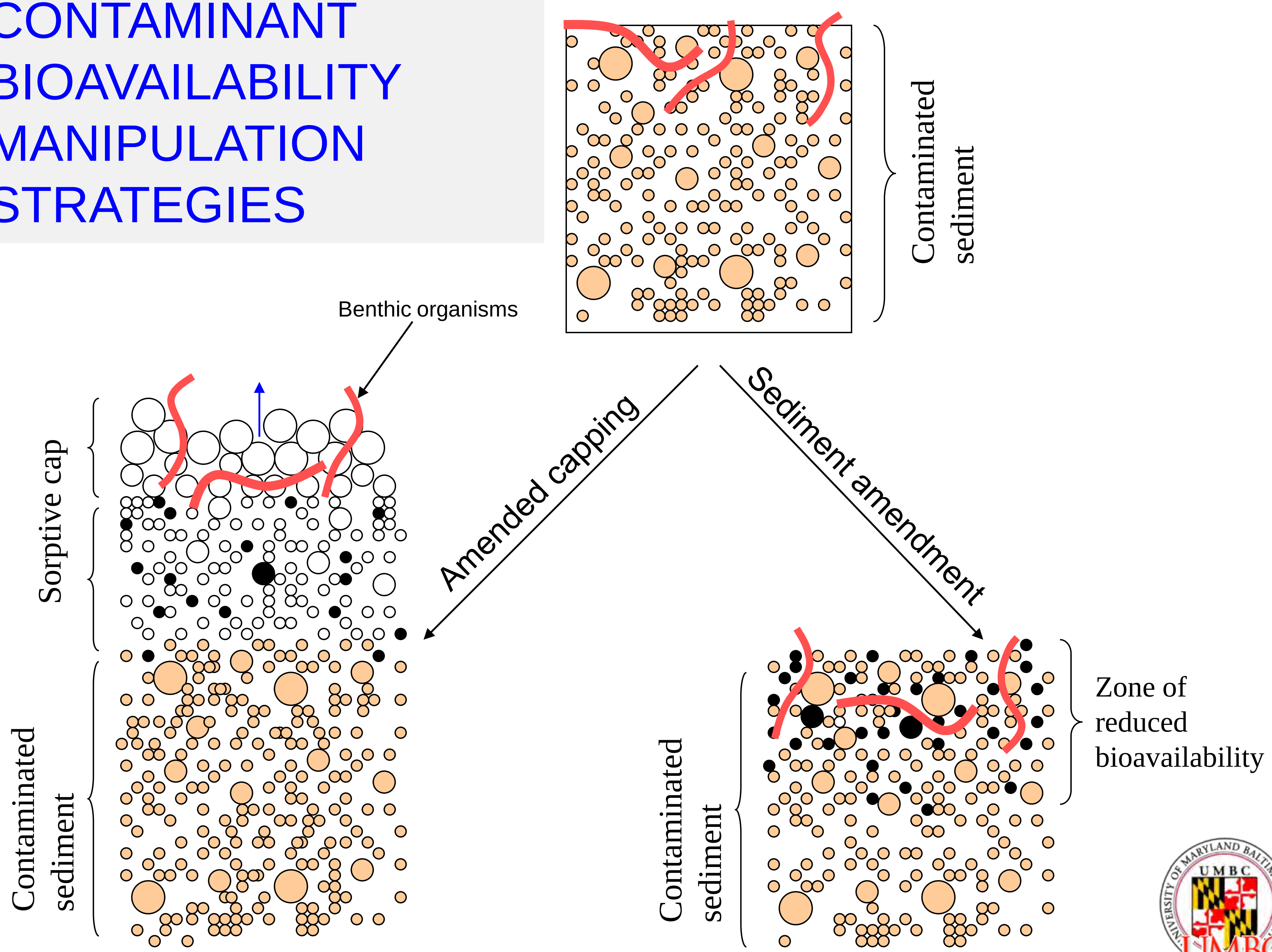
SEDIMENT AMENDMENT WITH CARBON



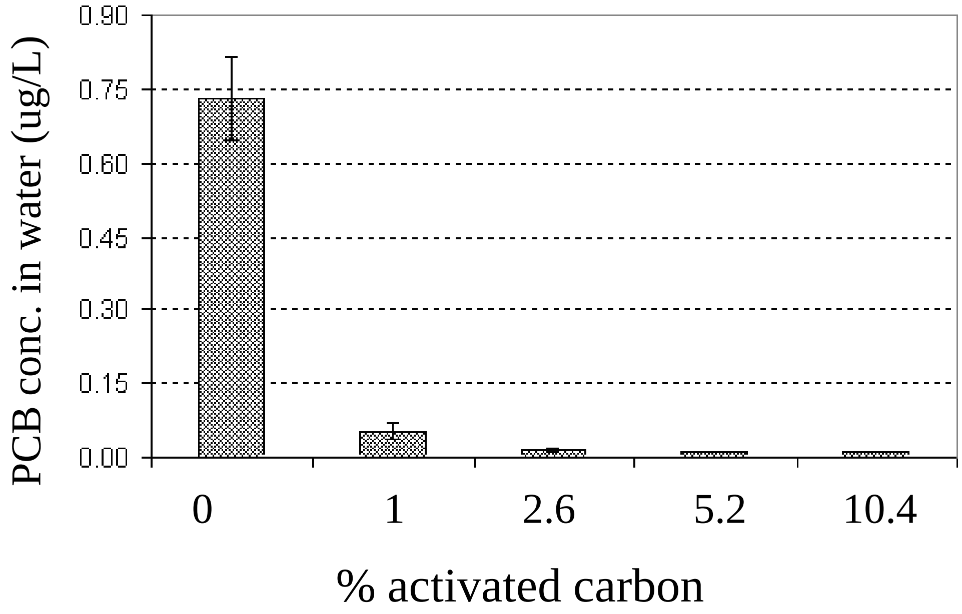
-Side view of aquarium 2 days after placing a layer of AC on sediment
-Carbon is slowly worked into the sediment through worm movement
-PCB accumulation in worms reduced by ~ 80%

Sun & Ghosh, ES&T 2007

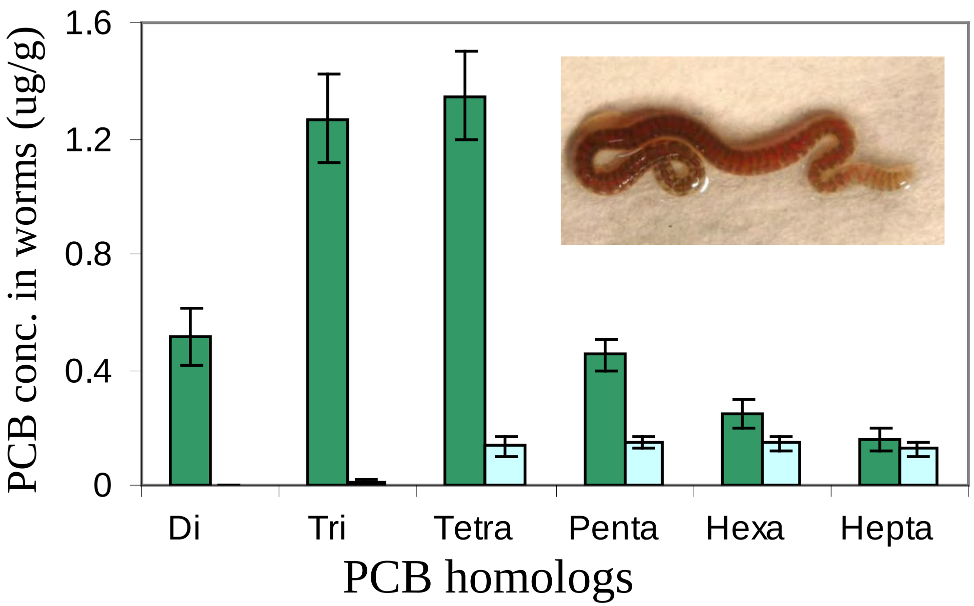
CONTAMINANT BIOAVAILABILITY MANIPULATION STRATEGIES



REDUCTION IN WATER AND WORM UPTAKE

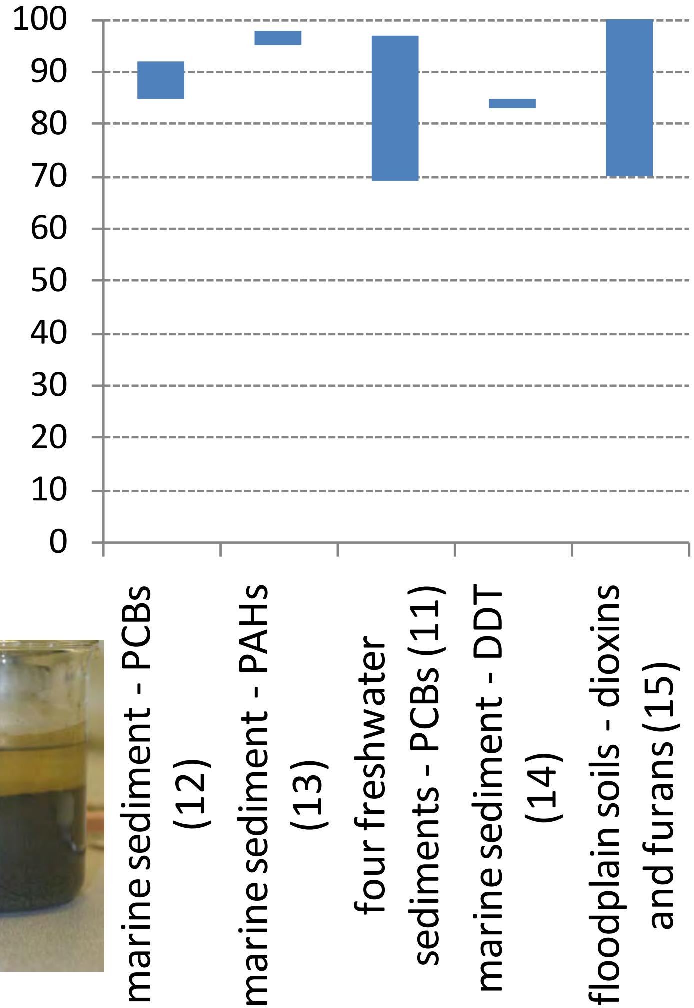


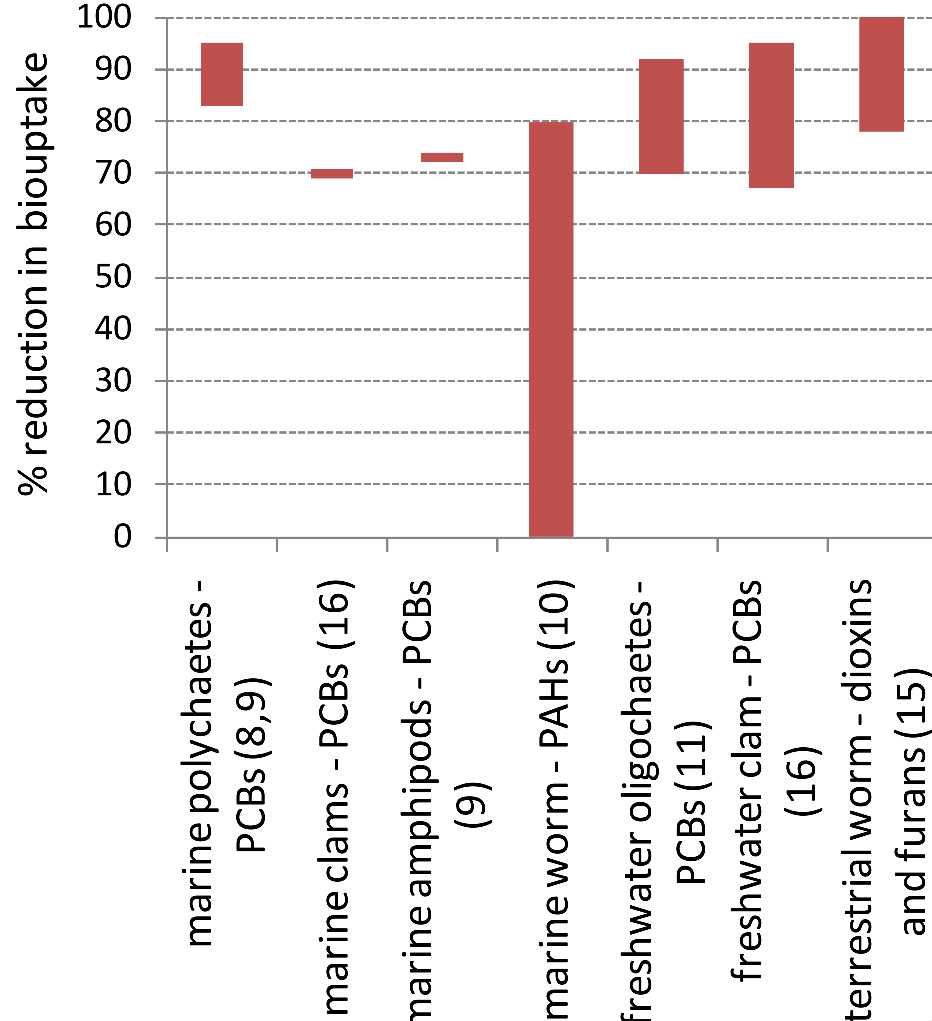
Pore water PCB concentration decreases with increasing dose of activated carbon



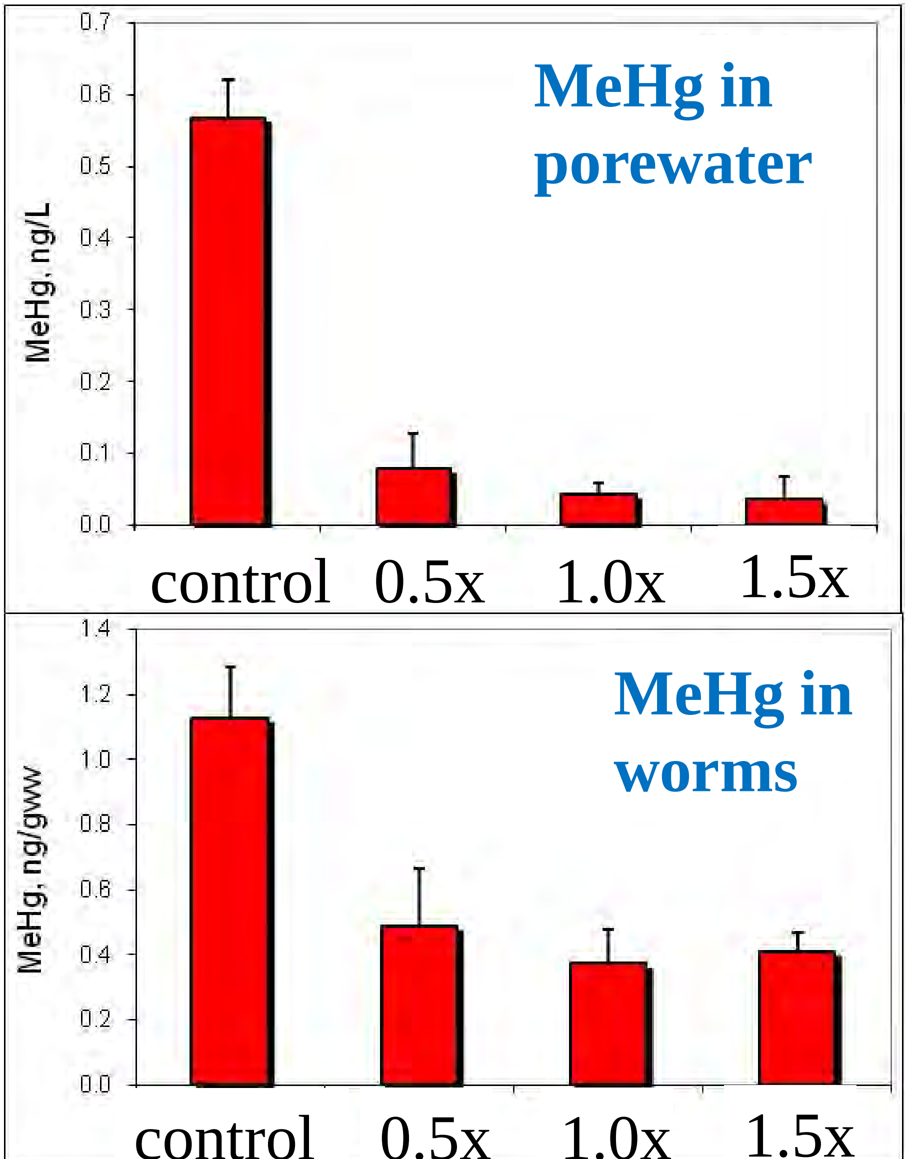
PCB uptake in freshwater worms reduced after amending sediment with activated carbon

RESULTS FROM SEVERAL LABORATORY STUDIES: ORGANIC CHEMICALS



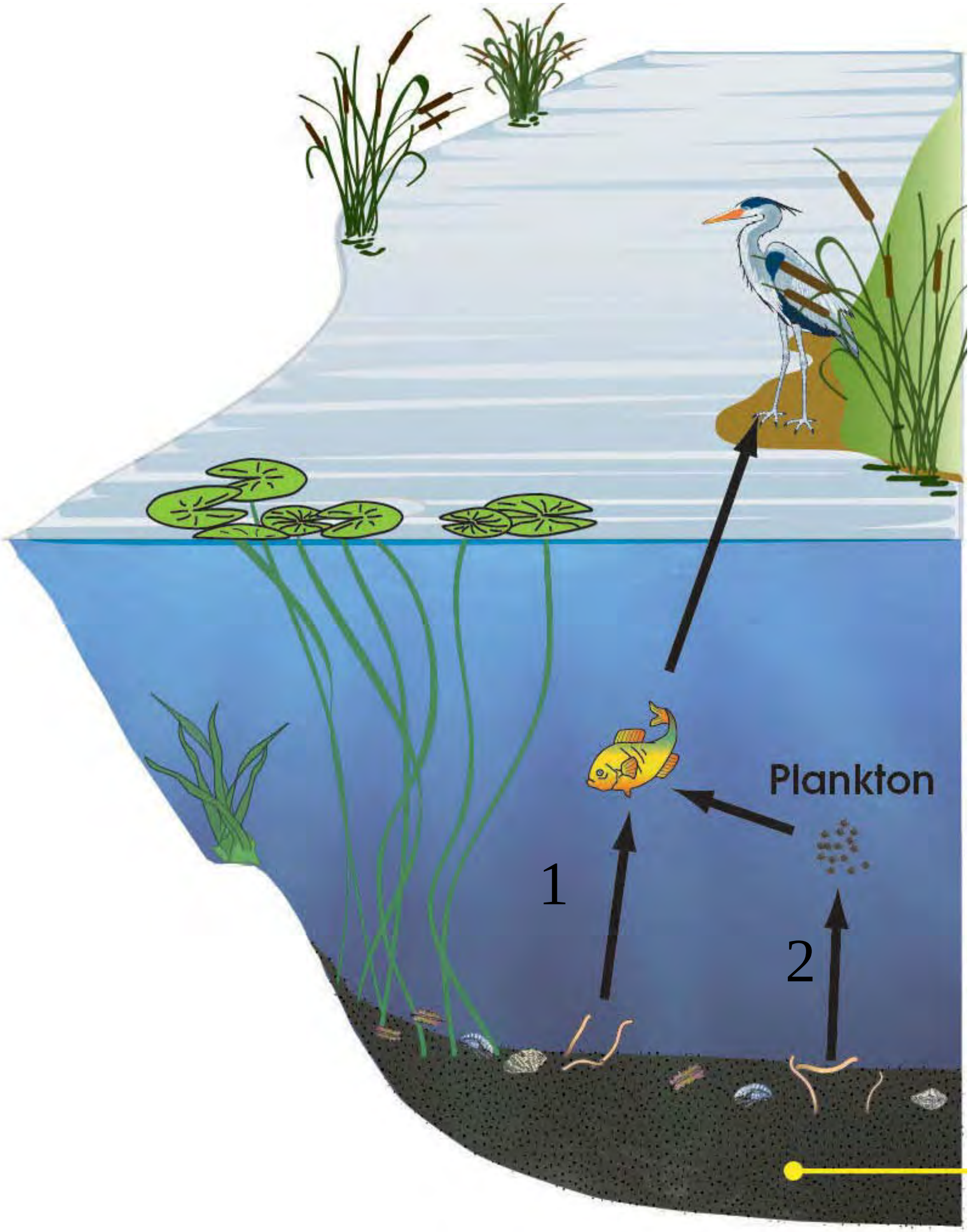


RESULTS FROM LABORATORY STUDIES: MERCURY AND METHYLMERCURY (CANAL CREEK)



- 3 doses of GAC: 0.5, 1, 1.5 times native TOC
- Pore water Me-Hg reduction by 86-92%
- Methylmercury reduction in worm tissue: 57-74%

