DEMONSTRATION OF IN SITU TREATMENT WITH REACTIVE AMENDMENTS FOR CONTAMINATED SEDIMENTS IN ACTIVE DOD HARBORS

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ABSTRACT

A demonstration project at the Puget Sound Naval Shipyard & Intermediate Maintenance Facility located in Sinclair Inlet, Puget Sound, WA is being conducted to demonstrate and validate placement, stability and performance of reactive amendments for the treatment of contaminated sediments in an area with elevated polychlorinated biphenyl (PCB) and Hg contamination. The legacy contamination was identified adjacent to Pier 7 during a fender pile replacement project. The contaminated area was amended with powdered activated carbon (PAC) using the AquaGate+PAC™ composite aggregate system to decrease the bioavailability of PCBs in contaminated sediment.

Pre-installation activities included site characterization, laboratory treatability studies, and amendment detection testing. A grid of diver-collected grab samples was analyzed on site using an immunoassay method for PCBs and identified elevated contamination levels adjacent to the southwestern end of Pier 7 that were subsequently sampled to obtain bulk material for a laboratory treatability study. The laboratory treatability study showed that total PCB bioaccumulation in polychaete worms was significantly reduced by the amendment, and that addition of the amendment did not cause toxicity. Based on these results, pre-installation monitoring was conducted in August 2012, the amendment was installed in October 2012, and post-installation activities are now underway. The pre- and post-monitoring events are utilizing 14-day in-situ bioassays conducted with the bent-nosed clam and the polychaete worm and chemical characterization using the sediment ecotoxicity assessment (SEA) Ring protocol and an in situ solid-phase micro-extraction (SPME) technique. Physical and biological conditions are being documented with the sediment profile imaging (SPI) camera, measurement of black carbon and total organic carbon content and traditional benthic infauna sampling. The monitoring will establish pre-placement conditions, verify that the placement meets minimum specifications, and evaluate amendment performance after 6, 18, and 30 months of placement.

BACKGROUND

Problem

Active, deep-water DoD harbor areas pose significant challenges for remediation of contaminated sediment. Effectiveness of traditional methods such as dredging, capping and monitored natural recovery is limited by typical DoD harbor conditions:

- Ships, tugs, prop wash
- Navigation requirements
- Uncontrolled sources
- Piers, bulkheads, quay walls
- Dewatering and disposal

Reactive amendments represent a more environmentally/cost effective solution for application in active DoD harbors and overcome limitations of traditional methods.

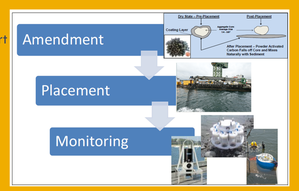
Technical Objectives

The primary objective of this work is to demonstrate and validate placement, stability and performance of reactive amendments for treatment of contaminated sediments in ***active DoD harbor settings.***

This project extends previous pilot-scale testing of the application of activated carbon (AC) to decrease bioavailability of contaminated sediment to near full-scale demonstration utilizing a delivery system that is applicable to realistic DoD harbor conditions.

Demonstration and validation focus on:

- Amendment placement in deeper water areas that support vessel traffic
- Physical stability and longevity of the amendment in the sediment
- Effectiveness of amendment in controlling contaminant bioavailability
- Response of the benthic community to the amendment application



Technical Approach

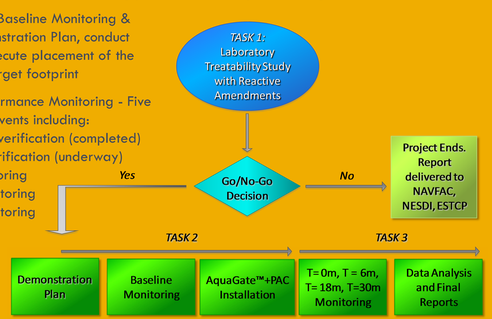
The technical approach is composed of three primary tasks including:

Task 1. Laboratory Amendment Treatability Studies - On-site delineation of contaminant concentrations, verification of site sediment treatability, toxicity studies to assess secondary effects of amendment, and verification of field-based methods for monitoring placement, stability and mixing of amendment

Task 2. Demonstration Plan, Baseline Monitoring & Installation - Develop Demonstration Plan, conduct baseline monitoring, and execute placement of the selected amendment to a target footprint

Task 3. Post-Placement Performance Monitoring - Five post placement monitoring events including:

