# ESTCP
# Cost and Performance Report

(ER-201131)


## Demonstration of *In Situ* Treatment with Reactive Amendments for Contaminated Sediments in Active DoD Harbors

**June 2017**

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The objective of this pilot-scale field demonstration was to evaluate and validate placement, stability, and performance of reactive amendments for in situ treatment of contaminated sediments in active DoD harbor settings. The approach to demonstrate and validate this in situ treatment using reactive amendments was focused on various performance issues. These demonstration and validation criteria form the basis of the POs. Data was collected in support of these POs and provided multiple lines of evidence that validated the effectiveness of amendment placement as an in situ strategy for limiting chemical bioavailability at contaminated sediment sites.

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# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| µg | microgram(s) |
| µm | micrometer(s) |
| AC | activated carbon |
| BC | black carbon |
| BNC | Bremerton Naval Complex |
| CERCLA | Comprehensive Environmental Response Compensation and Liability Act |
| CFR | Code of Federal Regulations |
| CL | confidence level |
| cm | centimeter(s) |
| CoC | contaminant of concern |
| Cu | copper |
| CVAA | cold vapor atomic absorption |
| cy | cubic yard |
| DoD | U.S. Department of Defense |
| ELISA | Enzyme Linked Immuno-Sorbent Assay |
| ESTCP | Environmental Security Technology Certification Program |
| g | gram |
| Hg | mercury |
| HOC | hydrophobic organic compound |
| in | inch(es) |
| IQR | interquartile range |
| J’ | Pielou’s Evenness Index |
| kg | kilogram |
| lw | lipid weight |
| MeHg | methylmercury |
| mg | milligram |
| MLLW | mean lower low water |
| mm | millimeter(s) |
| MNR | monitored natural recovery |
| NCP | National Oil and Hazardous Substance Contingency Plan |
| ng | nanogram |

| | |
|---|---|
| NOAA | National Oceanic and Atmospheric Administration |
| | |
| OC | organic carbon |
| OM | organic matter |
| OU | Operable Unit |
| | |
| PAC | powdered activated carbon |
| PAH | polycyclic aromatic hydrocarbon |
| Pb | lead |
| PCB | polychlorinated biphenyl |
| PO | Performance Objective |
| PSNS & IMF | Puget Sound Naval Shipyard and Intermediate Maintenance Facility |
| | |
| ROD | Record of Decision |
| RSC | Rapid Screening Characterization |
| | |
| SARA | Superfund Amendment and Reauthorization Act |
| SDI | Swartz Dominance Index |
| SEA Ring | Sediment Ecotoxicity Assessment Ring |
| SERDP | Strategic Environmental Research and Development Program |
| SITE | Superfund Innovative Technology Evaluation |
| SPI | Sediment Profile Imaging |
| SPME | solid phase microextraction |
| sq. ft. | square feet |
| SQC | sediment quality criteria |
| SQS | Sediment Quality Standards |
| SSC Pacific | Space and Naval Warfare Systems Command (SPAWAR) Systems Center Pacific |
| | |
| TOC | total organic carbon |
| | |
| USACE | U.S. Army Corps of Engineers |
| USEPA | U.S. Environmental Protection Agency |
| | |
| ww | wet weight |
| | |
| XRF | X-ray fluorescence |
| | |
| Zn | zinc |

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# EXECUTIVE SUMMARY

## OBJECTIVES OF THE DEMONSTRATION

The objective of this pilot-scale field demonstration was to evaluate and validate placement, stability, and performance of reactive amendments for *in situ* treatment of contaminated sediments in active U.S. Department of Defense (DoD) harbor settings. The approach to demonstrate and validate this *in situ* treatment using reactive amendments was focused on performance issues including:

- Proper design and selection of the amendment,
- Placement and physical stability of the reactive amendment in deeper water areas that support vessel traffic,
- Effectiveness of the amendment in reducing contaminant bioavailability over time, and
- Quantification of changes to benthic habitat and benthic community structure.