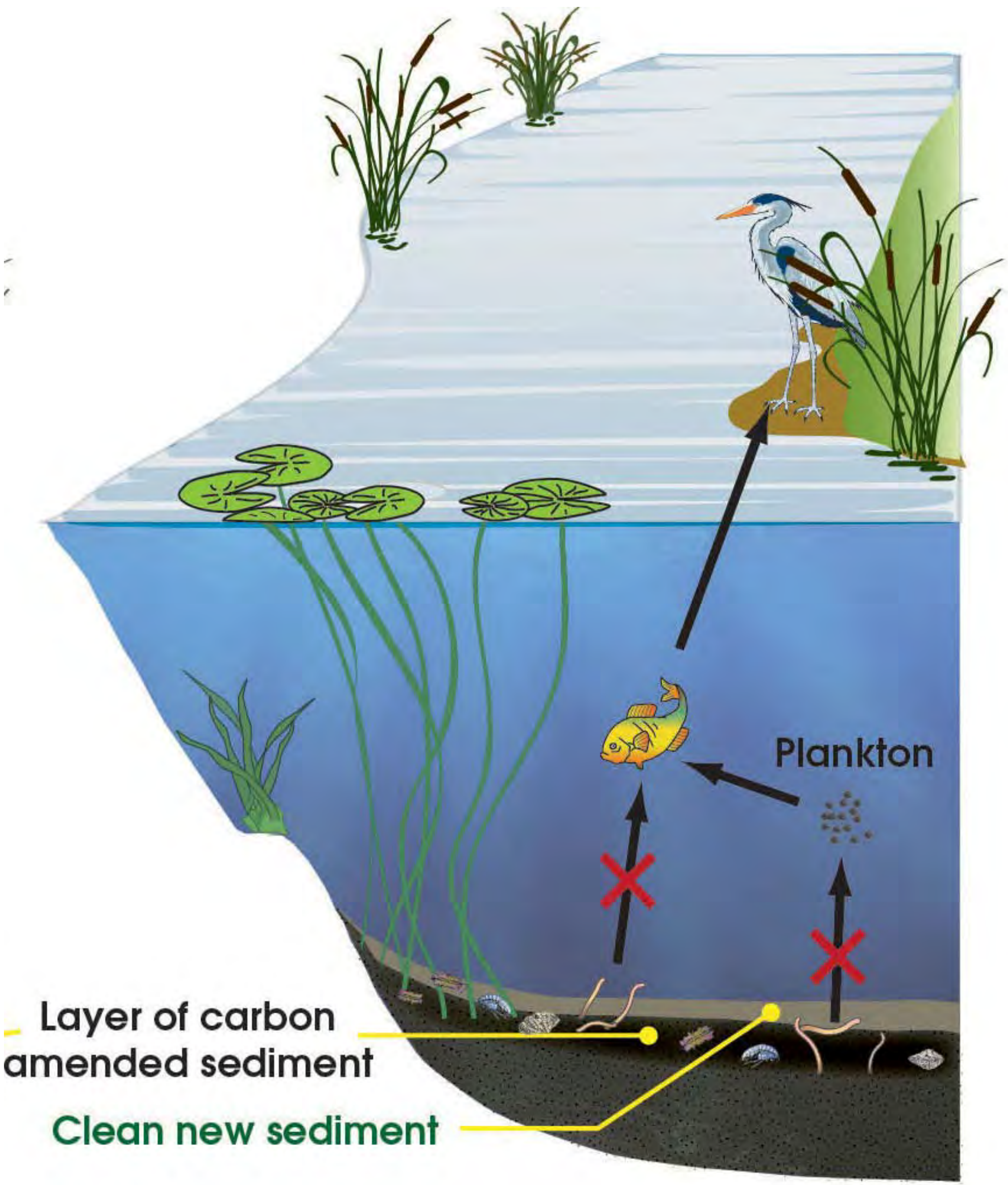
CONCEPTUAL MODEL: BEFORE TREATMENT



Legacy contaminants in exposed sediment contaminates the food chain through:

1) bioaccumulation in benthic organisms
2) flux into the water column, and uptake in the pelagic food web.

CONCEPTUAL MODEL: AFTER TREATMENT



Activated carbon amended to surficial sediments reduces contaminant exposure to food chain through:

1) Reduced bioaccumulation in benthic organisms

2) Reduced flux into water column and uptake in the pelagic food web.

3) In the long-term, the carbon amended layer is covered with clean sediment.

ONGOING DEMONSTRATION PROJECTS

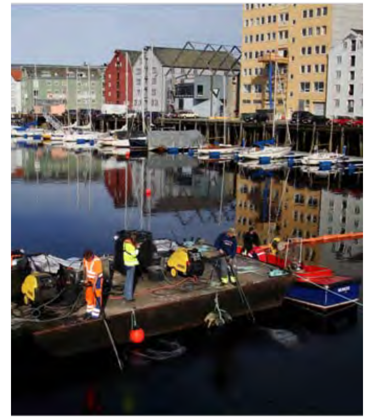
San Francisco Bay,
CA, USA, 2006

SLURRY INJECTION AND ROTOTILLER.

Grasse River,
NY, USA, 2006

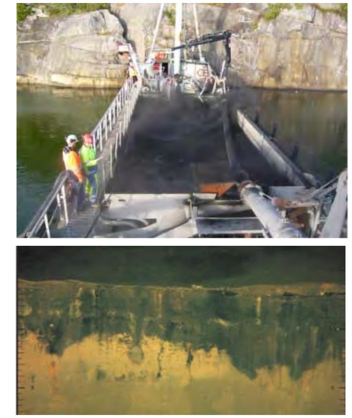
SLURRY INJECTION AND COVERED ROTOTILLER

Trondheim Harbor,
Norway, 2006



SLURRY INJECTION WITH AND WITHOUT CLAY

Grenlandsfjords,
Norway, 2009



ACTIVE CAP OF SITE CLAY AND ACTIVATED CARBON MIXTURE

Bailey Creek,
VA, USA, 2009

PELLETIZED CARBON DELIVERY (SEDIMITE)

Canal Creek,
MD, USA, 2010

PELLETIZED CARBON DELIVERY (SEDIMITE)

KEY MESSAGES

Amendment with AC will be most effective at:

- sites that are depositional in nature
- sites less prone to sediment erosion
- where native bioavailability of contaminants is high
- ongoing contribution from off-site sources have been controlled.

AC amendment provides several advantages over traditional methods:

- less disruption to benthic habitats in sensitive systems
- amenability to shallow or constricted locations
- potential for lower cost
- less concern about mobilizing buried contaminants

In-situ amendments can also be used in combination with other remedies:

- possible to incorporate AC into sediment caps
- apply AC during and immediately after a dredging hot spots to minimize aqueous contaminant release from resuspended sediments and residuals.

THE BIG PICTURE:

5% AC by dry wt in top 4” = 6 lb/sq. yd. = **30,000 lb/acre**
(equivalent to 2 mm sedimentation)

100 acre site: 3M lb of AC (<1% of US annual production of AC)

Material cost at $1.5/lb cost of AC = **$45,000/acre**
Application cost will depend on the method utilized

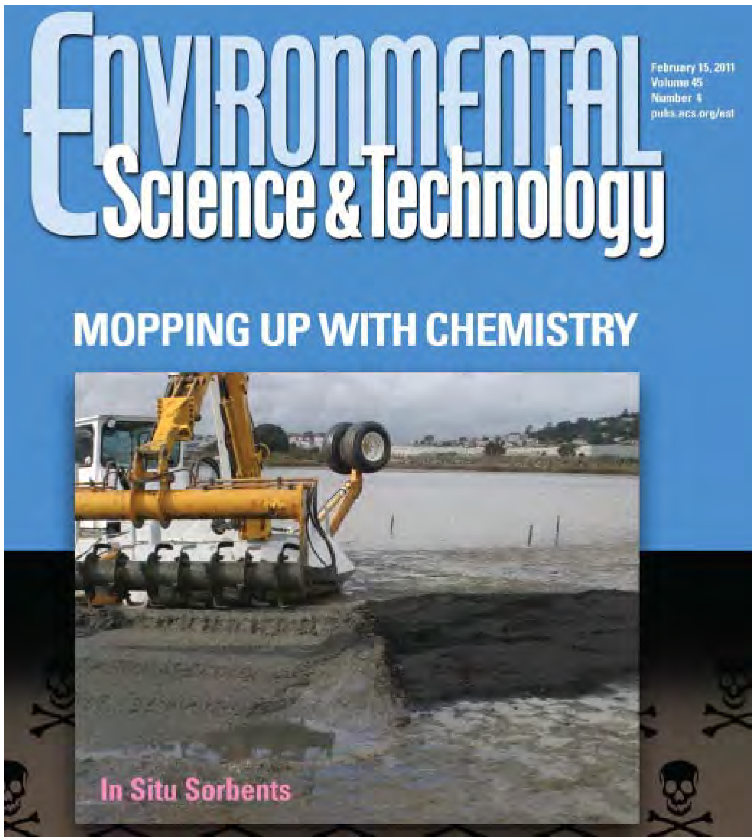
Promising considerations:

- Application of small increments over multiple years to incorporate into annually deposited sediments
- Use of activated biochars from agricultural residue can provide additional opportunity for carbon sequestration
- Low-impact delivery methods

RECENT FEATURE ARTICLE IN ES&T:

In-situ Sorbent Amendments:
A New Direction in Contaminated Sediment Management

Environ. Sci. Technol. 2011, 45, 1163–1168



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FEATURE
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In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management†

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Disclosure statement:

Upal Ghosh is a co-inventor of two patents related to the technology described in this paper for which he is entitled to receive royalties. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, UG is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

Bioavailability Reduction by Direct Amendment of Activated Carbon: A Demonstrated In Situ Sediment Immobilization Treatment Technology

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James Quadrini (Anchor QEA, LLC, Montvale, New Jersey, USA)
Gerard Cornelissen (Norwegian Geotechnical Institute, Stockholm, Norway)

Background/Objectives. In situ treatment via contaminant immobilization is an innovative sediment remediation approach that involves introducing sorbent amendments such as activated carbon (AC) into contaminated sediments to alter sediment geochemistry, increase contaminant binding, and therefore decrease bioavailability. Encouraged by bench-scale data suggesting that porewater concentrations and bio-uptake of hydrophobic contaminants can be reduced between 70 and 98 percent at AC doses similar to the native organic carbon content of sediment, more than ten field-scale demonstration projects spanning a range of environmental conditions have now either been completed or are currently underway in the United States and Norway.

Approach/Activities. Field-scale projects have demonstrated the efficacy of full-scale in situ sediment immobilization treatment technologies to reduce the bioavailability of organic and/or metal contaminants. The basic technology involves placement of targeted amendments using a range of options, all of which have now been demonstrated at the field scale, including:

- Mixing amendments with sand and mechanically placing the blended materials on the sediment surface
- Hydraulic slurry placement of the amendments onto the sediment surface (e.g., in a clay mixture)
- Sequentially placing amendments (mechanically or hydraulically) under a thin sand cover
- Mechanical mixing of amendments into shallow sediment
- Broadcast application of amendments in a pelletized form to improve settling characteristics—the pellet matrix subsequently settles onto the sediment surface and degrades, allowing the amendment to slowly mix into surface sediments through bioturbation

Results/Lessons Learned. In situ immobilization treatment techniques are less energy-intensive, less disruptive to the environment, and can be less expensive than conventional remedial technologies such as dredging and capping. This technology can also significantly reduce ecosystem exposure by binding contaminants to organic or inorganic sediment matrices. This presentation examines the following:

- Potential benefits of in situ immobilization treatment relative to other technologies
- Site conditions that are particularly promising for in situ immobilization treatment
- The role of pilot studies to verify the efficacy of the technology in different settings
- Potential ecological effects of amendments to benthos and other aquatic communities, and how potential impacts may be mitigated
- Lessons learned on the most promising application options
- Recommended long-term remedy effectiveness monitoring

Grasse River, NY
Activated Carbon Pilot Study

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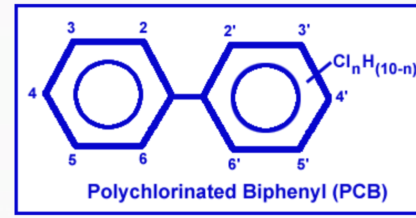
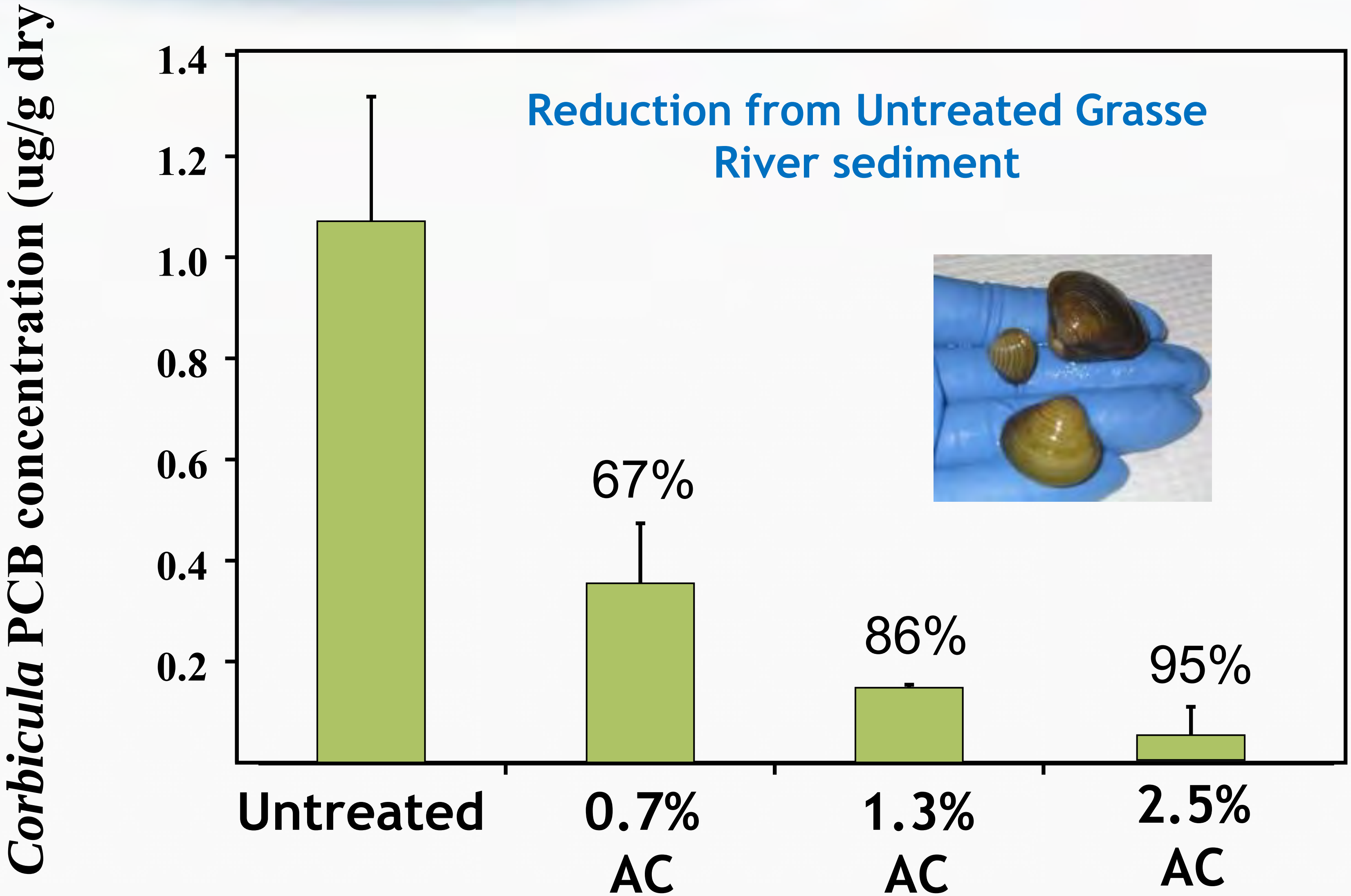
Grasse River, New York, USA



- Massena, NY
- Historic use & release of PCBs

- Near Saint Regis Mohawk Tribe
- Fish consumption advisory
- Managed land sources at plant site
- Past remedial action includes sediments—1995 NTCRA

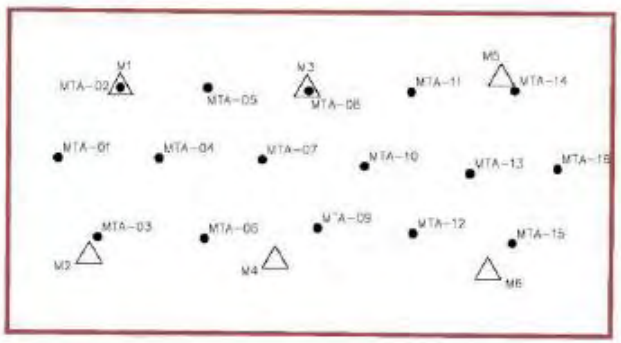
Stanford Lab Bioaccumulation Study



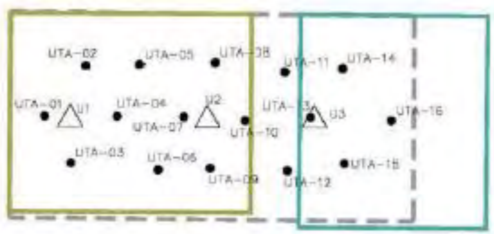
DELIVERY DEVICES USED AT GRASSE RIVER, NY

Tine injection system
Designed and built by Brennan with inputs from collaborators

Injection and mixing in an enclosed rototiller
Designed and built by Brennan with inputs from collaborators

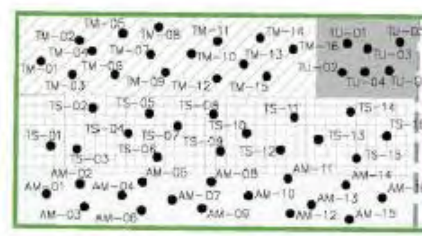


Mixed Tiller (75’ x 100’)



Tine Sled (50’ x 60’)

Unmixed Tiller (50’ x 50’)



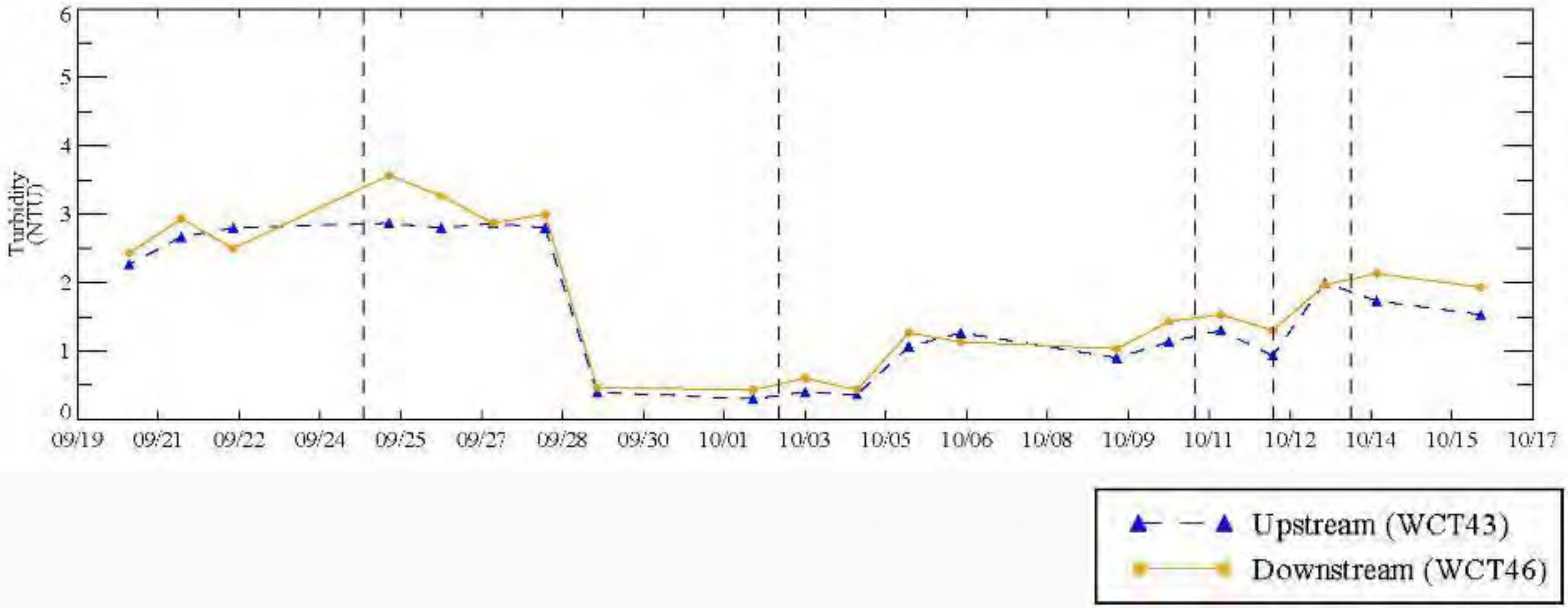
Initial (50’ x 100’)