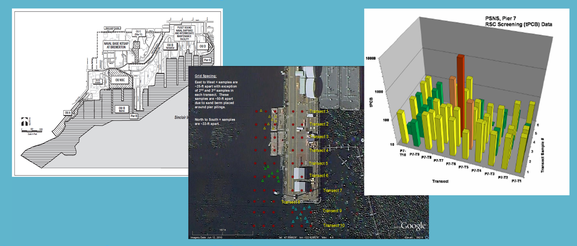
- T=0 months – placement verification (completed)
- T=3 months – stability verification (underway)
- T=6 months – perf. monitoring
- T=18 months – perf. monitoring
- T=30 months – perf. monitoring



Pre-Installation Activities

Site Characterization at Puget Sound Naval Shipyard, Pier 7

- Sediment sampling and analysis to further delineate contaminant concentrations in the target area & collect treatability samples.
- Sediment core samples (6") collected by Navy divers (n=51 samples).
- Rapid screening for tPCBs using Immunoassay technique.
- RSC tool identified 50 ppb - 6 ppm range total PCB in surface sediments.
- Subsequent sampling revealed > 30 ppm total PCBs in subsurface sediments (near T6 – 3).
- **Cleanup Goal**: 3 mg/kg PCB OC normalized (~100 ppb PCB un-normalized).



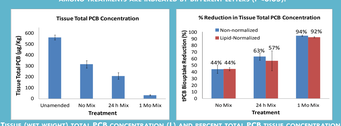
Laboratory Toxicity and Bioaccumulation Treatability Studies

- **Study Design:** A principal component of the lab study was to verify the effectiveness of the amendment material in terms of reduction in contaminant bioavailability to benthic organisms. The dosing experiments were carried out using a standard formulation of the AquaGate+PAC™ , the activated carbon-based reactive amendment selected for testing. Equal parts of AquaGate+PAC™ and Pier 7 (BNC) sediment were mixed in 2 L pre-cleaned glass jars to create an estimated 3.5% final PAC concentration, on a dry weight basis. The tests also evaluated different degrees of mixing including a No Mix, a Partial Mix (24 hour) and a Full Mix (1 month).
- Toxicity testing involved running standard 10-day amphipod and 28-day polychaete bioassays to assess any potential adverse toxic effects/risk (via growth and mortality endpoints) from a) the unamended sediment, b) the uncoated aggregate that acts as the delivery mechanism for the AquaGate+PAC™ , and c) the activated carbon-coated AquaGate+PAC™ . Bioaccumulation testing involved running standard 28-day bioaccumulation studies on the reactive amendment/sediment mixtures.

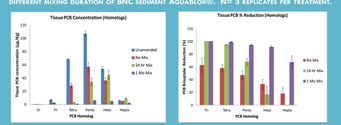
Parameter	Preliminary Study (Toxicity)	Treatability Study (Bioaccumulation)
Species	Polychaete (Neanthes arenaceodentata) Amphipod (Eohaustorius estuarius)	Polychaete (N. arenaceodentata)
Replication	Three per treatment	Nine per treatment
Treatments	1) Control (Yaquina Bay) 2) BNC, unamended 3) BNC + AquaGate (BNC + Aq) 4) BNC + uncoated AquaGate (BNC + AqNC)	1) Control (Yaquina Bay) 2) BNC, unamended 3) BNC + Aq no mix (No Mix) 4) BNC + Aq 24-hour mix (24-h Mix) 5) BNC + Aq 1-month mix (1-mo Mix)
Mixing period(s)	One month	Range from no mixing to one month
Endpoints	Survival, growth only	Survival, growth, bioaccumulation

	Survival (%)			Individual Wet Wt. (mg)			Lipid (%, wet wt.)		
Sample ID	Mean	s.d.	Sig.	Mean	s.d.	Sig.	Mean	s.d.	Sig.
Control	96	2.7	A	19.6	2.0	A	1.7	0.51	A
Unamended	97	5.1	A	23.5	3.0	B	2.0	0.15	A
No Mix	97	3.9	A	18.4	1.4	A	2.0	0.13	A
24 Hr Mix	96	5.0	A	18.9	1.1	A	1.9	0.69	A
1 Mo Mix	97	3.2	A	22.5	2.7	B	1.4	0.06	A

Treatability study results from 28-day exposures with the marine polychaete *Neanthes arenaceodentata*. N=9 for survival and wet weight; N=3 for lipid data. Statistical differences among treatments are indicated by different letters (P<0.05).