These demonstration and validation criteria form the basis of the Performance Objectives (POs). Data was collected in support of these POs and provided multiple lines of evidence that validated the effectiveness of amendment placement as an *in situ* strategy for limiting chemical bioavailability at contaminated sediment sites.

## TECHNOLOGY DESCRIPTION

In this study, *in situ* remediation of surface sediment contaminated with hydrophobic organic compounds (HOCs) was demonstrated by placing a reactive amendment consisting of powdered activated carbon (PAC) at a site (Pier 7) contaminated with polychlorinated biphenyls (PCBs) located at the Puget Sound Naval Shipyard and Intermediate Maintenance Facility (PSNS & IMF), Bremerton, Washington. The PAC was successfully placed on the seafloor of a half-acre target site to sorb PCBs in sediments, thereby reducing bioavailability and limiting bioaccumulation of contaminants into the tissues of benthic invertebrates, and subsequently the food web. The sorbent material, AquaGate®+PAC (referred to here as AquaGate) (AquaBlok, Ltd., Toledo, Ohio) was specifically manufactured by coating an aggregate core with PAC held in a bentonite clay binder, to enable deep water placement of the material on the sediment surface. The AquaGate, which is denser than water, sinks rapidly through the water column directly to the surface of the sediment. Over a short period of time (days), the PAC coating of the AquaGate releases from the aggregate and becomes mixed with the underlying sediment. Natural mixing—specifically bioturbation—incorporates the PAC into the surface sediments over time. AquaGate was placed with a conveyor belt-type equipment, which demonstrated the ability to rapidly and evenly place the material both in the open water and areas under structures such as piers and between pilings.

## DEMONSTRATION RESULTS

In a laboratory treatability study, concentrations of total PCBs in tissue of *Neanthes arenaceodentata* exposed to the control sediment (unamended) were compared to tissue concentrations from amended site sediment. The AquaGate amended sediment resulted in up to a 94% reduction of total PCBs in tissues. Following the success of the laboratory study, a field scale demonstration was carried out by placing AquaGate on the seafloor of a half-acre target site.

The field scale demonstration resulted in a reduction of freely dissolved PCBs in porewater by >75% from the baseline. Additionally, PCB biouptake in a polychaete worm *Nephtys caecoides* and bent-nose clam *Macoma nasuta* was reduced by >68% from baseline. Overall, the biological and porewater results generally indicated an average decrease in bioavailability of 84% from the baseline. The reduction in concentrations of total PCBs in *M. nasuta* (88%), *N. caecoides* (97%), and sediment porewater (81%) from baseline to a 33-month event indicate that these reductions were sustained over time.

Successful placement and stability of the reactive amendment around piers and structures utilizing conventional placement equipment was demonstrated by using a number of monitoring tools. The approximate amendment thickness was on average >4 inches (in) and was present within the target area (80% of the target area received measurable or trace deposits of AquaGate). Additionally, an increase in total organic carbon (TOC) content in surface sediment was an average of 50% greater than in the baseline. Approximately 65% of the target area retained measurable or trace deposits of the amendment over the course of the 33 months, indicating the relative stability of the amendment. Additionally, the amendment placement did not negatively impact the native benthic community, as measured by six biotic endpoints.

Results from this demonstration illustrated the effectiveness of the AquaGate at reducing contaminant bioavailability over 33 months, without negatively impacting resident biota. The amendment also exhibited satisfactory placement and stability in an active DoD harbor.