Target dose of activated carbon = 0.5x TOC in surficial sediments (+50% safety factor)

Grasse River ACPS
Baseline & Long-Term Monitoring

Parameter	Baseline (Aug/Sep '06)	After Placement (Oct '06)	Year 1 (Fall '07)	Year 2 (Fall '08)	Year 3 (Fall '09)
Carbon in sediment cores (BC)	√	√	√	√	√
Field PCB biouptake	√		√	√	√
Lab PCB biouptake	√		√	√	√
Equilibrium	√		√	√	√
Desorption	√		√	√	
Benthic community	√		√	√	√
Erosion potential	√		√	√	
Impact of AC on aquatic plant growth					√

Fall 2006 Water Quality Monitoring Results

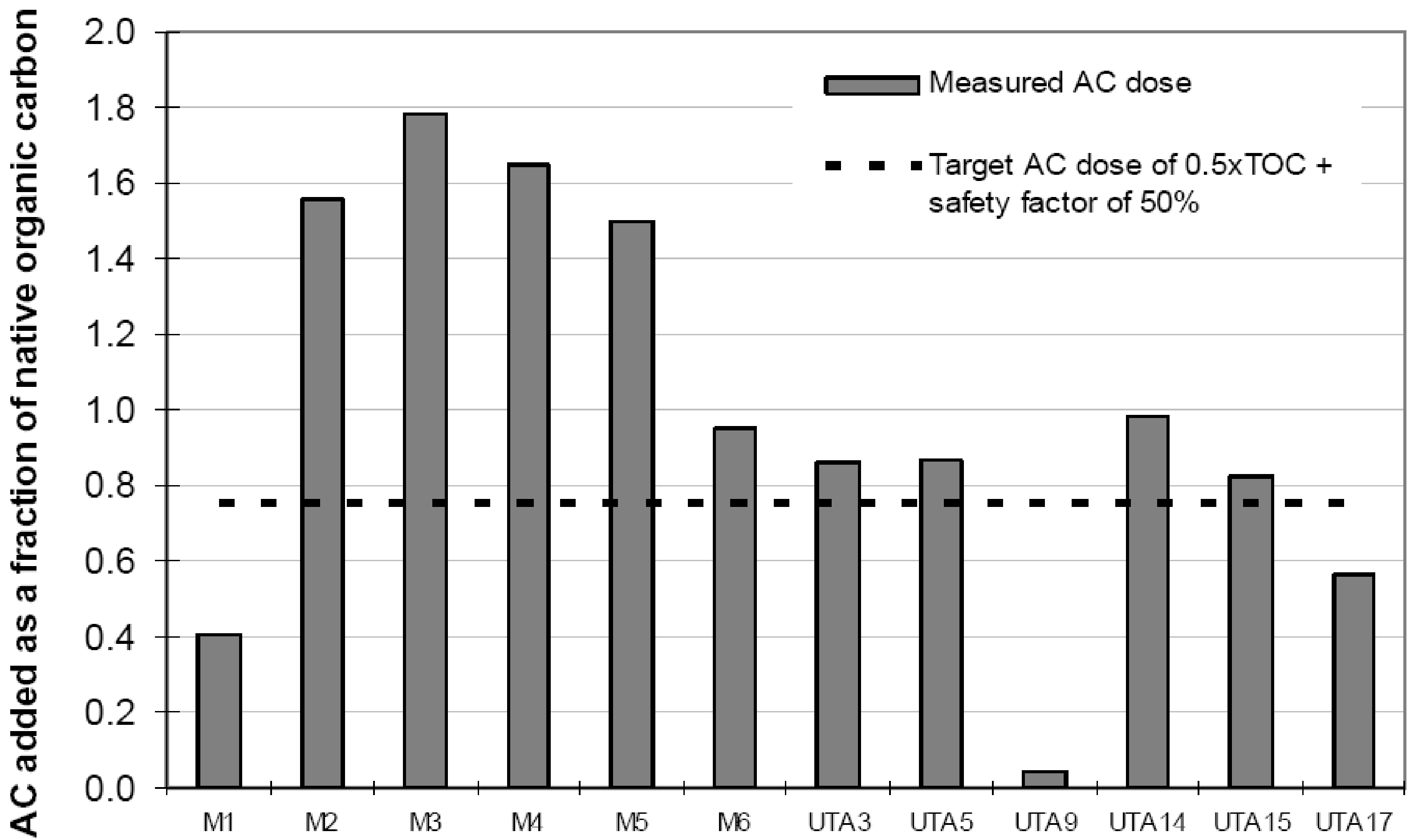


- **Water column PCB monitoring during construction**
  - No measurable changes in water column PCB concentrations observed downstream of the study area during application

Data from Alcoa

Post-Application Core Sampling

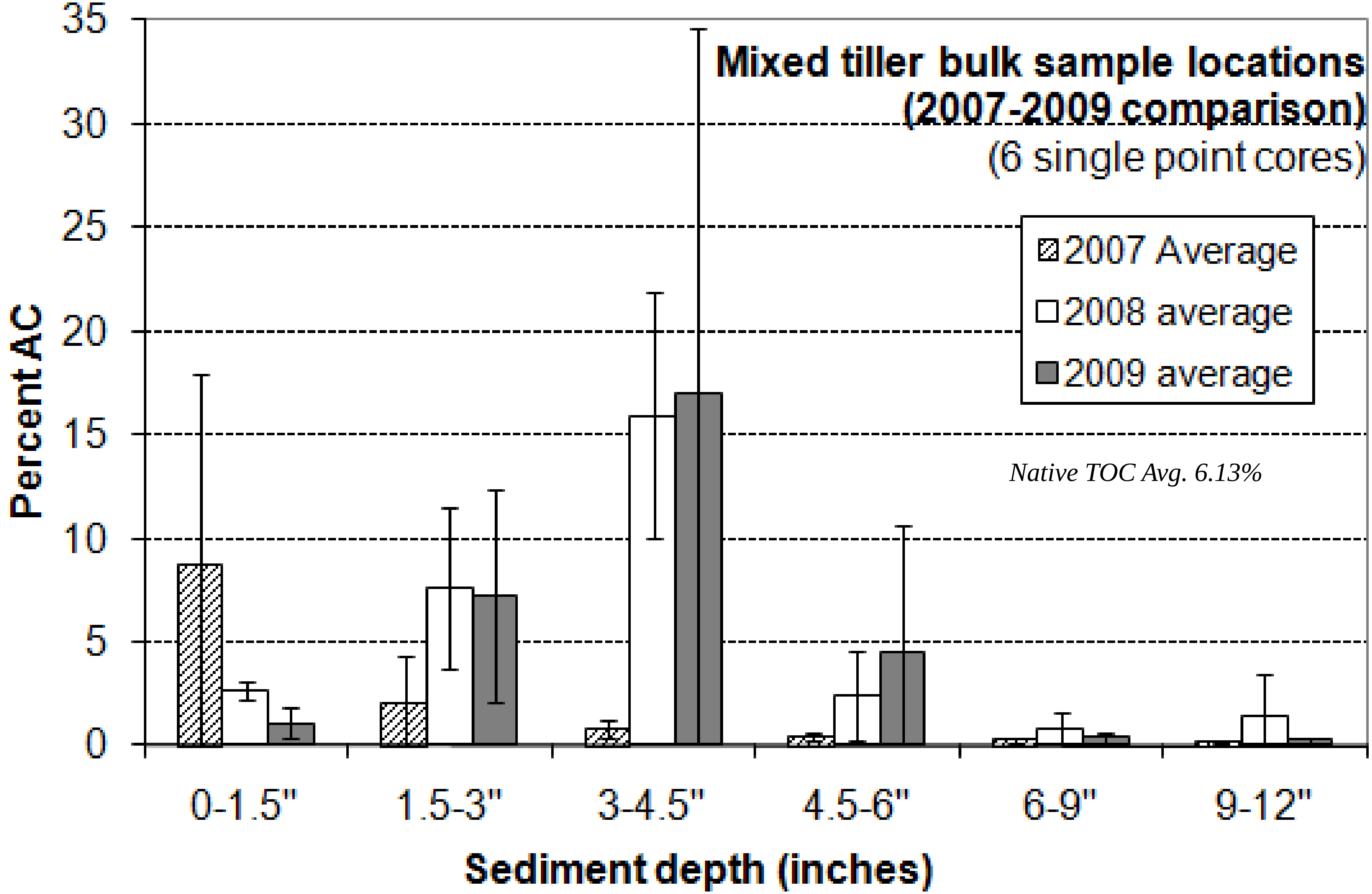
Dose of AC achieved in sediment 2007 sampling data



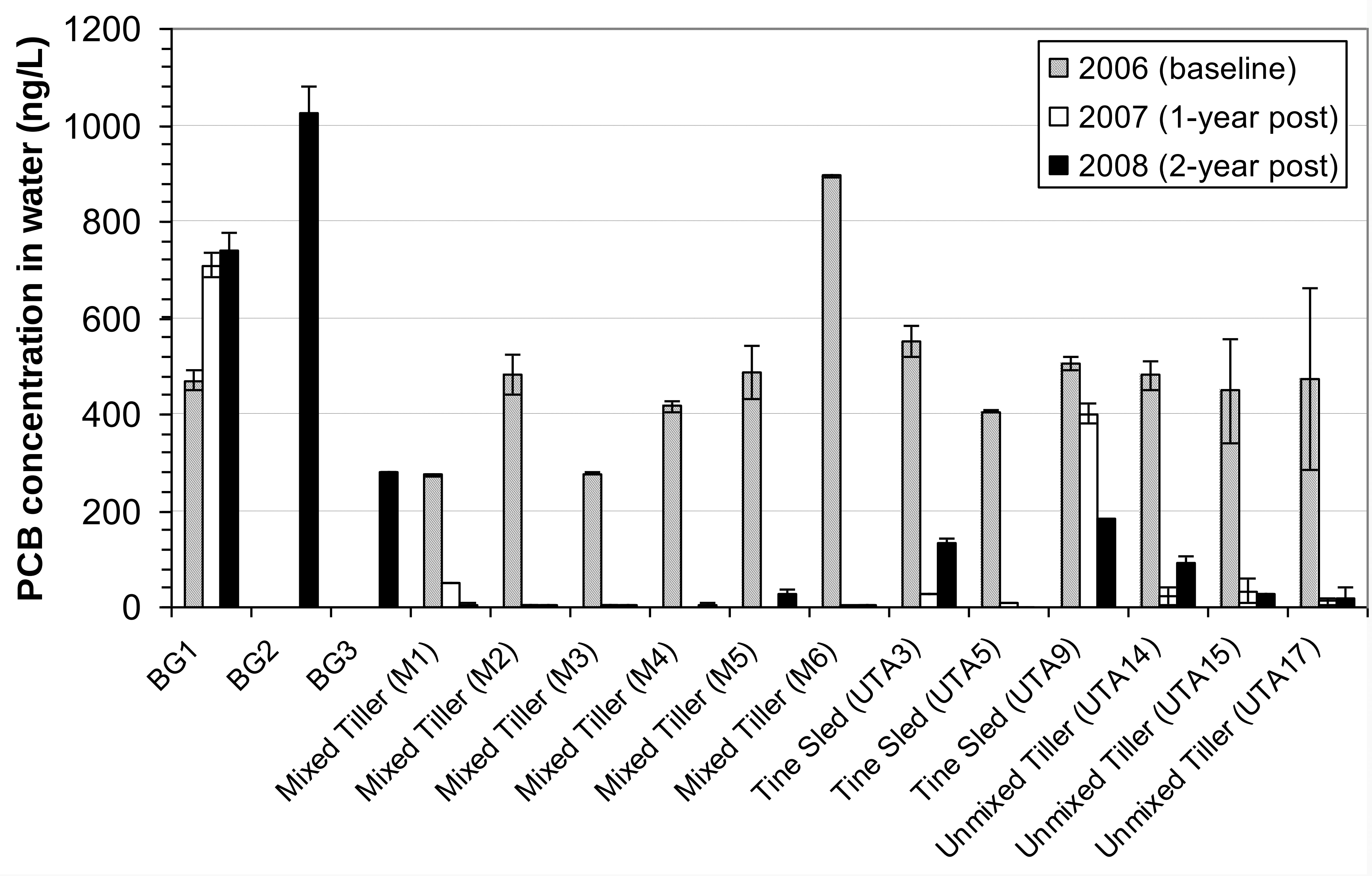
- Measured AC addition achieved at sampling sites compared to the target dose of half of native TOC plus safety factor of 50%

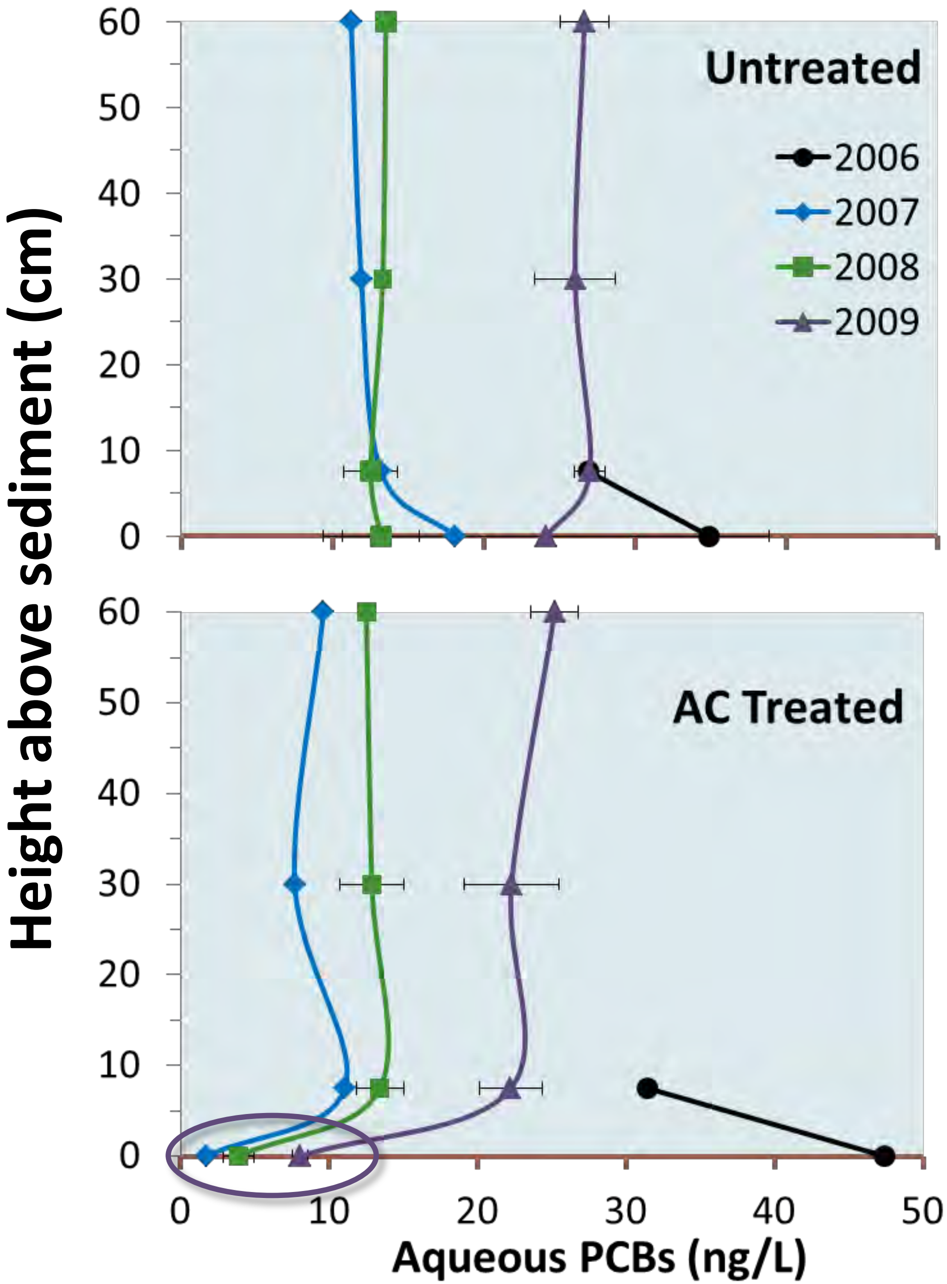
Data from Alcoa

Carbon Profile with Time



Aqueous Equilibrium



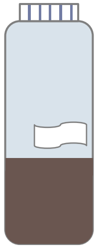


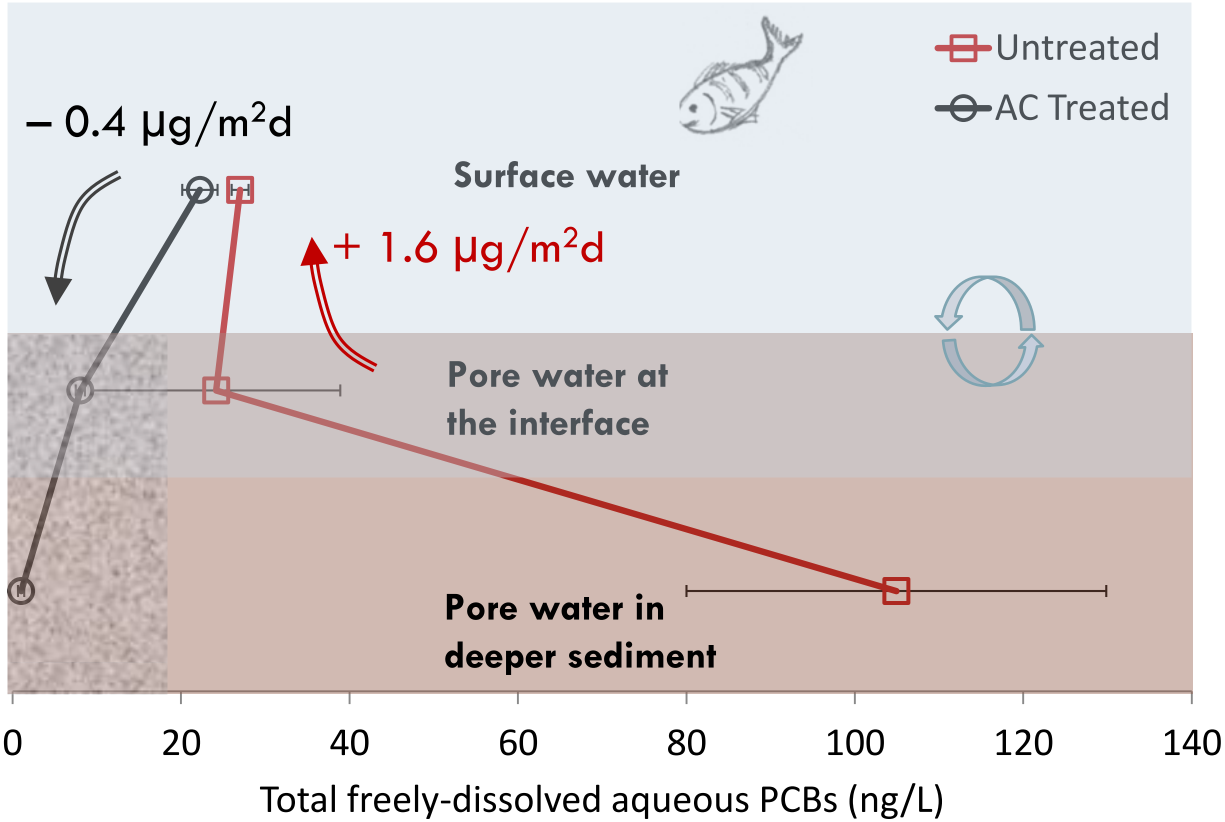
PCB IN WATER BASED ON IN-SITU PASSIVE SAMPLERS

Reduced aqueous PCB on sediment surface at AC treated sites compared to overlying water