Tissue (wet weight) total PCB concentration (L) and percent total PCB tissue concentration reduction (R) in *Neanthes arenaceodentata* following 28-day laboratory exposures following different mixing duration of BNC sediment. AquaBlok®. N= 3 replicates per treatment.



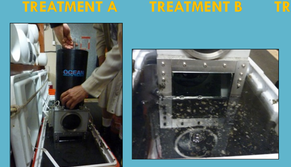
Tissue (wet weight) PCB concentration, expressed as sum of congeners in each homolog (R) and percent total PCB tissue concentration reduction, by homolog (L), in *Neanthes arenaceodentata* following 28-day laboratory exposures following different mixing duration of BNC sediment with AquaGate ©. N= 3 replicates per treatment.

- **Toxicity Results:** Polychaete survival was very high (Table 3-3), with ≥ 96% survival in all treatments. Growth was not adversely affected when compared to the control sediment for any treatment, nor when the unamended sediment was compared to the 1 Month Mixed treatment (p>0.05). However, the No Mix and 24 Hr Mix treatments did result in statistically lower final weights relative to the unamended BNC treatment. Lipid content of polychaetes tissues was lowest in the 1 Month Mix treatment (Table 3-3), but the reduced value (1.4%, as a mean of 3 replicates of 6-8 organisms each) was not statistically significant, even though variability within treatments was very low.
- **Bioaccumulation Results:** Increasing AquaGate+PAC™ contact time with the BNC sediment resulted in progressively lower bio-uptake with up to 94% tPCB reduction for the 1 month mixed treatment. Lipid normalization of the data resulted in similar reductions. The substantial reduction of bioaccumulated PCBs under a worst case scenario (no mixing) and fine particle size associated with the PAC used in AquaGate+PAC™ (providing greater surface area and more sorption sites for PCB binding relative to AC) suggests that field scale applications of AquaGate+PAC™ should result in near immediate PCB sequestration to benthic invertebrates. On a homolog-specific basis, biouptake reduction was inversely correlated PCB chlorination. Tetra- and Penta- homologs, however, made up 75% of the PCBs detected in tissue exposed to the unamended Pier 7 (BNC) sediment, 97% of which were not detectable in the 1 month mix treatment. Therefore, considering the homolog distribution at the site, the reduced efficiency associated with the highest levels of biphenyl chlorination should be of little concern.

Amendment Detection Testing

- **Study Design:** Laboratory testing was conducted to evaluate the amendment detection capability of the Sediment Profile Imaging (SPI camera) system with digital image analysis. The testing consisted of comparative analysis of a series of treatments with different vertical mixing strength as well as un-amended controls.

Treatment	Description	Materials: Sediment and Amendment
Treatment A	Unamended sediment. Represents native sediment prior to addition of AquaGate+PAC™.	Sediment from MCRD (~ 15 gallons)
Treatment B	Amended sediment with AquaGate+PAC™ placed on sediment surface. Represents initial application of amendment (T=0).	Sediment from MCRD (~15 gallons) + 10lbs of AquaGate+PAC™
Treatment C	Amended sediment with a 1: 1 mixture of sediment and AquaGate+PAC™ placed on sediment surface. Represents partial mixing of amendment into sediment surface (short-term mixing).	Sediment from MCRD (~15 gallons) + 13lbs of AquaGate+PAC™ (17.5 lbs sediment ww + 13 lbs. amendment)
Treatment D	Amended sediment with a 3: 1 mixture of sediment and AquaGate+PAC™ placed on sediment surface. Represents full mixing of amendment into sediment surface (long-term mixing).	Sediment from MCRD (~15 gallons) + 11lbs of AquaGate+PAC™ (45lbs sediment ww + 13 lbs. amendment)

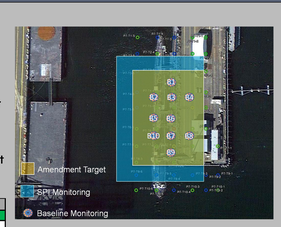


- The SPI Camera was able to distinguish two distinct layers (darker amendment layer on top; lighter native sediment layer below) in all of the amended treatments (B, C, D).