## IMPLEMENTATION ISSUES

*In situ* remediation of HOC-impacted sediments with activated carbon (AC) has been demonstrated to meet placement objectives for target area and thickness in deep waters as well as stability to remain in place over three years in an active shipyard. In this demonstration, AquaGate has been shown to reduce concentrations of PCBs in tissue and sediment porewater in the third year following placement in surface sediment by 81–97%. *In situ* reactive amendment with AquaGate is well suited to be implemented in a variety of environmental conditions from shallow, quiescent, flat-bottom settings to deep water, variable, or sloping water depths, and tidal environments with active vessel traffic and infrastructure. This technology could be of great interest as a remedy to HOC-impacted (e.g., PCBs, polycyclic aromatic hydrocarbon [PAHs], and pesticides) surface sediments in association with Superfund sites and sites implementing remediation in response to equivalent state and local regulations associated with contaminated surface sediments. *In situ* treatment technology may be limited to sites with contamination to depths within the site-specific bioturbation mixing zone (generally 10–20 centimeters [cm] below sediment-water interface) unless it is determined that there is little or no advective transport of contaminant from depths below the bioturbation mixing zone. AquaGate has an advantage in the ability to place amendments around infrastructure (e.g., piers and bulkheads) where dredging may be found to be more expensive or infeasible. Another advantage of AquaGate is the ability to place the amendment in navigational channels and berthing areas where capping may be infeasible due to water depth requirements. Costs of implementing AquaGate are competitive with alternative remedial methods; however, as with selection of any remedy, cost is depending on site-specific conditions and complexity. Additionally, AquaGate has an advantage as a green remediation strategy, which is of interest to the U.S. Environmental Protection Agency (USEPA) to minimize environmental footprints after cleanup.

Placement of *in situ* reactive amendment to sediments at Pier 7 presented significant challenges associated with amendment placement in active harbors including security access, scheduling, deep water placement, working near and under waterfront structures, complex bathymetry and dredge cuts in berthing areas, strong and variable tidal currents, and possible disturbance from ship movement and other harbor activities. Also, as with any pilot project, the small size of the area limited the ability of the operator to gain efficiency or improve the potential uniformity or coverage within the placement area. In total, 141 tons of AquaGate were placed on surface sediments at Pier 7 within 4 days from the arrival of the tugs to the verification of the placement by U.S. Navy divers. Improvements could be made to placement, such as achieving placement within the entire target area and avoiding placement in areas outside the target area. Additionally, the evenness of the amendment thickness could be improved to place a more uniform distribution. Monitoring at Pier 7 was limited by diver assistance for deployment and retrieval of the Sediment Ecotoxicity Assessment Rings (SEA Rings) and passive samplers. Also, measurements of TOC and black carbon (BC) content in sediment with presence of shell hash presented further challenges.

Although AC has been shown for decades to be effective at treatment of air, water, and wastewater, there remains some uncertainty as to the long-term effectiveness of sequestration treatment in the field. Because of public perception and a predisposition by the regulatory community, dredging continues to be the most common and accepted means of sediment remediation. Any remedy that leaves untreated contaminants in place, such as *in situ* sequestration, may have the potential for risk of re-exposure of the contaminants. A similar risk would be encountered for sites utilizing monitored natural recovery (MNR), capping, or dredging when high concentrations in residuals are left in place. However, the risk from potential effects of re-exposure may be less if low concentrations of contaminants remain in the sediment.

It is recommended that further research be performed. However, since the initiation of this project, the application of *in situ* sequestration at full-scale has been performed successfully. Long-term monitoring of these sites will be required to further support the expanded application of this technology.

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# 1.0 INTRODUCTION

The objective of this project was to demonstrate and validate placement, stability, and performance of reactive amendments for treatment of contaminated sediments in active U.S. Department of Defense (DoD) harbor settings. This project extends prior pilot-scale testing of the application of activated carbon (AC) to decrease the bioavailability of contaminants of concern (CoC)—specifically polychlorinated biphenyls (PCBs)—in contaminated sediment to a full-scale demonstration under realistic, deep water, and under pier conditions at an active DoD harbor site. The evaluation was conducted at Pier 7 of the Puget Sound Naval Shipyard and Intermediate Maintenance Facility (PSNS & IMF) in Bremerton, Washington. Performance Objectives (POs) were developed to evaluate the amendment performance. Because AC and the clay mineral (sodium bentonite) associated with the amendment may also sorb methylmercury (MeHg) in sediment thereby reducing MeHg bioavailability, POs also evaluated the effectiveness of MeHg-related endpoints.