Data from UMBC, Beckham & Ghosh

Pore water – Surface water PCB Gradient in Grasse River, 2009

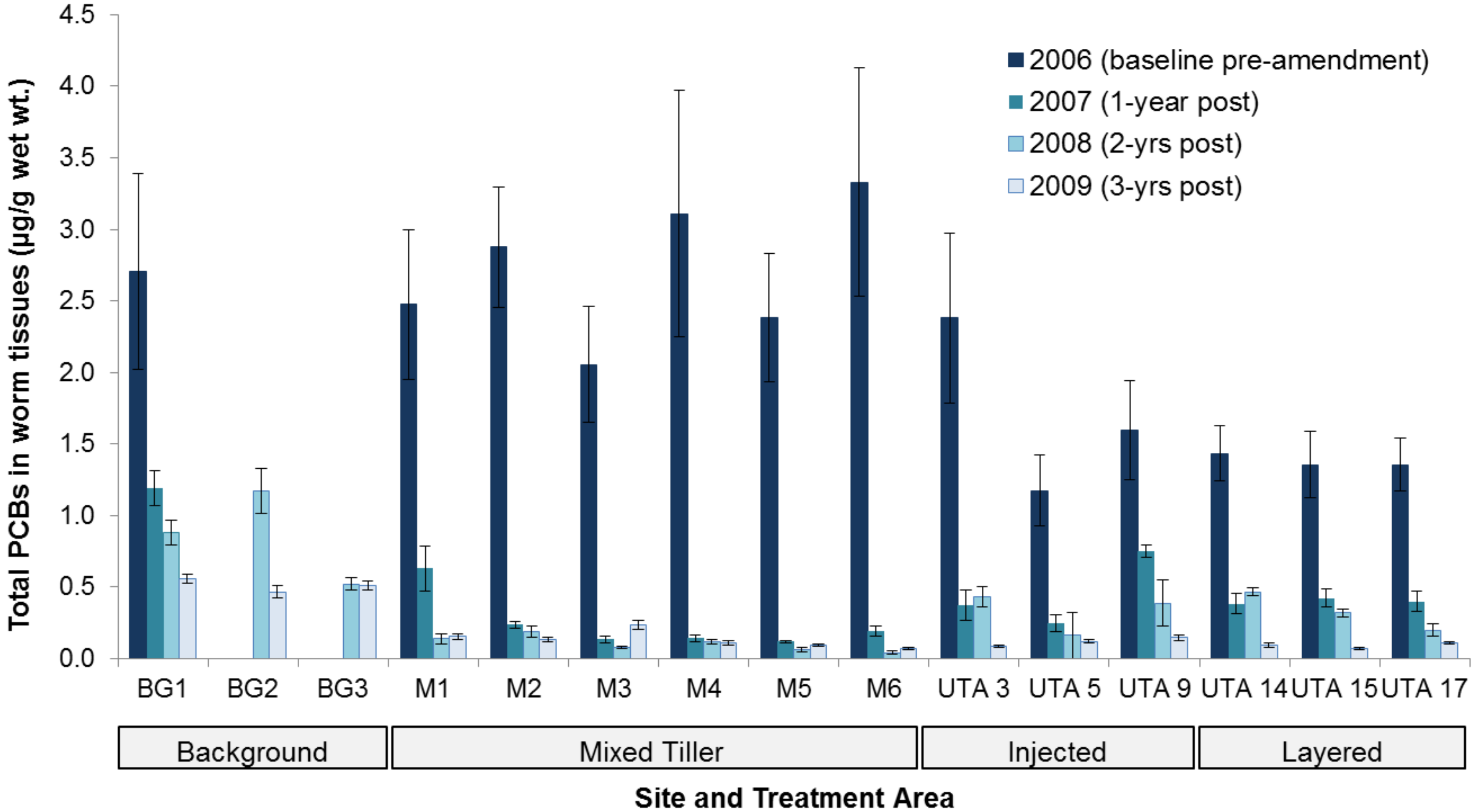




$$\text{Flux } (\mu g/m^2 d) = k_f(C_{pw} - C_{sw})$$

Data from UMBC, Beckham & Ghosh

Laboratory Bioaccumulation in *L. variegatus*



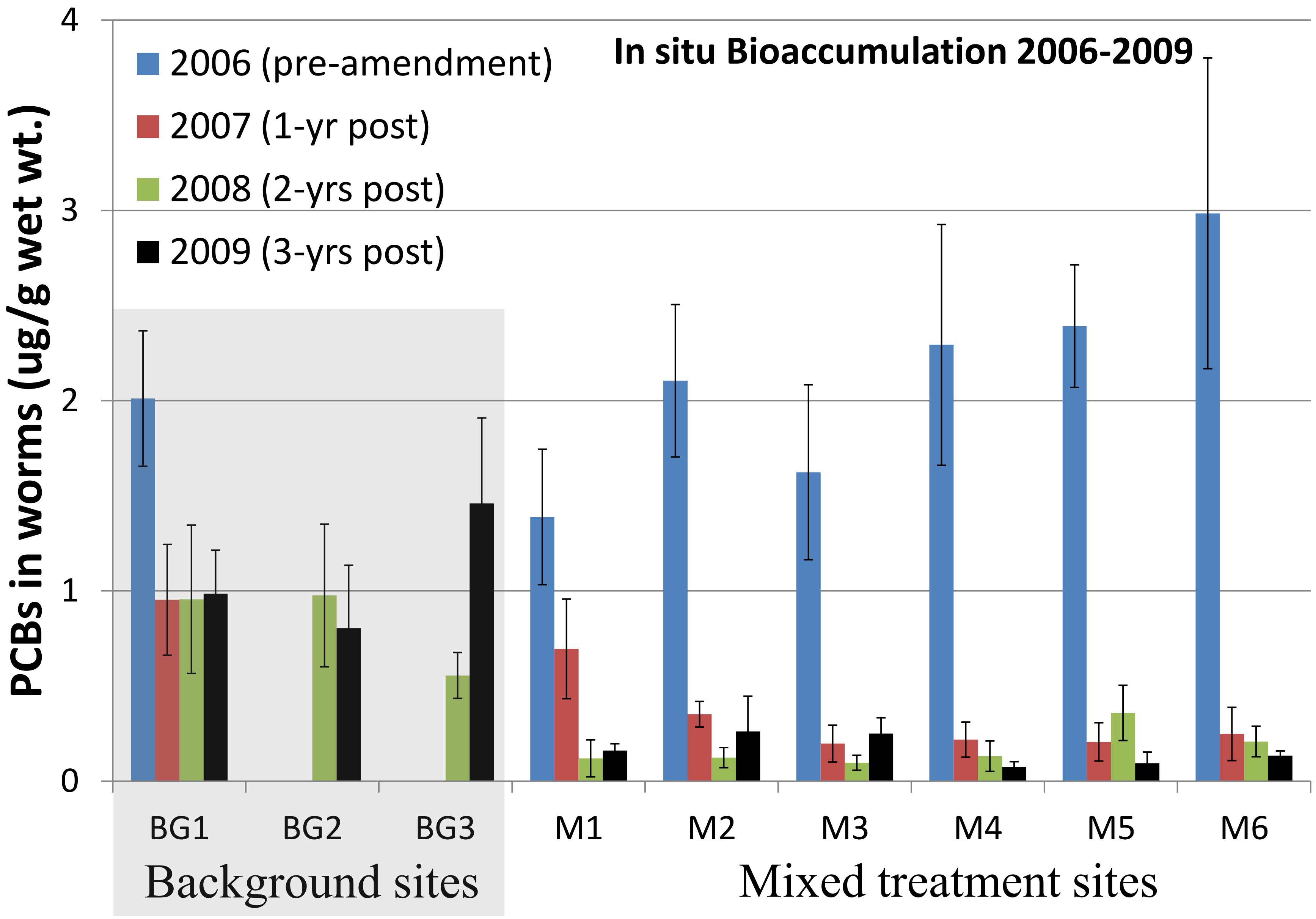
Data from UMBC, Beckham & Ghosh

IN-SITU PCB MONITORING STUDIES

In-river deployment of field exposure cages with *L. variegatus* for baseline study (method adapted from Burton et al. 2005)

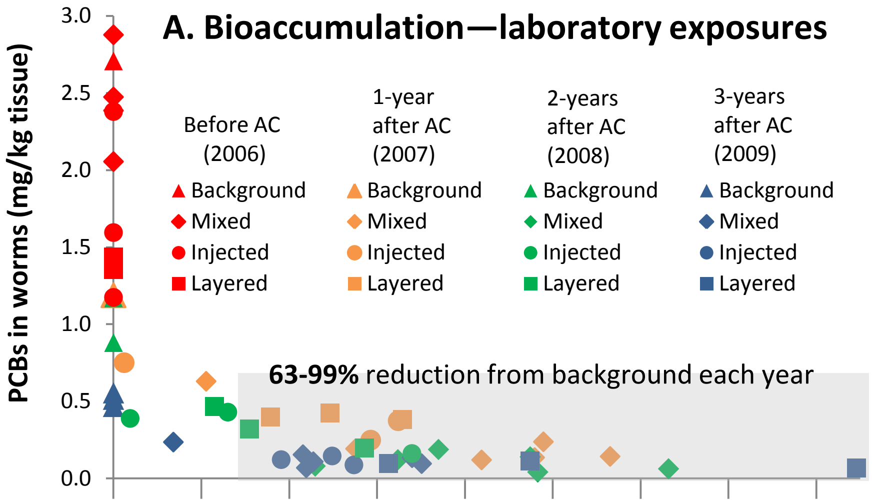
PCB IN L. VARIEGATUS IN-SITU EXPOSURE

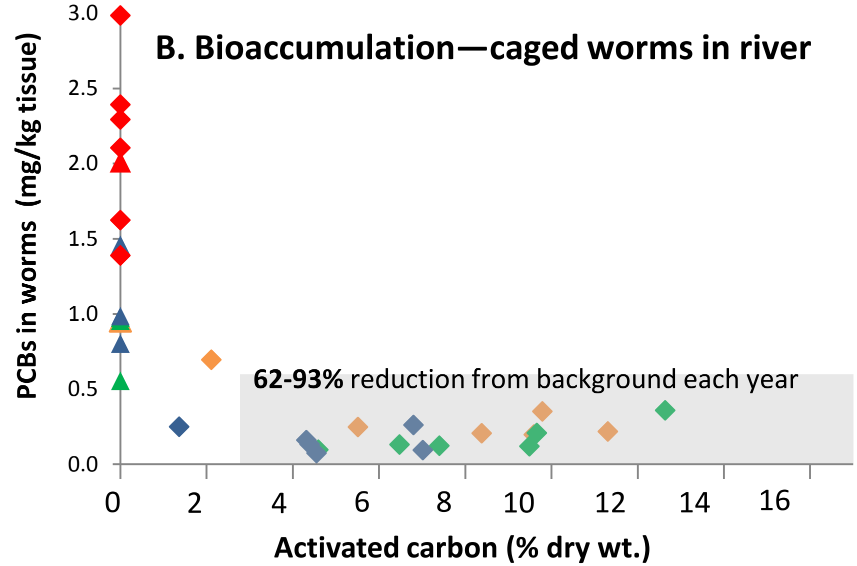
Data from UMBC, Beckham & Ghosh

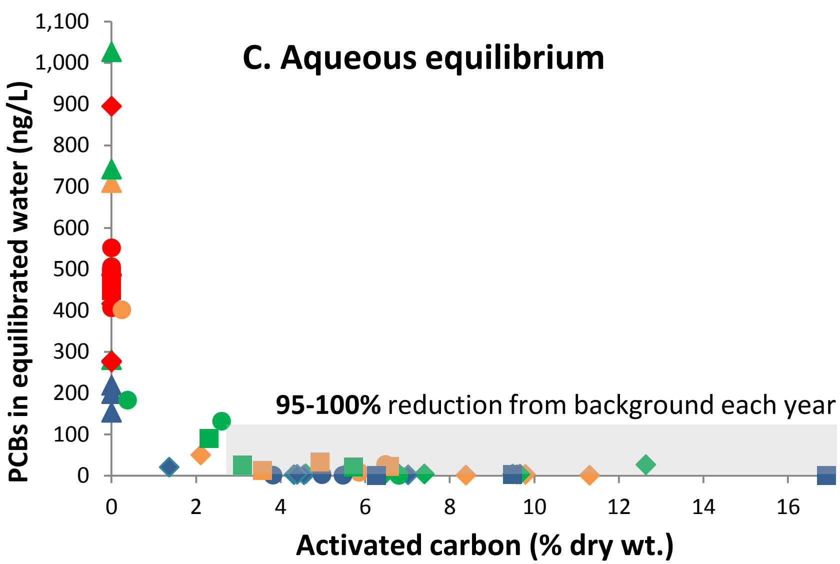


- % reduction over 3 years: 46% in BG sites and 92% for Mixed Tiller sites

PCB IN WORMS AND WATER VS. CARBON DOSE



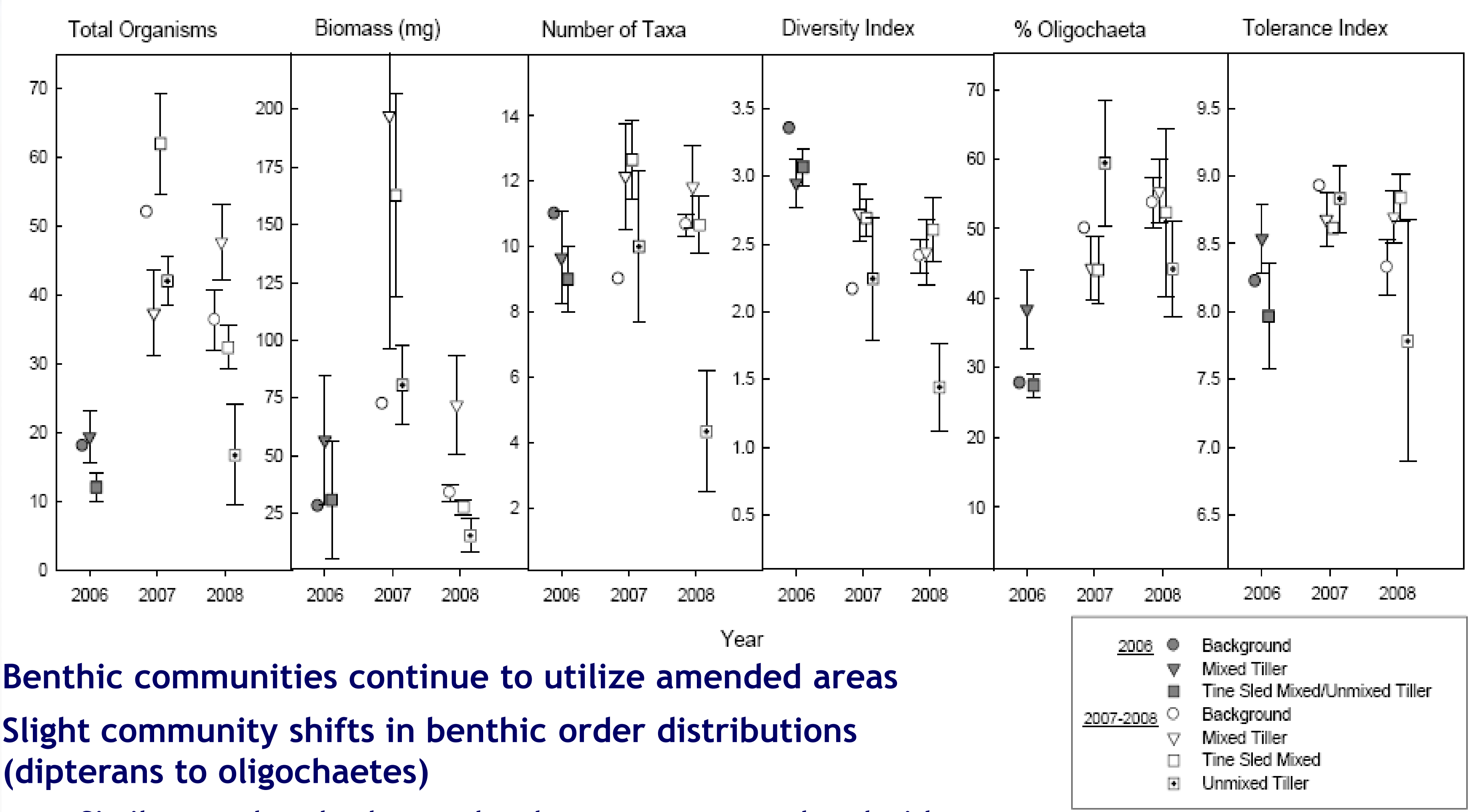




- Reduced uptake in field plots with increasing AC dose
- **> 90% reduction for all treatment sites by 2009 for AC dose >4%**
- Little incremental benefit above 5%AC
- Tighter range in aqueous PCBs compared to worms

Data from UMBC, Beckham & Ghosh

Benthic Invertebrate Monitoring



- Benthic communities continue to utilize amended areas
- Slight community shifts in benthic order distributions (dipterans to oligochaetes)
  - Similar trends at background and treatments, correlated with temporal variability in grain size
- Possible 2008 benthic community effect in Unmixed Tiller area

Data from Alcoa

Moving forward

- Carbon amendments appear to be promising enough for serious consideration in remedies
- AC can be applied to sediment at the field scale
- AC remained in place 3 years after placement
- Reductions in porewater PCB levels & desorption
- Reductions in tissue PCB levels
- No major changes to benthic community due to amendment
- Over time, the AC-amended sediment is covered with new sediment deposits
- Successful pilot scale demonstration of reduction in bioavailable PCBs in the sediments

Acknowledgements

Young Chang, EPA Region 2, Grasse River Study Area RPM

Larry McShea, Alcoa Project Manager

Drs. Upal Ghosh and Barbara Beckingham University of Maryland, Baltimore County

THANK YOU FOR YOUR ATTENTION TODAY

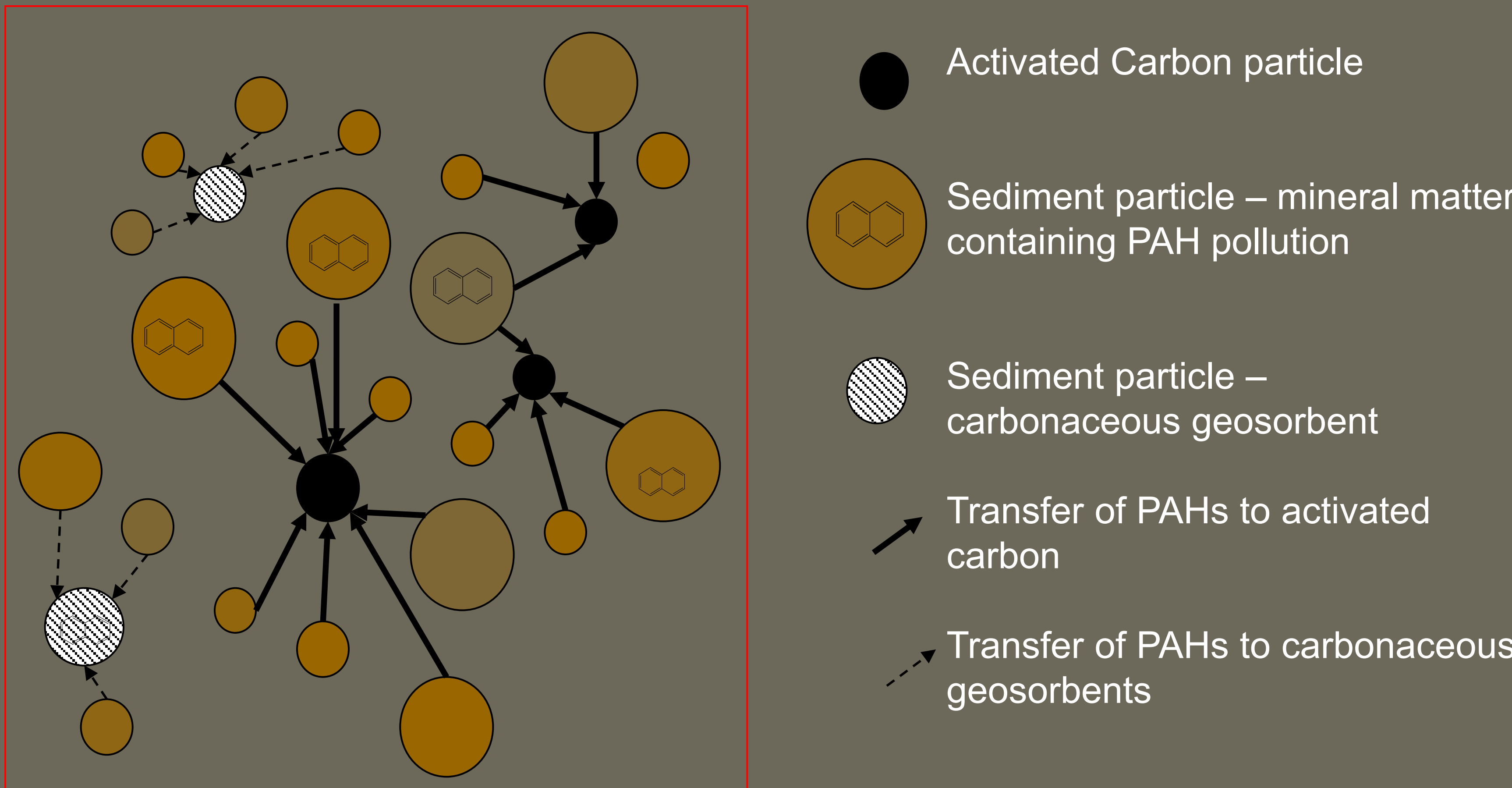
In-situ sediment remediation through activated carbon amendment: Trondheim Harbour and other field trials