Installation and Monitoring

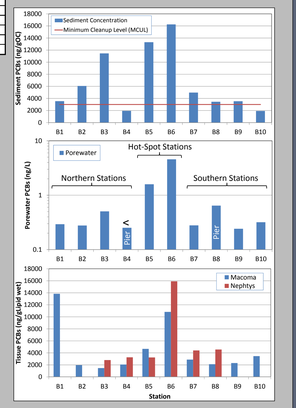
Baseline Monitoring

- **Study Design:** Conduct characterization to define the performance baseline for comparison of post-amendment monitoring events
  - Prior to amendment placement
  - Physical, chemical and biological characterization at 10 stations within footprint
  - SPI Camera at ~ 50 location, extending beyond target footprint



PRE-PLACEMENT BASELINE MONITORING					
PHYSICAL/GEOPHYSICAL		CHEMICAL		BIOLOGICAL	
Bathymetry	tran	TOC	10	Marine Polychaete PCBs	10
Tides/Currents	1	Black Carbon	10	Marine Polychaete Hg/MeHg	10
Grain Size	10	Whole Sediment PCBs	10	Mollusk PCBs	10
Permeability	10	Whole Sediment Hg/MeHg	10	Mollusk Hg/MeHg	10
Bulk Density	10	PED Porewater PCBs	10	Benthic Community Census	10
Sediment Profile Images (SPI)	50			Sediment Profile Images (SPI)	50

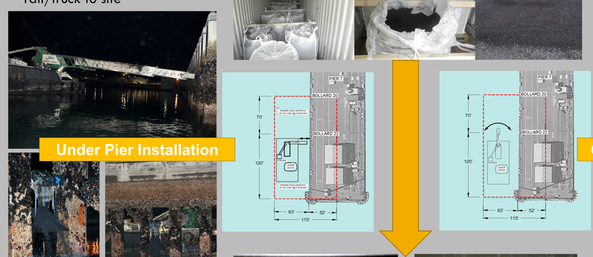
- **Preliminary Results:**
  - PCB concentrations above MCUL in hot spot area, at or near MCUL in surrounding areas
  - Porewater concentrations (average of SeaRing and cores) show similar patterns to sediment
  - Bioaccumulation also elevated in hot spot area, also in area B1 to the north
  - Two species showed similar uptake in two week exposures



See also the presentations "Improved In Situ Approach for Assessing Sediment Ecological Risk, Remediation Effectiveness and Stormwater Impacts" in session D3 and "Two-Week In Situ Method for Measurement of PCBs in Sediment Porewater Using SPME" in session D5

Amendment Placement

- Final placement and logistics considered:
  - Bathymetry
  - Pier structure
  - Tides
  - Fish windows
  - Shipyard work/schedule
- Amendment delivered by rail/truck to site



- Installation utilized articulated conveyor operating from a flat deck barge
- Dry-land testing of delivery system prior to installation
- 141 tons of amendment installed to target area
- Low-tide only for under dock (night ops)

Under Pier Installation

- Under dock articulated telebelt between pilings
- Varied angle to access behind pilings
- Multiple passes to reduce "windrows"

Open Berth Installation

- Open water - rotate/retract telebelt (2 ft increments)
- Step barge back as required
- Multiple passes to reduce "windrows"

See also the presentation "Installing an Activated Carbon Sediment Amendment at the Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, WA" in session B4. Challenges in Ports and Harbors Management

Post Placement Monitoring

T=0 MONTHS – PLACEMENT VERIFICATION

- Placement was evaluated through the SPI images and collection of core samples. SPI imagery at 50 baseline stations; Cores at 10 baseline stations
- Characterize thickness and spatial uniformity of the placement, and the surface area covered during the initial placement

T=3, 6, 18, 30 MONTHS – PERFORMANCE MONITORING

- Conduct during four post-placement monitoring events
- 3-month post installation stability (cores and SPI)
- Physical, chemical and biological characterization at ~10 stations
- Comparison to baseline conditions
- Performance metrics for stability and reduction in bioavailability

POST-PLACEMENT PERFORMANCE MONITORING					
PHYSICAL/GEOPHYSICAL		CHEMICAL		BIOLOGICAL	
Grain Size	10	TOC	10	Marine Polychaete PCBs	10
Sediment Profile Images (SPI)	50	Black Carbon	10	Marine Polychaete Hg/MeHg	10
		Whole Sediment PCBs	10	Mollusk PCBs	10
		Whole Sediment Hg/MeHg	10	Mollusk Hg/MeHg	10
		PED Porewater PCBs	10	Benthic Community Census	10
				Sediment Profile Images (SPI)	50

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