Demonstration and validation was focused on placement of the amendment in areas that support vessel traffic; physical stability; longevity of the amendment in the sediment following placement; effectiveness of the amendment in controlling contaminant bioavailability over time; and response of the benthic community to the amendment application. POs are specifically designed to assess physical endpoints (including placement, distribution, mixing, and stability), chemical endpoints (including changes in PCB partitioning/sorption in the presence of the amendment), and biological endpoints (including tissue concentrations of contaminants and assessment of benthic community effects following placement). These monitoring endpoints allow examination of multiple facets to the amendment performance under an active harbor setting, including the feasibility of deep water material placement, the stability of material placement, the extent to which material placement reduces tissue residue concentrations of PCBs and MeHg, together with the potential changes in the benthic community.

## 1.1 BACKGROUND

Active, deep-water DoD harbor areas pose a number of challenges to the effective use of traditional sediment remedies such as dredging, capping, and monitored natural recovery (MNR). Successful demonstration of delivery, stability, and effectiveness of *in situ* treatment materials to address these challenges has the potential to reduce costs and recovery time frames for a wide range of active DoD sites and provide a more effective alternative to traditional methods of remediation.

Cleanup costs for contaminated sediments at DoD sites are estimated to exceed $1 billion. Cost-effective remedies for sediment remediation at contaminated DoD sites are limited, particularly for active harbor areas. Currently, the primary remedial options for DoD sites include dredging, isolation capping, and MNR (USEPA 2005). Although *in situ* treatment is described in the U.S. Environmental Protection Agency (USEPA) *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (2005), large-scale demonstrations, implementation, and acceptance remain limited, and at the time of this project, there had been no demonstrations in active DoD harbors. Dredging is expensive, energy intensive, can have adverse short-term effects such as impacts to the benthic community and surface water, and often cannot be applied near structural bulkheads and beneath piers. Also, dredging effectiveness is often hampered by the inability to remove contaminated sediments in and around piers and structural areas common to active DoD harbors.

Conventional sand-based isolation capping also impacts the benthic community; may be limited by vessel draft requirements; can be unstable in the face of tides, currents, ship, and tug movements; and has minimal capacity to control sources. MNR is generally targeted to quiescent, depositional environments and is generally thought to be poorly suited to high-energy environments subject to significant vessel traffic. The use of amendments, such as AC, promises to provide a cost-effective approach to overcome these challenges and to remediate active DoD harbor areas.

At the start of this project, the majority of the *in situ* reactive amendment applications had been small, pilot-scale efforts generally targeted to areas with minimal vessel traffic, obstructions, or harbor activities. In addition, most of these efforts focused on the use of granulated AC, which is not considered to be suitable for delivery and stability in deep-water active harbors due to its low density. Extending these efforts to an active DoD harbor area with propeller wash, piers, bulkheads, deep water, and a range of other common challenges associated with coastal installations is necessary to demonstrate the broader, more critical application for solving DoD's contaminated sediment challenge. No cost-effective technology had been demonstrated that can meet this range of challenges at the time of this project.

## 1.2 OBJECTIVES OF THE DEMONSTRATION

The objective of this pilot-scale field demonstration was to evaluate and validate placement, stability, and performance of reactive amendments for *in situ* treatment of contaminated sediments in active DoD harbor settings. The approach to demonstrate and validate this *in situ* treatment using reactive amendments was focused on performance issues including:

- Proper design and selection of the amendment,
- Placement and physical stability of the reactive amendment in deeper water areas that support vessel traffic,
- Effectiveness of the amendment in reducing contaminant bioavailability over time, and
- Quantification of changes to benthic habitat and benthic community structure.