Amy Oen[1], Gerard Cornelissen[1,2,3]

Marie Elmquist[1], Sarah Hale[1], Katja Amstätter[1], Espen Eek[1], Gijs Breedveld[1], Morten Schaanning[4], Jenny Hedman[2], Gøran Samuelsson[2], Jonas Gunnarsson[2]

[1] Norwegian Geotechnical Institute (NGI), Norway
[2] Stockholm University, Sweden
[3] Universitetet for miljø og biovitenskap (UMB), Norway
[4] Norwegian Inst for Water Research (NIVA), Norway

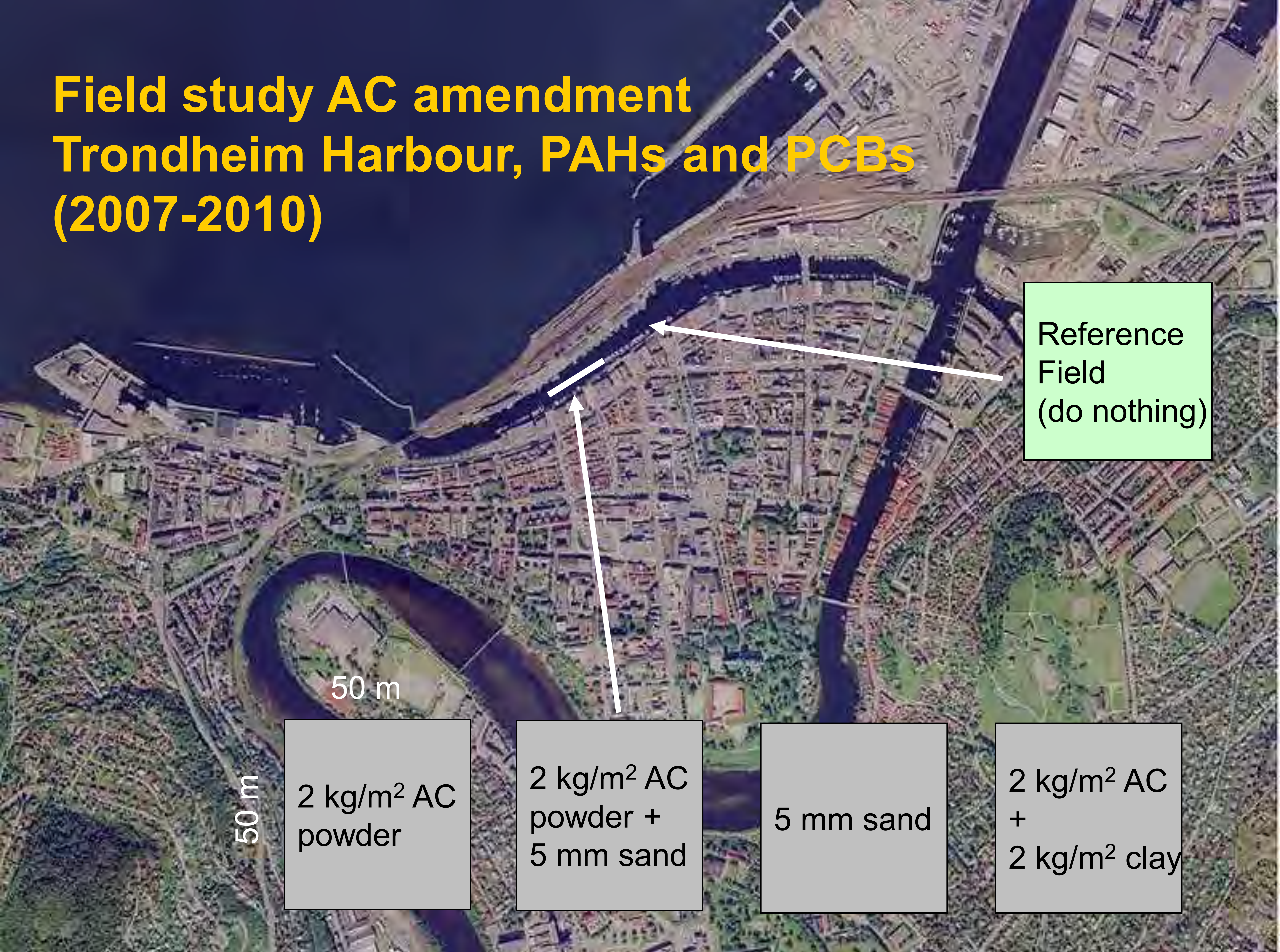
Principle of in-situ amendment



Transfer from polluted sediment particles to added activated carbon

Hale and Werner, 2010

Field study AC amendment Trondheim Harbour, PAHs and PCBs (2007-2010)

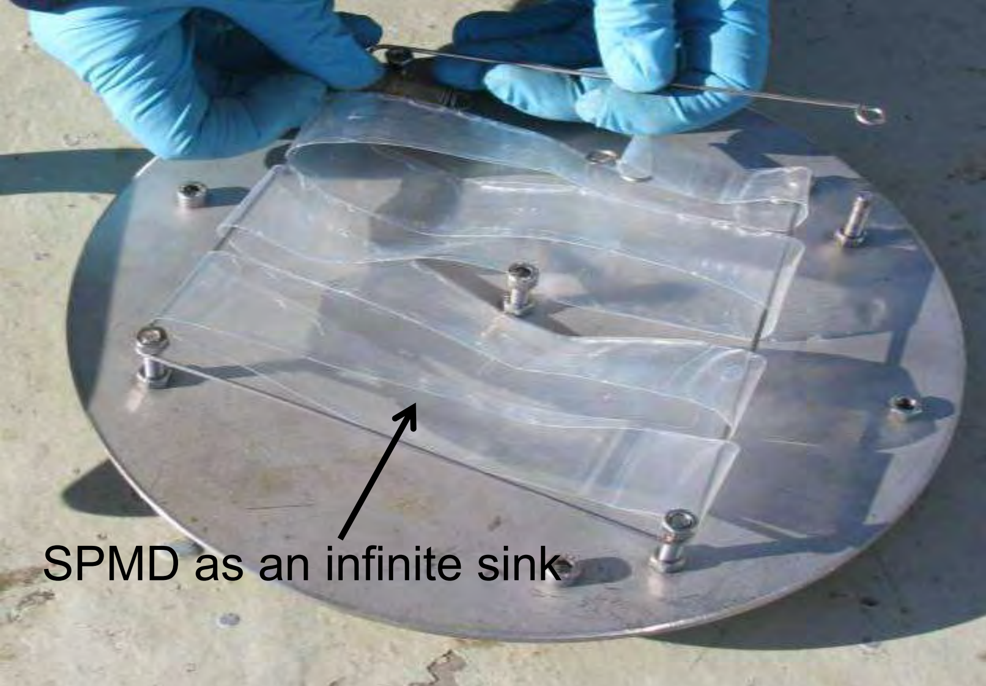


Implementation

Powder AC (0.02 mm)
AC:clay (1:1) or AC was mixed with 10% salt

1:1 AC:bentonite suspension after 1 day

1:1 AC:bentonite suspension after 5 months

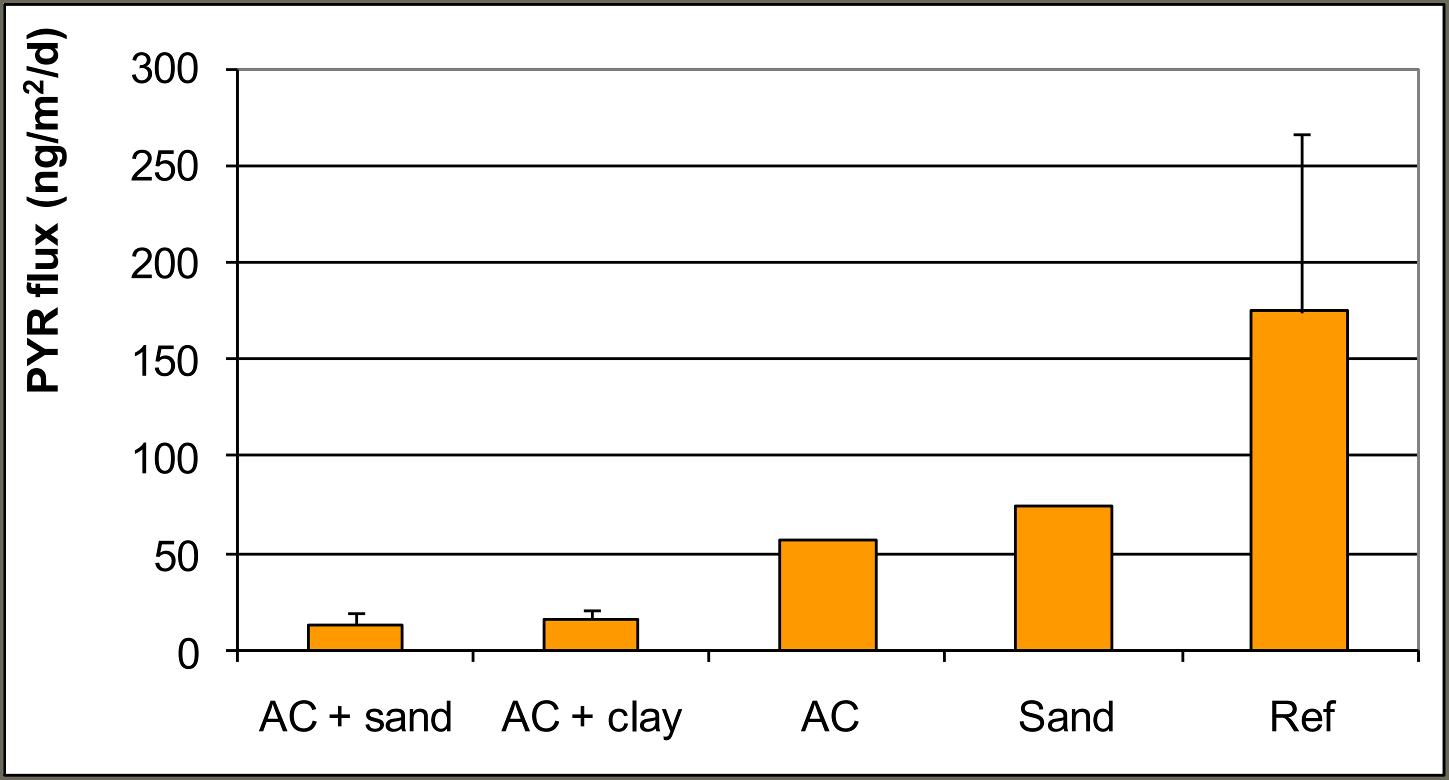

SPMD as an infinite sink


Benthic flux chambers
After deployment


Underwater camera
V5 HG5 249HD+2 CA-45 02FEB07
D5 0015.4MS 05C 14:10:30
Eek et al. 2010, Environ. Sci. Technol, 44, 17, 6752


SPMD after deployment

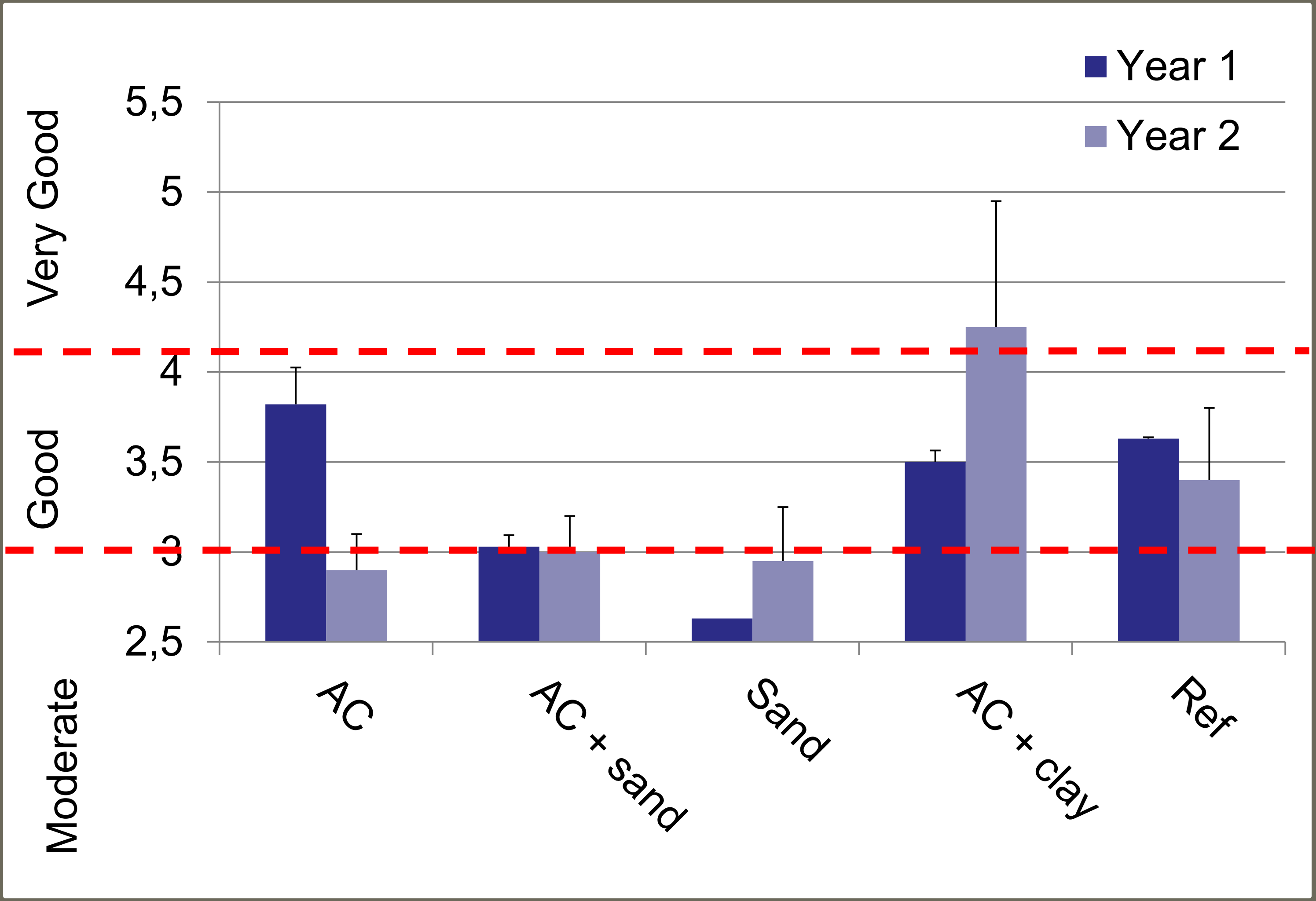
Results: Chemical - Pyrene flux from sediment



Factor 3-10 reduction

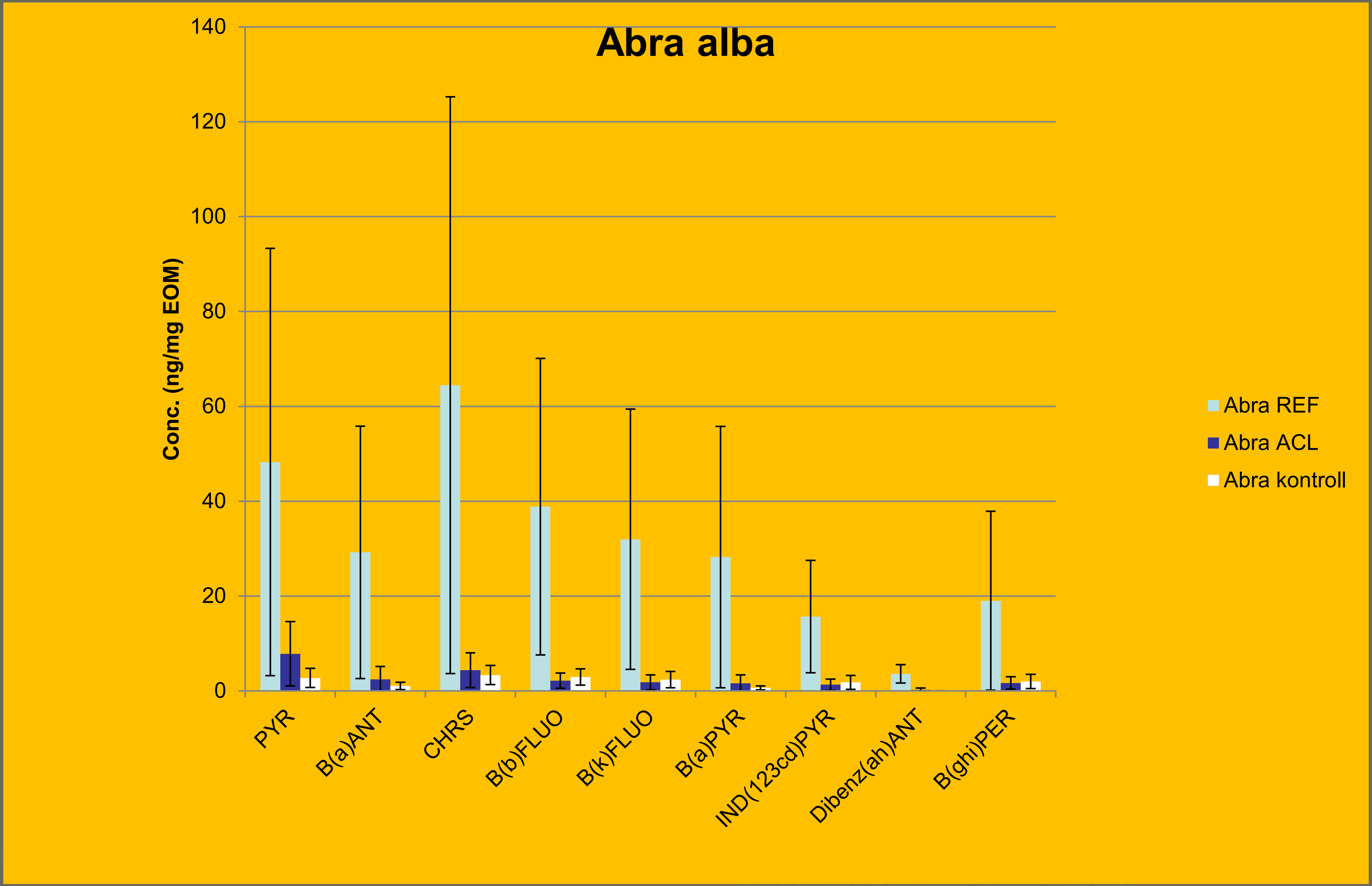
Measured after a 3 month deployment of the benthic flux chambers

Results: Biological - biodiversity index (Shannon)



Species number, species evenness

Results: Biological - bioaccumulation

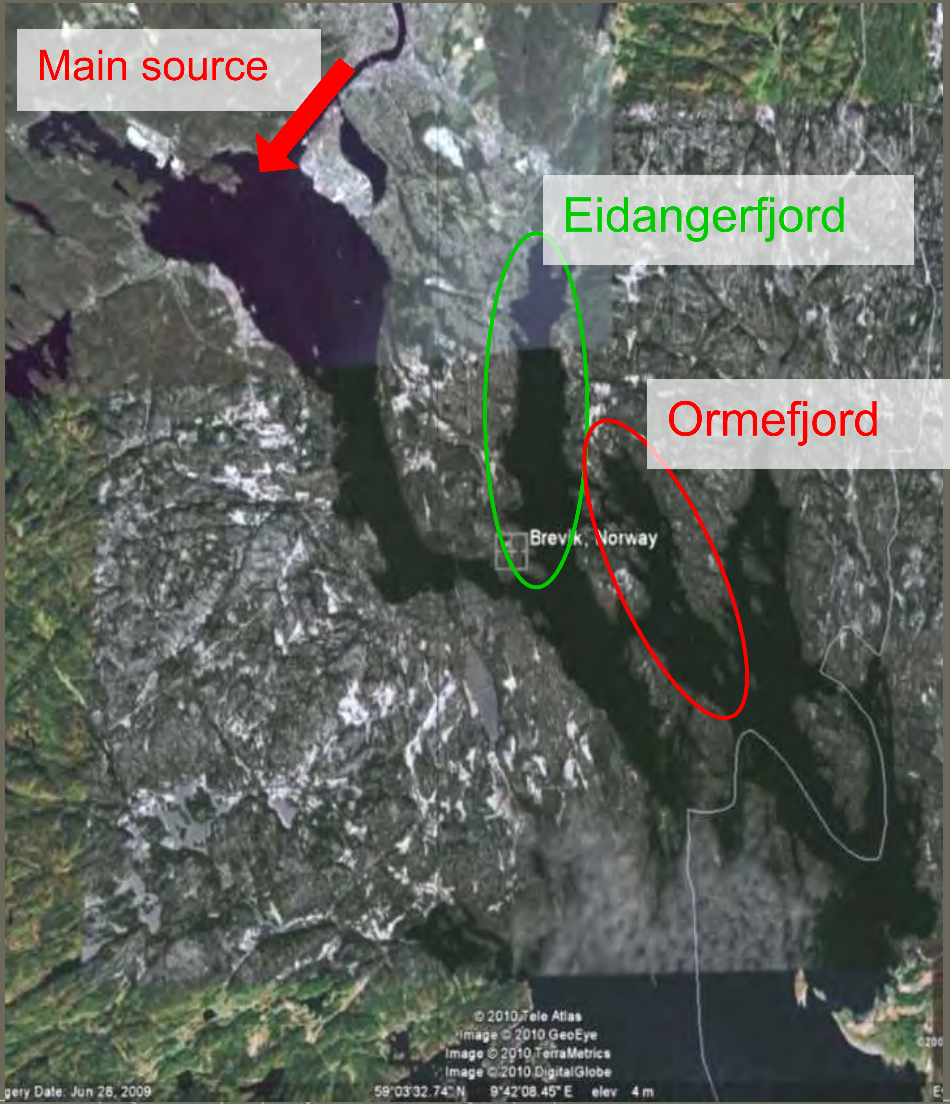


Grenlandfjord, september 2009 – december 2011 (Hydro, Klif, NFR)

”Europe’s worst dioxin contamination”

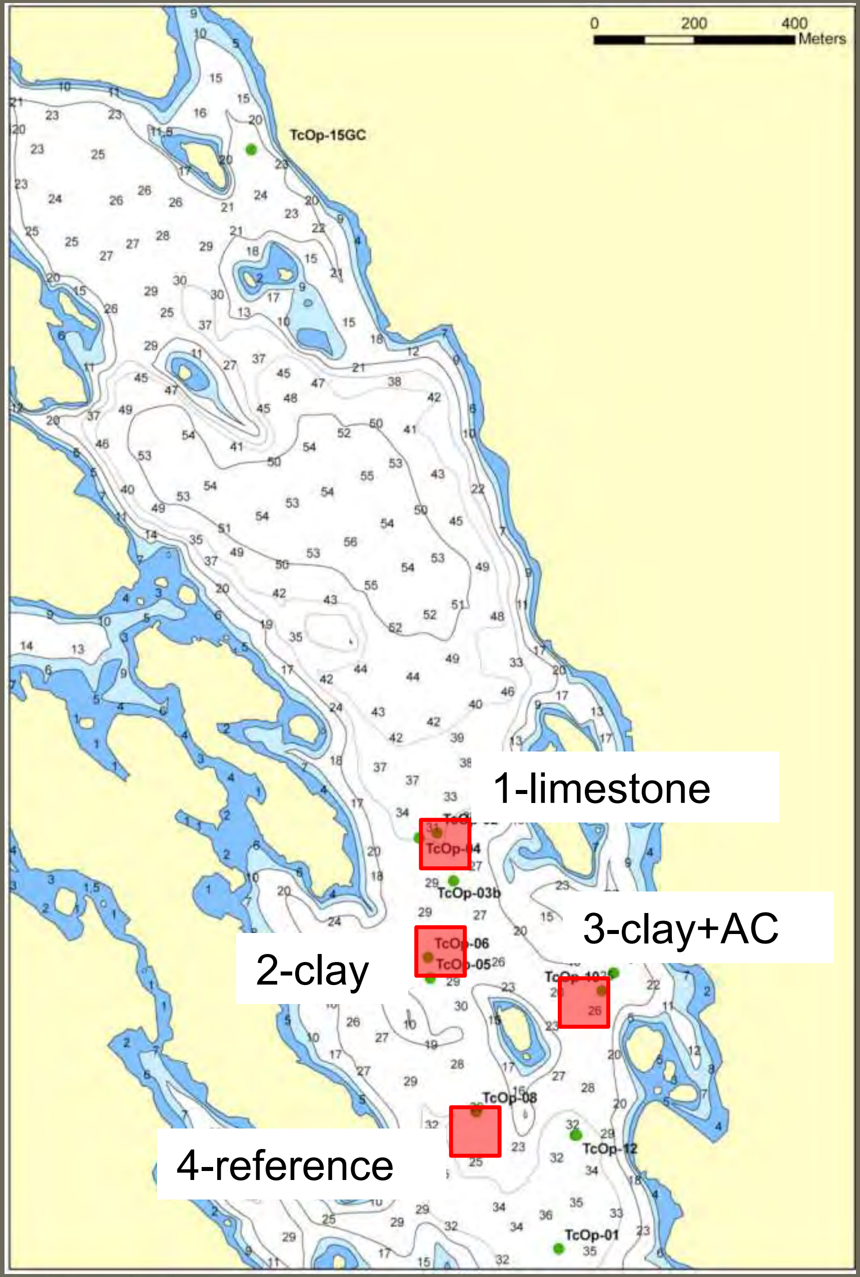
A case of thin layer capping

- Mg smelter caused dioxin pollution (production closed in 2002)
- Remediation of 28 km^2 is needed
- Thin capping is tested



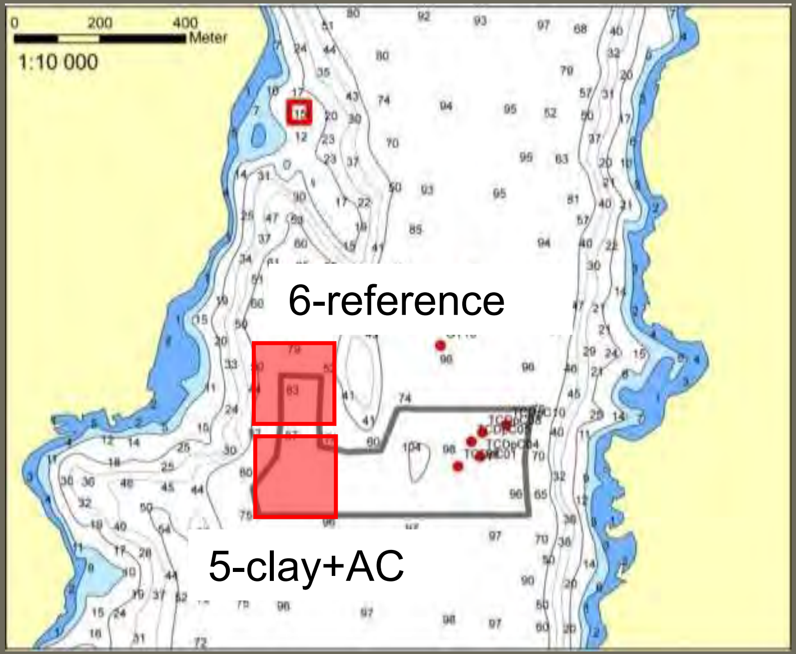
Ormefjord

- 30 m depth, 100 m x 100 m
- 3 fields
  - 5 cm cap crushed limestone
  - 5 cm cap clay
  - 5 cm cap clay + 2 kg AC/m^2
- + control field



Eidangerfjord

- 100 m depth, 200 m x 200 m
- 1 field
  - 5 cm clay + 2 kg/m^2 AC
- + control field
- Total capped area: 70 000 m^2



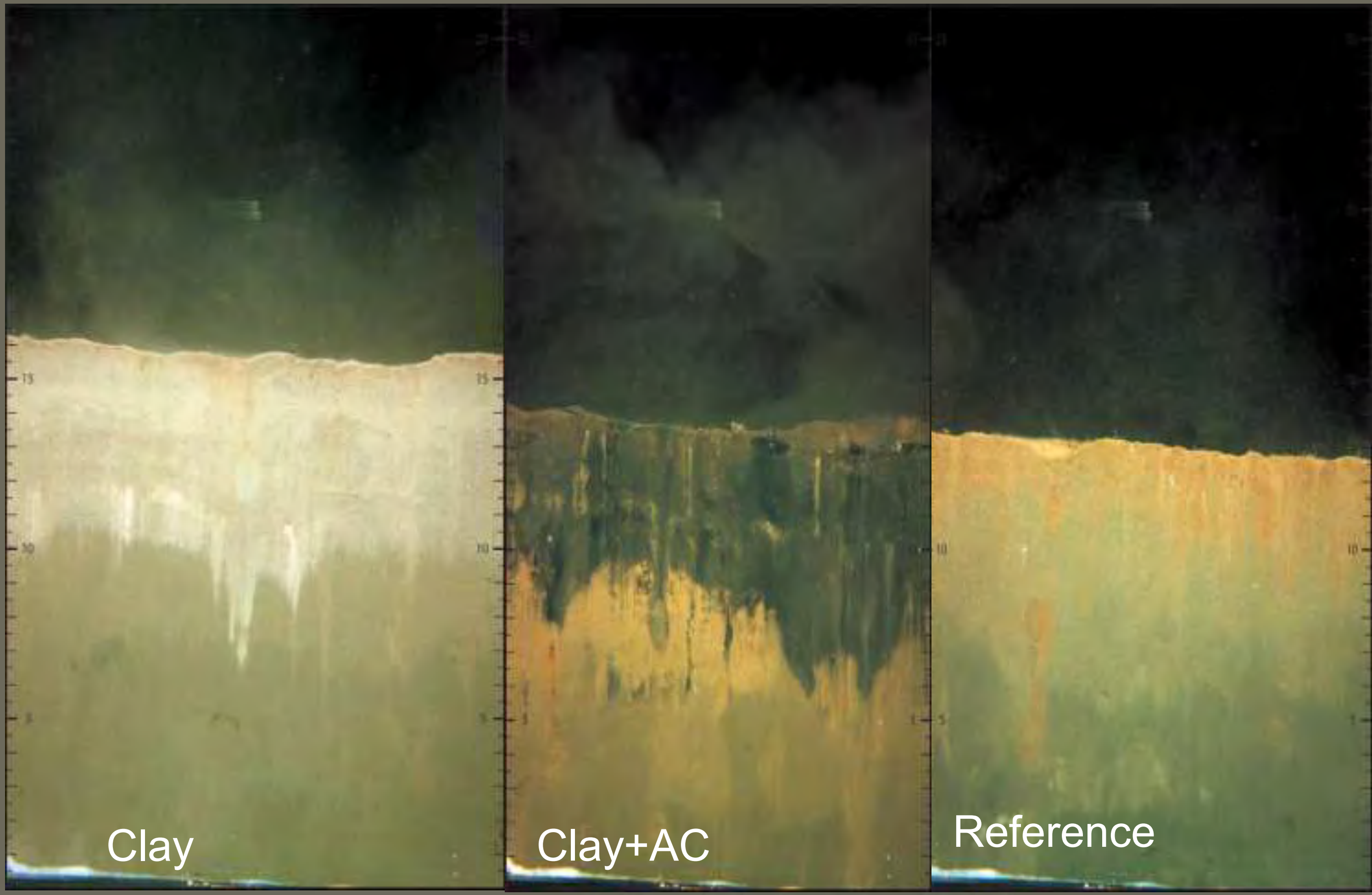
How should 80 t activated carbon and 20 t salt be added to the seafloor?

Material mixing on board

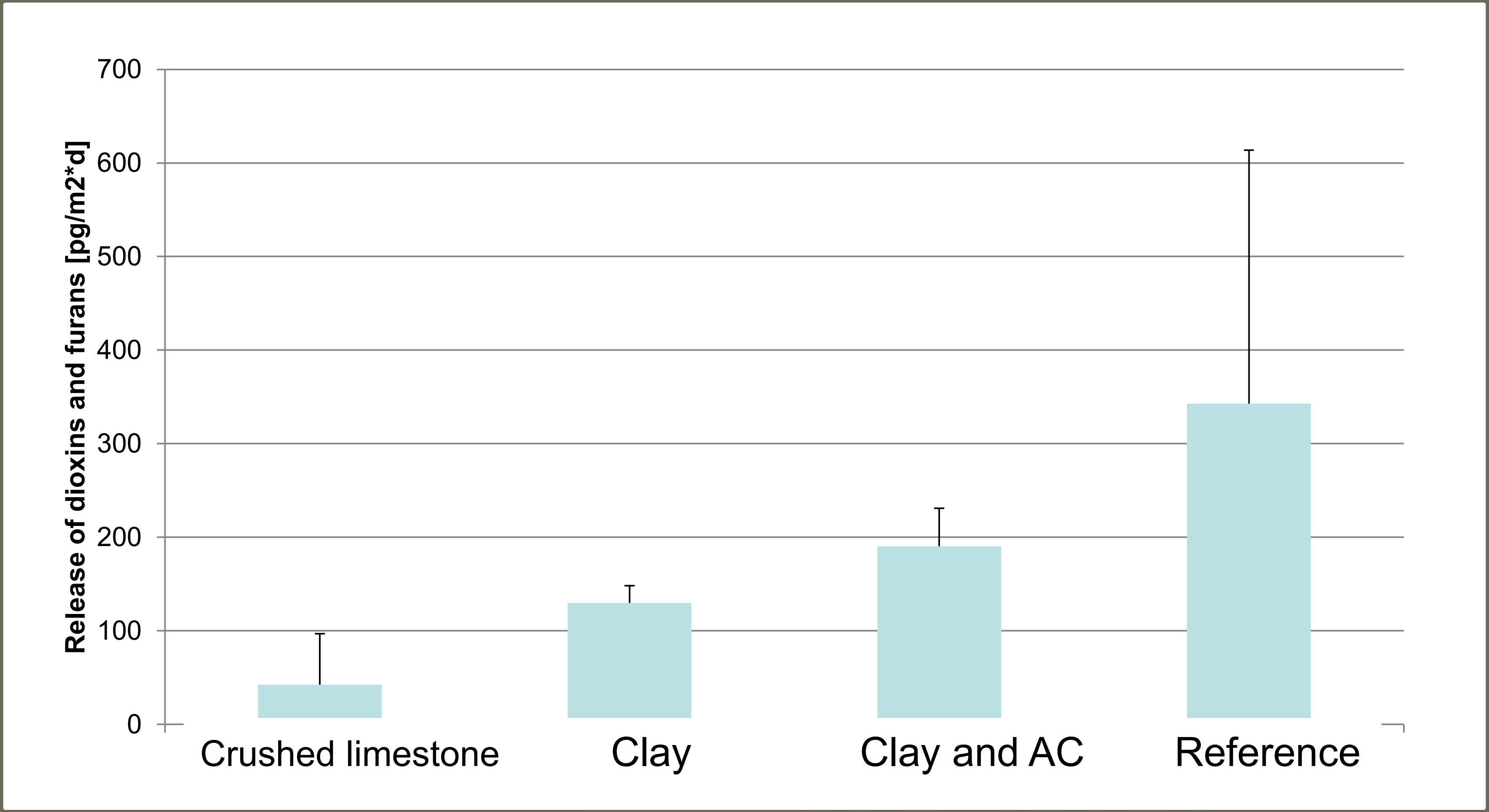
During dredging


Following mixing the amendment with the dredged material

Determination of the cap thickness: Ormefjord (30 m)

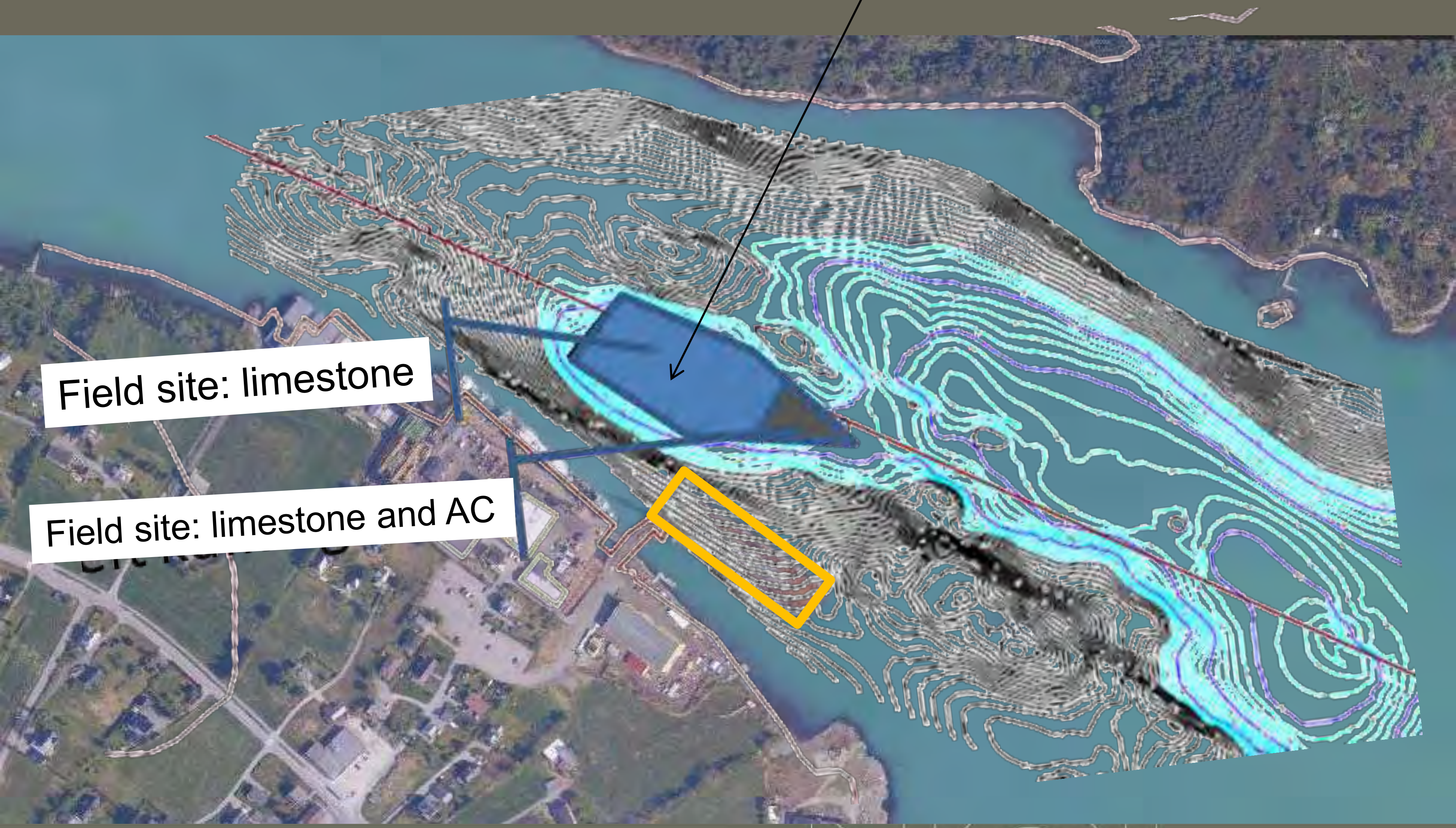


Results: flux from the seabed with and without capping



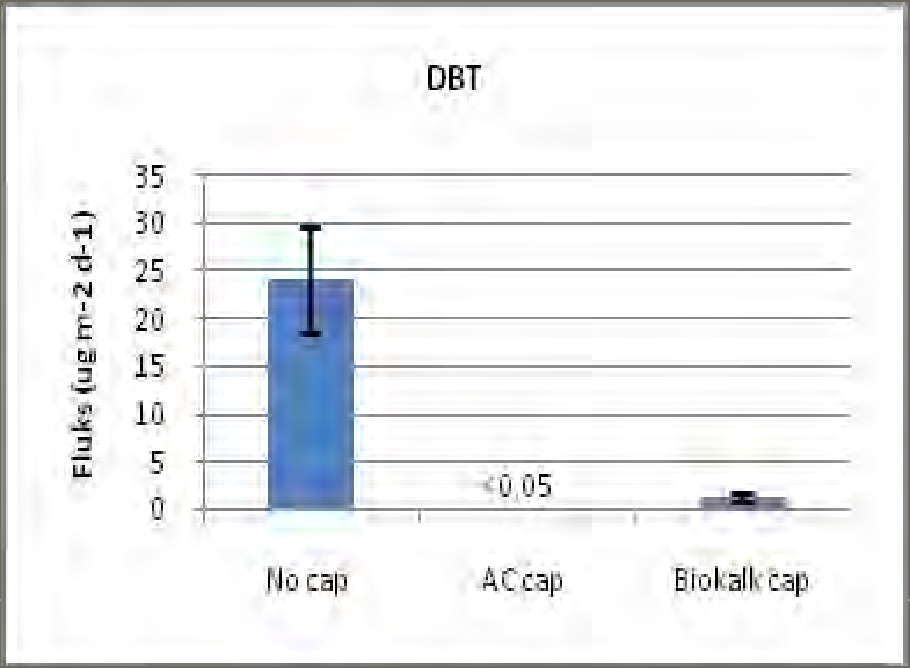
Fiskerstrand, september 2010, TBT

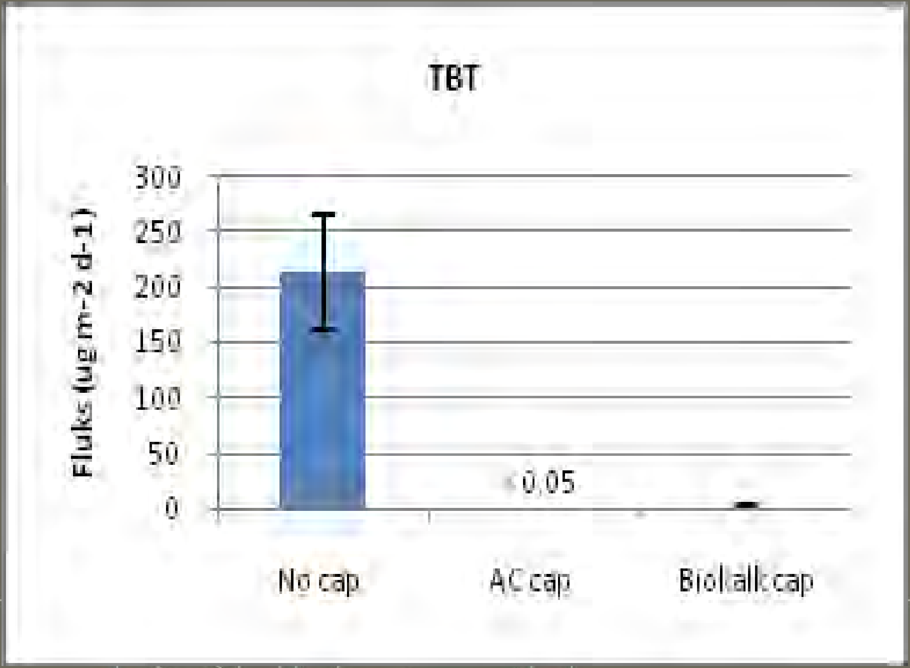
Field site


Area of greatest contamination
Field site: limestone
Field site: limestone and AC

Field test near Fiskerstrand shipyard

- Test limestone as a capping material
- Test increased effect with activated carbon in the cap
- Lab results show good capping by both materials





Summary

AC amendment to soil and sediment can reduce pollutant flux

Many different monitoring methods are needed to assess treatment effectiveness

may play a less important role in determining PBDE bioavailbility than for PCDD/Fs.