These demonstration and validation criteria form the basis of the POs. Data was collected in support of these POs and provided multiple lines of evidence for assessing the effectiveness of amendment placement as an *in situ* strategy for limiting chemical bioavailability at contaminated sediment sites.

## 1.3 REGULATORY DRIVERS

The demonstration project at Pier 7 was conducted as a remedial action for Operable Unit (OU) B in accordance with the Record of Decision (ROD) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA). Implementation of the CERCLA remediation process is outlined in Title 40 of the Code of Federal Regulations (CFR) Part 300, National Oil and Hazardous Substance Contingency Plan (NCP).

## 2.0 TECHNOLOGY

### 2.1 TECHNOLOGY DESCRIPTION

The technology incorporates a combination of a reactive amendment, a conventional placement equipment, and a suite of monitoring tools. The novel aspect of the technology involves the demonstration of a composite particle system that enables the delivery of the amendment to an active DoD harbor environment, particularly in areas where piers and structures limit traditional dredging and capping methods (Figure 1). The amendment was placed using a composite particle system based on the AquaGate®+PAC (referred to here as AquaGate) technology platform (AquaBlok, Ltd., Toledo, Ohio). AquaGate is powdered activated carbon (PAC) bound to a dense, aggregate particle with clay minerals. AquaGate utilizes a coated aggregate particle as the means for achieving uniform placement of reactive amendments through deep water to the surface of the sediment. This technology has been used to deliver a range of mineral-based reactive amendments (AquaBlok Ltd. 2010). The formulation for this demonstration incorporates a nominal 5% PAC, 10% clay (sodium bentonite), and the remaining fraction of aggregate, by weight.

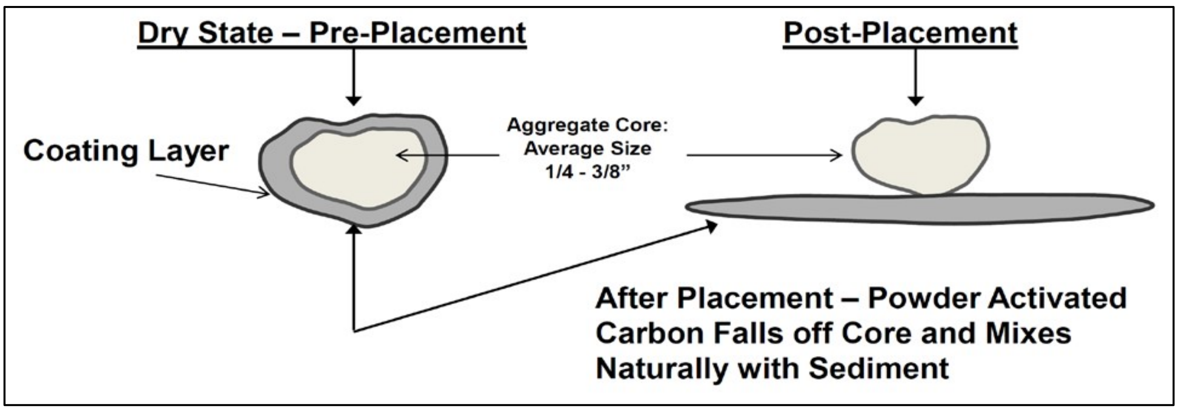


**Figure 1. Composite Particle Approach (AquaGate).**

From a placement perspective, the AquaGate particles resemble small stones and can be handled and applied with a wide range of conventional construction equipment. Due to the physical setting at this site, broadcast application with conveyor belt-type equipment (e.g., Putzmeister's Telebelt®) provided a suitable option for rapid, relatively uniform placement. The concurrent demonstration of robust monitoring techniques for assessing delivery, stability, and effectiveness in reducing bioavailability were integrated for this project.