759 Biodynamic Modeling of Remedial Success of In Situ Activated Carbon Amendment to Sediment and Possible Secondary Effects on Benthic Invertebrates E.M. Janssen, Stanford Univ, graduate student, Stanford Univ; R.G. Luthy, Stanford Univ, Civil and Environmental Engineering. The primary goal of sediment remediation is to reduce risk to ecosystems and humans by reducing contaminant release to overlying water and exposure to biota. A secondary goal is that the remedial approach should allow ecosystem recovery, e.g., the restoration of the benthic community. Our previous work showed that at full-scale, in situ sorbent amendment with activated carbon (AC) may reduce bioaccumulation of polychlorinated biphenyls from sediment by up to 85 to 90% under favorable field and treatment conditions. We demonstrate a biodynamic modeling framework for benthic organisms with different feeding strategies to assess how the remedial success of a sorbent amendment that lowers the contaminant availability can be compared to reference conditions and traditional cleanup goals, which are commonly based on bulk sediment concentrations. In situ AC amendment is a promising yet novel sediment remediation alternative and possible secondary effects on benthic invertebrates by sorbent addition need to be better understood. The presence of ingestible and non-ingestible AC in three reference sediments slightly increased weight loss but had no effect on survival, lipid, glycogen or protein content of *Neanthes arenaceodentata*, a deposit feeding polychaete, which does not discriminate against AC in its diet.

760 Reducing PAH (Bio)availability by In Situ AC Amendment to Soils and Sediments S. Hale, Norwegian Geotechnical Institute; G. Cornelissen, Norwegian Geotechnical Inst; E. Eek, G. Breedveld, K. Amstatter, M. Elmquist, Norwegian Geotechnical Institute; T. Hartnik, L. Jakob, Soil and Environment Division, Norwegian Institute for Agricultural and Environmental Research (Bioforsk); T. Henriksen, Lindum Ressurs og Gjenvinning AS; J. Gunnarsson, J. Hedman, G. Samuelsson, Stockholm Univ, Dept of Systems Ecology; O. Stokland, Marine Bunndyr AS. Activated carbon (AC) has a very high sorption capacity for organic pollutants and when added to contaminated soil or sediment can sequester and reduce the (bio) availability of these pollutants. We present a series of field AC amendments in Norway in which PAH -contaminated soils and sediments have been treated. A variety of innovative analysis techniques were used to assess the effectiveness of the amendment, such as the deployment of in situ porewater passive samplers and benthic diffusion flux chambers. At Trondheim harbor, AC was applied as a thin layer cap to a marine underwater sediment. Caps consisting of AC-alone, AC+clay and AC with a sand layer on top were compared to sand only and no cap. Underwater imaging showed successful cap placement and up to 60 % of the AC was recovered for the AC+clay cap. The sediment-to-water PAH flux was reduced for all AC treatments and the greatest reduction (factor of 10) was observed for the AC+clay. Porewater PAH concentrations were reduced up to 50 % in the biologically active 0-5 cm deep sediment layer which contained AC. Bioaccumulation of PAHs to worms and benthic mussels decreased 80-90% for the AC+clay cap. AC+clay was recommended as the best amendment method because it showed; i) best AC recoveries; ii) best chemical and biological effectiveness; iii) lowest detrimental secondary effects to the benthic communities. At Drammen, powdered and granular (PAC and GAC) AC were added to a soil. Freely dissolved aqueous PAH concentrations in drainage water and soil pore water were monitored with passive samplers. More than one year after amendment, the free aqueous concentrations in the drainage water were reduced by 93 % and 55 % for the PAC and GAC, respectively, and the free aqueous PAH concentration in the soil pore water itself, as measured by innovative dug-in passive samplers, was reduced by 93 and 70 % for PAC and 84 and 61 % for the GAC. The secondary chemical effects of the AC amendment were considered by monitoring the concentration of DOC and nutrients. Both PAC and GAC bound DOC while the concentrations of nutrients were variable and likely affected more by external environmental factors than the AC amendment. Biological testing showed that the amendment of 2% PAC had a negative effect on plant growth, but GAC actually improved growth. PAC was toxic to earthworms as it reduced the worm's weight. Both kinds of AC significantly reduced Biota to Soil Accumulation Factors (BSAFs) in earthworms and plants.

761 Activated Biochars for the In Situ Sequestration of Organics, Mercury and Carbon in Sediments J.L. Gomez-Eyles, Univ of Maryland Baltimore County; B. Beckingham, Univ of Maryland Baltimore County, Civil & Environmental Engineering, Univ of Maryland Baltimore County, Dept of Civil & Environmental Engineering; S. Kwon, UMBC; U. Ghosh, Univ of Maryland Baltimore County, Civil & Environmental Engineering. In aquatic environments that are impacted by contaminated sediments, contaminant transport pathways can be interrupted by enhancing the binding capacity of natural sediments. This study evaluates the potential of a series of especially formulated biochars (derived from pine wood, peanut hull, barley straw and acai pit) and activated poultry litter biochars to sequester organic and metal contaminants in sediments, while reducing or even reversing the carbon footprint of sediment remediation efforts. PAH, PCB and DDT isotherm studies were conducted at environmentally relevant concentrations using polyoxymethylene solid-phase extraction (POM-SPE), to evaluate the sorption capacity of the different biochars. Freundlich isotherms were constructed and biochar performance was compared with that of commercially available activated carbons (CACs). Biochars were effective at sorbing organics with Kf values ranging from 6.4 to 7.2 for PCB 47, a mid-range tetra-PCB. This sorption was highly non-linear, with n values ranging from 0.53 to 0.81 for PCB 47. However, CACs consistently removed more PCBs from solution, followed by the activated poultry litter biochars suggesting surface area is a key parameter controlling organic contaminant sorption potential. The difference in sorption potential between CACs and biochars was greater for the less chlorinated PCBs with lower Kow. Sorption studies were also carried out for mercury at a range of pH concentrations (pH 3-11). The activated poultry litter biochars removed >99% mercury from solution over the whole pH range, whilst the CAC's removed between 18 and 95% depending on pH level. This suggests the surface functionality of the biochars make them more effective for mercury removal, than the CACs. A better understanding of how biochar characteristics affect contaminant sorption is necessary to improve biochar quality and to help in the selection of the appropriate biochar amendment necessary to achieve site specific contaminated sediment remediation goals.

762 Biochar-Herbicides Antagonism: Can They Stand Each Other? A. Freddo, Univ of East Anglia; B. Reid, Univ of East Anglia, Environmental Sciences. The benefits on plant growth and improvement of soil structure following biochar addition to soil have been previously reported. However the physic-chemical structure of biochar allows the sorption of organic compounds (for example pesticides), thus, while on one hand biochar might increase crop yields the beneficial role of pesticides might be undermined through alteration of their bioavailability to pests and weeds. The purpose of this study was to establish the efficacy of four herbicides (mesotrione, pendimenthaline, terbuthilazine, isoproturon) upon three common broadleaf weeds (Amaranthus retroflexus, Solanum nigrum and Abutilon theophrasti) when applied to soil amended with 0%, 1% and 5% biochar. The results indicated that in all the treatments the presence of higher concentration of biochar in soil significantly reduced the effectiveness of all herbicides tested. The viability of targeted weeds in the herbicide amended 5% biochar soil was not significantly ($p< 0.05$) different to the number of viable weeds observed in the control treatments (no biochar and no herbicide). Physiologic characteristics were also taken into account. Results regarding stem- and root-length and fresh weight of biomass indicated that weeds present in the 5% biochar plus pendimenthaline treatments were not significantly ($p< 0.05$) different to the control. Thus, biochar was found to be effective in reducing the bioavailability of the dissimilar herbicides to contrasting broadleaf weeds. These results are significant in so much as they suggest biochar incorporation to soil could undermine food security on account of the potential for biochar to deactivate herbicidal activity.

763 An NMR-based Metabolomic Analysis of Cobia Health in Response to Dietary Manipulation T. Schock, National Institute of Standards and Technology, Analytical Chemistry Division; S. Newton, Univ of Arkansas, Pine Bluff; K. Brenkart, J. Leffler, South Carolina Dept of Natural Resources; D. Bearden, National Institute of Standards and Technology, Analytical Chemistry Division, National Institute of Standards and Technology. Commercial aquaculture feeds rely heavily on fishmeal and fish oil, which can be expensive and ecologically unsustainable. The environmental impact of various aquaculture practices because of the need to harvest fish for fish meal and the need to properly handle the waste stream in intensive aquaculture systems leads to investigation of alternative, plant-based foods.

Exponent

SediMite®
A delivery system for amending contaminated sediment with activated carbon and/or other amendments

Prepared for LDW Carbon Workshop
February 2012

Charles A. Menzie, Ph.D.
camenzie@exponent.com

Acknowledgements

- SediMite® was developed through a Small Business Innovative Research (SBIR) Grant from U.S. Environmental Protection Agency (USEPA)
- SediMite® demonstration projects have been supported by:
  - ESTCP/SERDP
  - NIH NIEHS
  - Industry
- Support for projects and/or permits received
  - USEPA, NOAA. ACOE. States

SediMite® as a means of delivering in-situ treatment amendments

Tens of grams/day production in the laboratory

2-5 Million lb/year at a production facility

30 lb buckets

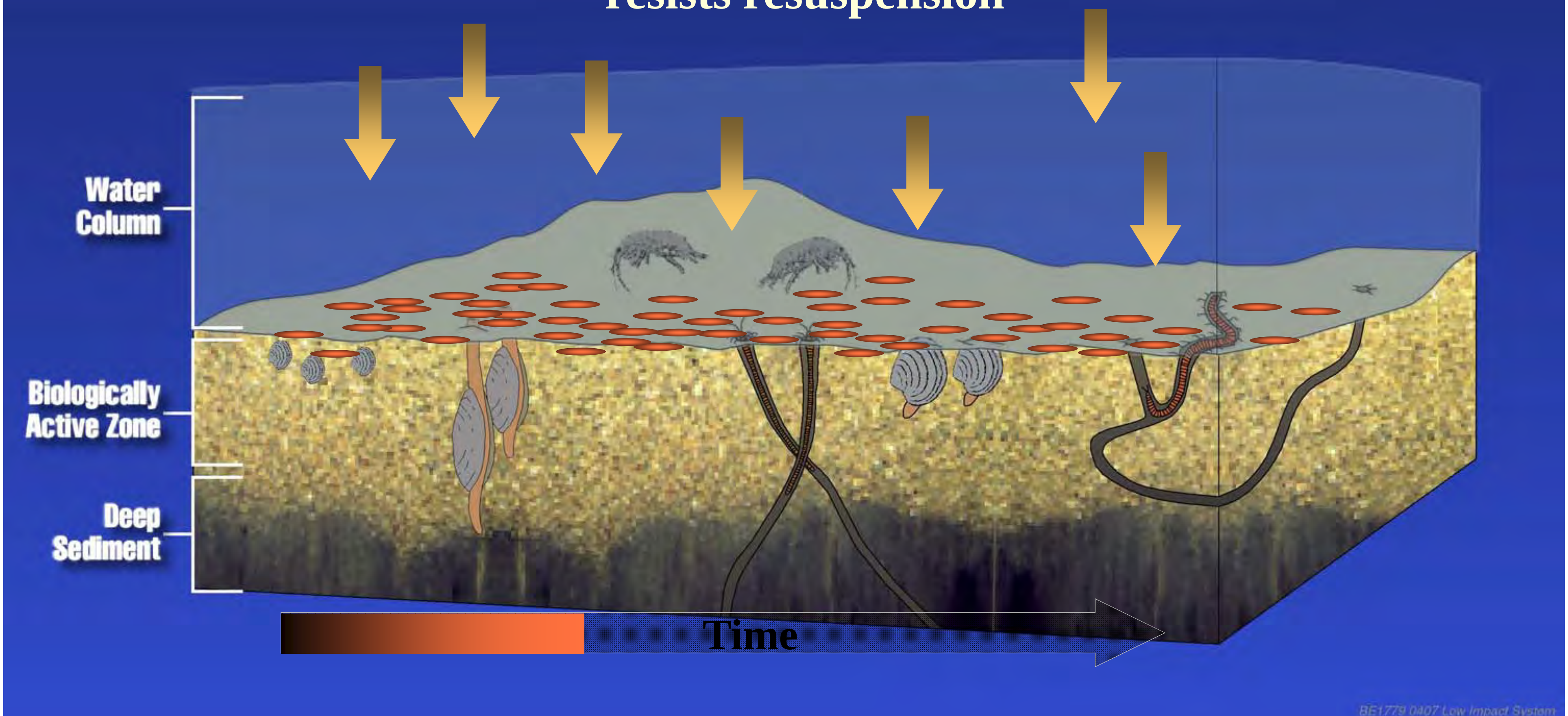
1800 lb bulk bags

An example of application

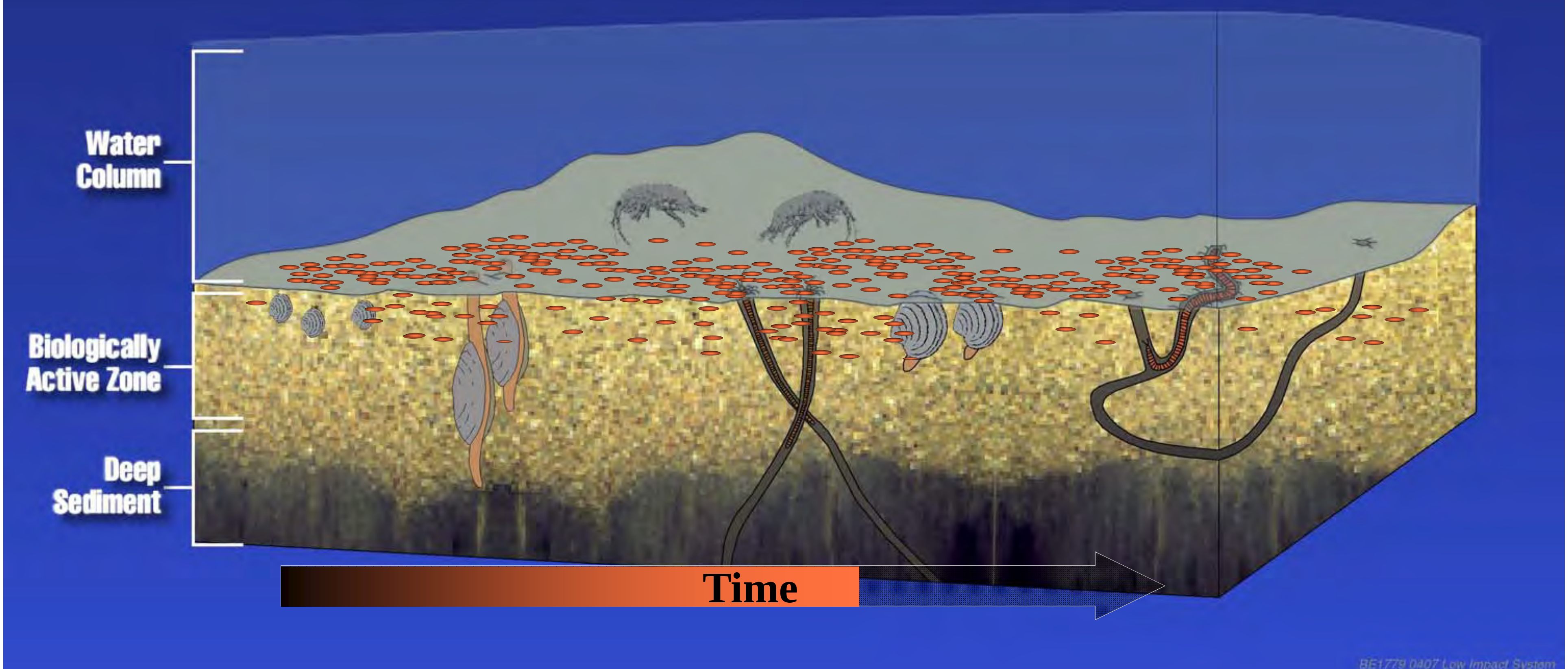
An example of application

SediMite® is designed to provide a low-impact delivery system for AC and other amendments

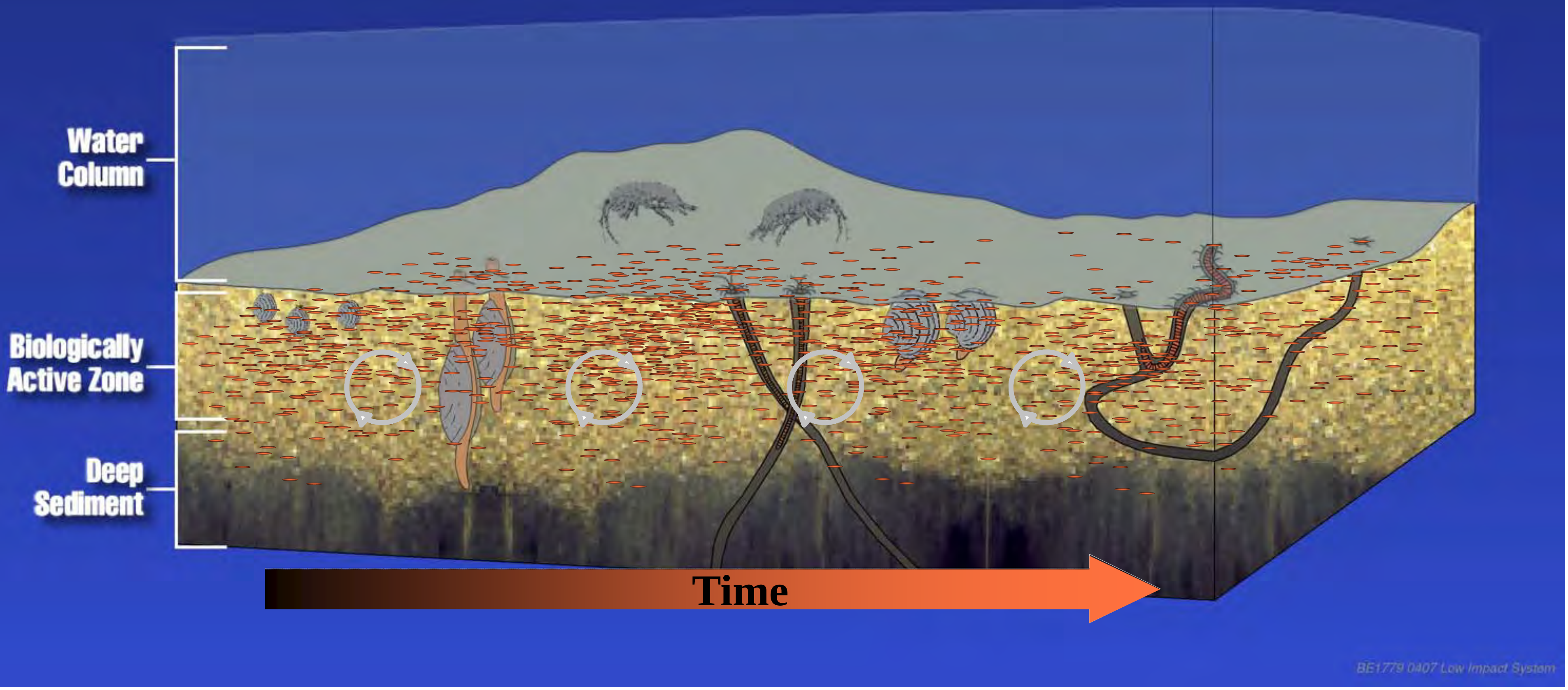
Agglomerate containing treatment agent delivered from water surface or above the sediment— sinks to sediment surface and resists resuspension



SediMite® granules break down over time



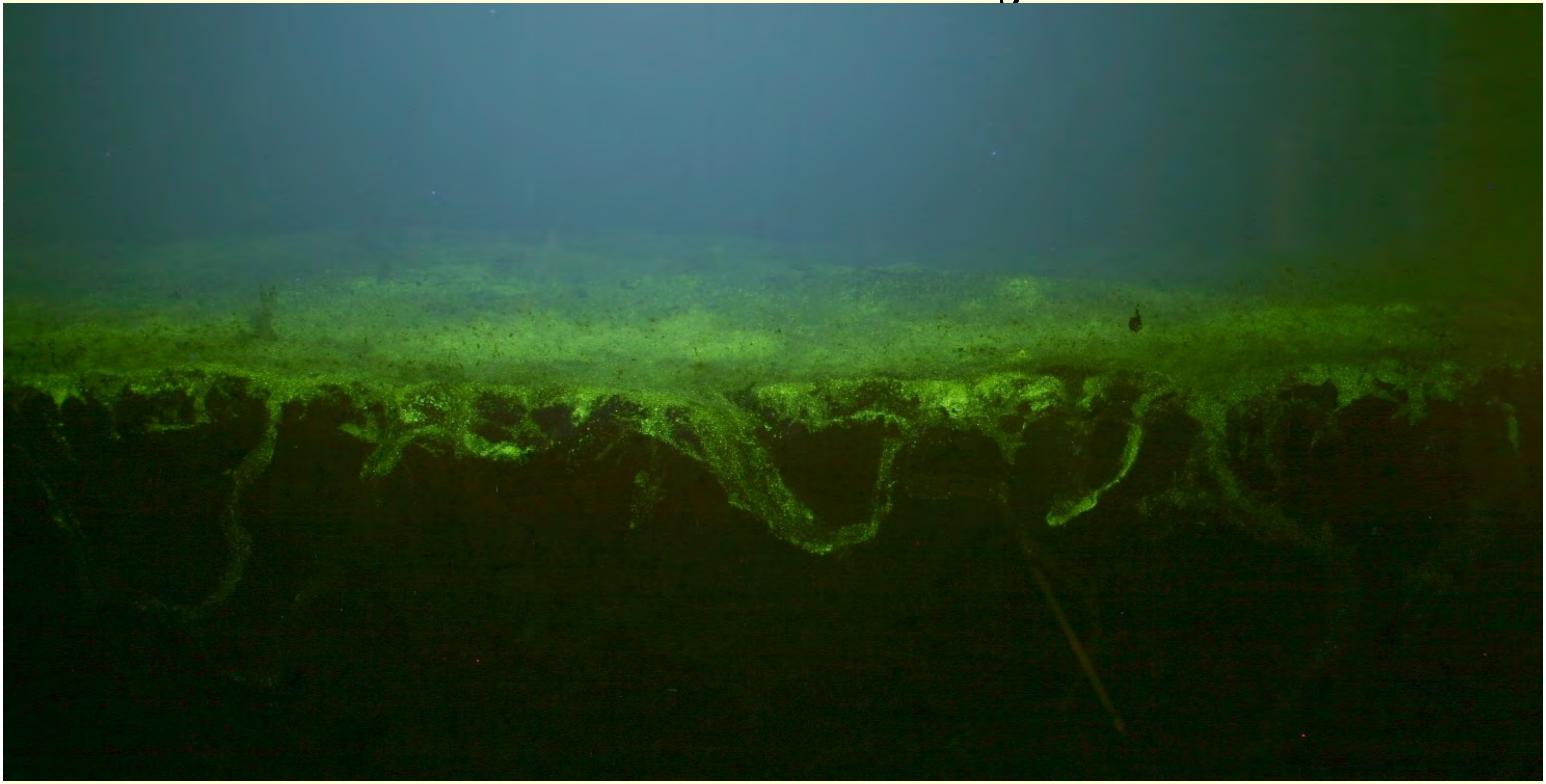
and are mixed by bioturbation, thus targeting the biologically active zone



The Workers

(burrowing depth increases left to right)

SediMite-delivered fluorescent particles mixed by marine benthic invertebrates after 30 days



A low-impact in-situ approach is attractive when natural resources may be impacted by more invasive methods (dredging and capping)

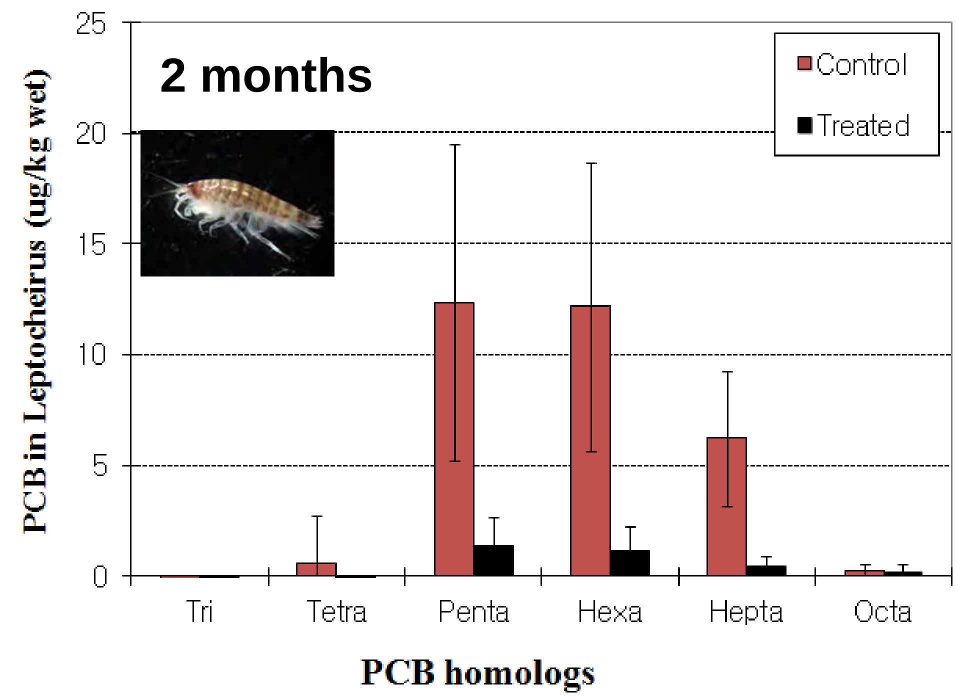
Note: these same areas are often the most productive regions of a lake or river and can make a proportionally greater contribution to chemicals in aquatic food webs

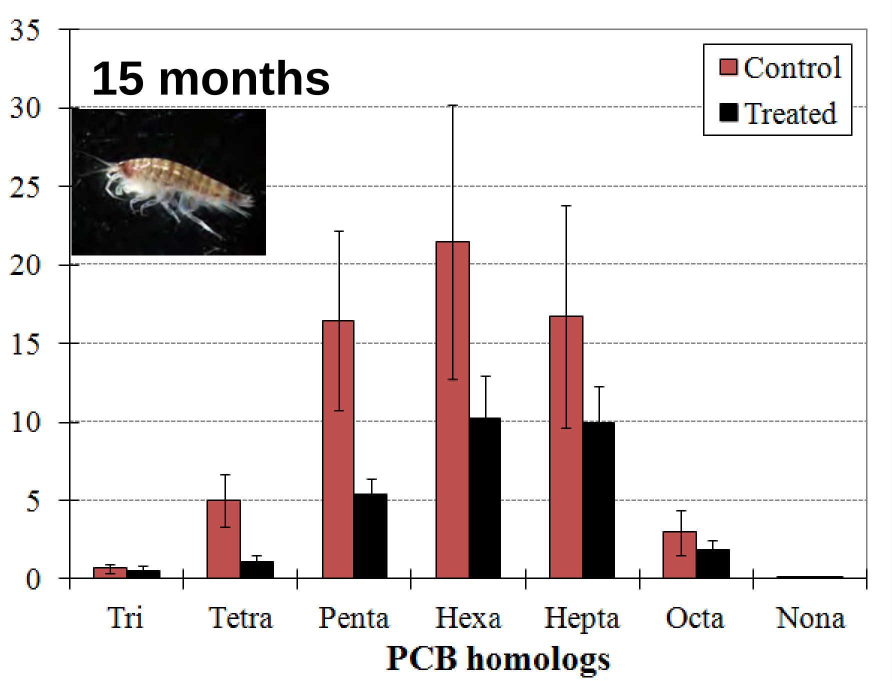
SEDIMITE® application in a tidal creek and wetland contaminated with PCBs

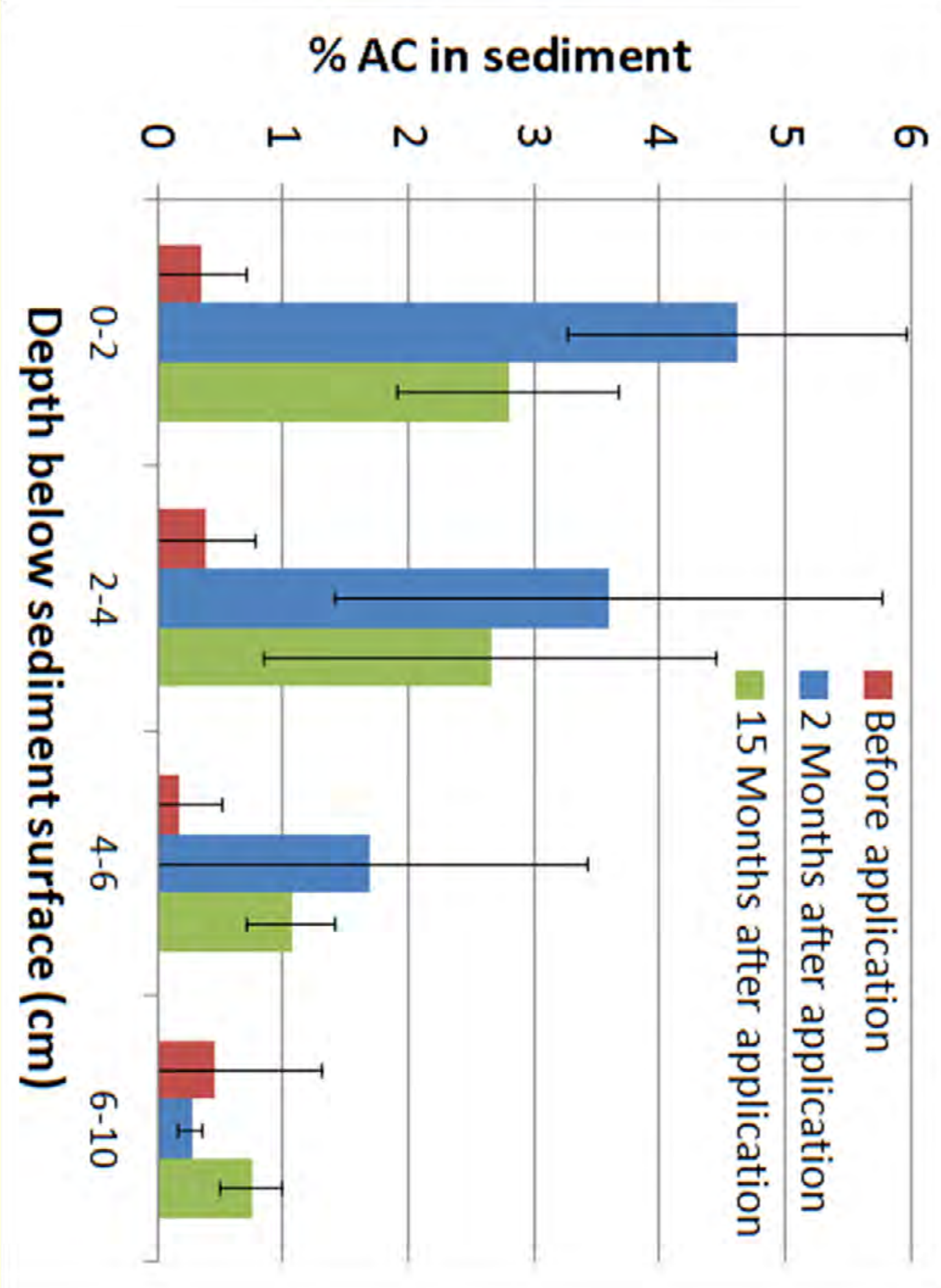
August, 2009

Efficacy of PCB treatment in Baily's Creek sediment at 2 and 15 months

- Reduction after 2 months ~ 90% (measured using 2-week test)
- Mixing and dilution of AC dose in 15 months reduced effectiveness (edge effect)







Distribution of activated carbon with sediment depth in Bailey's Creek after 2 and 15 months

SediMite projects

- Fort Eustis tidal creek and salt marsh – PCBs
- Aberdeen Proving Ground tidal creek – mercury
- Aberdeen Proving Ground marsh – PCBs
- Berry's Creek NJ marsh – mercury and PCBs
- South River – mercury
- Confidential site – PAHs
- Delaware freshwater creek and pond - PCBs

SediMite® makes sense when…

- You have dealt with contaminant sources
- In-situ and/or ENR remedies are compatible with nature of system (currents, waves, sediment dynamics)
- You want to amend natural sediment with AC or other amendments for *in-situ* treatment without impacting what is living there
- You want to amend added sand or habitat mix with AC
- You want to treat hard-to-reach places (under docks and around pilings)

Questions?

AquaGate+PAC™

Background

AquaGate+PAC (Powdered Activated Carbon) is a patented, composite-aggregate technology resembling small stones typically comprised of a dense aggregate core, clay or clay-sized materials, polymers, and fine-grained activated carbon additives.

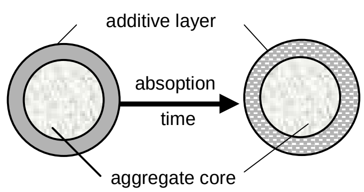


Figure 1. Configuration of PAC-coated particle.

AquaGate+PAC serves as a delivery mechanism to reliably place reactive capping materials into aquatic environments.

Product Specifications

Aggregate:	Nominal AASHTO #8 (1/4-3/8”) or custom-sized to meet project-specific need * Limestone or non-calcareous substitute, as deemed project-appropriate
Clay:	Bentonite (or montmorillonite derivative) ** Typically 5 – 10% by weight*
Activated Carbon:	Powdered – Iodine Number 800 mg/g (minimum) ⊙ 99% (minimum) through 100 mesh sieve ⊙ 95% (minimum) through 200 mesh sieve ⊙ 90% (minimum) through 325 mesh sieve ** Typically 2 – 5% by weight*
Binder:	Cellulosic polymer
Permeability:	1×10^{-1} to 1×10^{-2} cm/sec
Dry Bulk Density:	85 – 90 lbs/ft^3

AquaBlok®
Composite Particle System

For more information, Contact AquaBlok, Ltd. at:

Phone: (800) 688-2649
Email: services@aquablokinfo.com visit us at our
Web: www.aquablokinfo.com

Last Revised: January 1, 2010

AquaGate+PAC™

Activated Carbon - A Recognized Material for a Wide Range of Contaminants

Key Benefits:

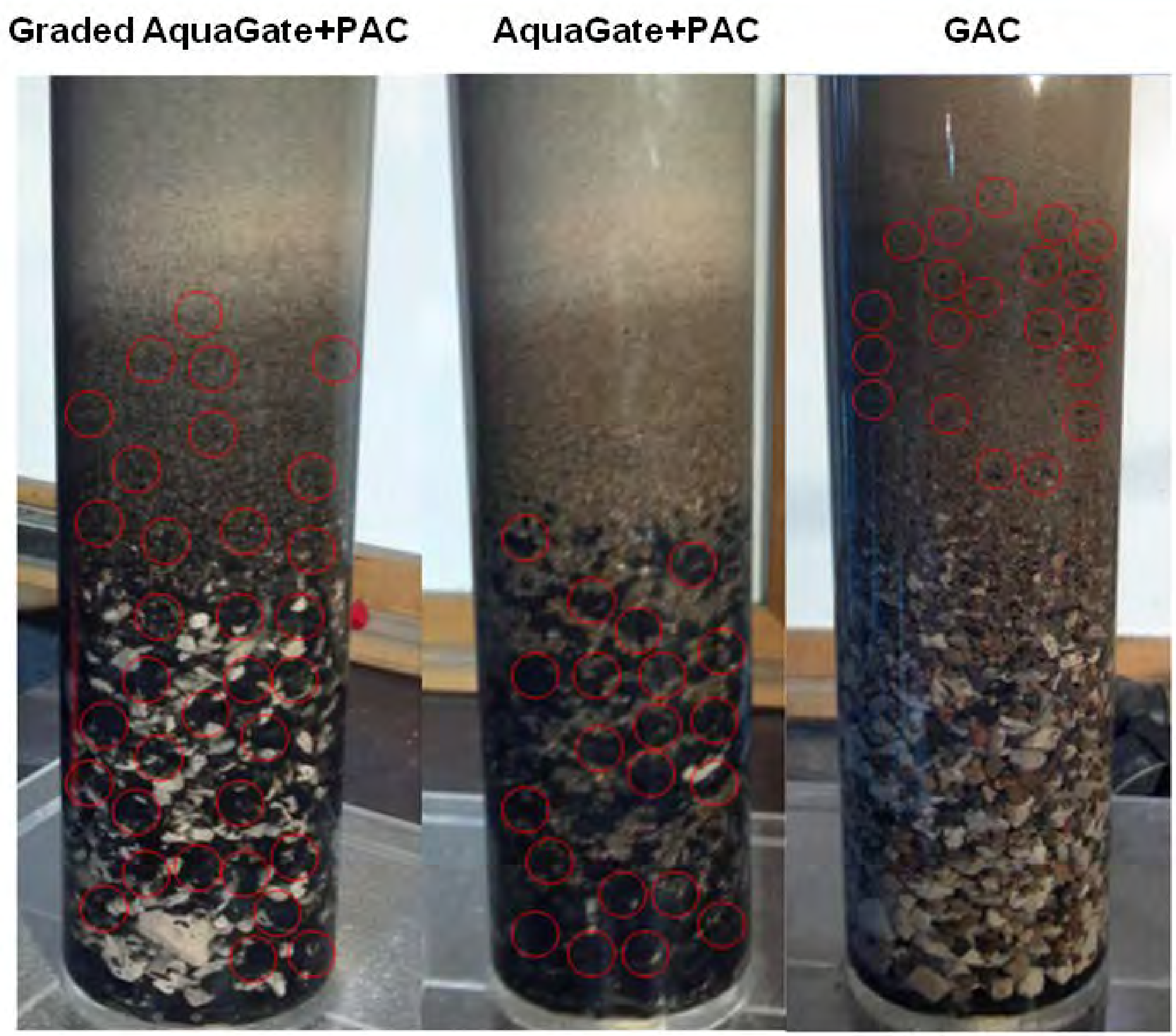
1. Allows delivery through a water column
2. No Mixing - Uniform Delivery without Risk of Material Separation
3. Creates Thicker (uniform) Layers with Less Material Usage
4. Powder Form (PAC) provides higher rate of adsorption than Granular

Above: Intact AG+PAC 5% after perm test

Activated Carbon:	Powdered – Iodine Number 800 mg/g (minimum) ⦿99% (minimum) through 100 mesh sieve ⦿95% (minimum) through 200 mesh sieve ⦿90% (minimum) through 325 mesh sieve ** Typically 2 – 5% by weight*
Binder:	Cellulosic polymer
Permeability:	1 x 10^{-1} to 1 x 10^{-2} cm/sec
Dry Bulk Density:	85 – 90 lbs/ft^3
Moisture:	10 – 12% (maximum)

Above: Flex-wall permeameter – Flow 14,774 cm/day or greater used in three runs - ***Significantly in excess of a conservative 5 cm/day without material loss through sand pack***

AquaGate+PAC – Uniform Distribution of a Small Quantity of Adsorptive Material in a Single Lift



Red circles indicate relative location of particles within the as-placed cap.
They do not denote the number of particles in a given location.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