#### 2.1.1 Development of Sorbent (Reactive) Sediment Amendments

Persistent hydrophobic organic compounds (HOCs), such as PCBs, when released into the aqueous environment can eventually become associated with sediment, where they may reside for long periods of time due to a combination of properties including strong sorption and slow degradation (Millward et al. 2005). PCBs have been identified as the most common CoC in contaminated sediments in the United States (NRC 2007). At elevated concentrations, these contaminants pose long-term risks to ecosystems and human health.

Reactive amendments are chemical or mineral-based materials designed to react *in situ* with sediments and porewater through direct contact. Contaminant bioavailability is decreased, though the total concentration of chemicals in sediment is expected to remain constant. Bioavailability is decreased by increasing the sorptive capacity of the sediment and thus decreasing dissolved concentrations of HOCs in porewater and surface water. As more emphasis is being placed on the development of alternative *in situ* sediment remedial technologies (SERDP/ESTCP 2004, USEPA 2005) and research has demonstrated strong binding of HOCs in anthropogenic and naturally occurring particulate in sediments (Zimmerman et al. 2004), there is a growing movement towards the development and application of *in situ* sorbent amendments for contaminated sediment management.

There are numerous reactive amendments—both natural mineral sorbents (e.g., apatite, barite, bentonite) as well as engineered materials (e.g., ATS, Thiol-SAMMS)—that have been bench-scale tested for their organic and metal sorption capacity (Ghosh et al. 2008, Ghosh et al. 2011). For HOCs such as PCBs, AC has been demonstrated to be the most effective type of sorbent. Other carbon types such as coke, charcoal, and organoclays have been suggested, but the sorption capacity for PCBs in AC is at least an order of magnitude higher than in the other sorbents (Ghosh et al. 2003).

Laboratory studies have demonstrated field-collected contaminated sediment amended with AC amendments in the range of 1–5% reduced the equilibrium porewater concentrations of HOCs in the range of 70–99%, thereby reducing the diffusive flux of the HOCs into the water column and bioaccumulation in benthic organisms (Hale and Werner 2010, Ghosh et al. 2011, Kupryianchyk et al. 2015). In addition to reduced uptake of HOCs, increased survival in invertebrates exposed to 1% AC amended sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) relative to unamended sediments was observed (Kupryianchyk et al. 2011).

Ghosh et al. (2011) summarizes five on-going pilot-scale field studies in which AC is used to reduce the bioavailability of HOCs in sediment. The field sites include a tidal mudflat, a freshwater river, a marine harbor, a deep-water fjord, and a tidal creek and marsh. In each case, the form of AC used, the application technique employed, and suite of contaminants differed. However, each study had similar objectives: (1) assess the feasibility of field-scale application using large equipment, (2) assess the persistence of AC and binding capacity in the natural environment, (3) assess the effectiveness of the AC in reducing contaminant bioavailability, (4) assess the reduction in porewater concentrations and sediment-to-water fluxes, and (5) evaluate the effects of AC addition on the existing benthic community. Results from the tidal mudflat demonstration at Hunters Point Shipyard in San Francisco Bay showed that AC can be placed in sediment in large scale, is physically stable in the environment, and remains effective in binding contaminants in sediments several years after application (Cho et al. 2009, Ghosh et al. 2011). PCB bioaccumulation in benthic invertebrates at Hunters Point was reduced by 85–90% (Janssen et al. 2011).

A more recent review (Patmont et al. 2015) reports that in the past decade, there have been 25 full- or pilot-scale studies of AC *in situ* treatment of contaminated sediments. Studies reviewed included placement of AC via directly applying a thin layer of amendments (which potentially incorporates weighting or binding materials) to surface sediment with or without initial mixing, and incorporating amendments into a premixed blended cover material of clean sand or sediment also applied to the sediment surface. Notable studies reviewed include:

(1) Lower Grasse River, Massena, New York, where three separate application techniques were proven to effectively deliver AC slurry with no water quality impacts, and resulted in 99% reduction of porewater concentrations of PCBs; and (2) Upper Canal Creek, Aberdeen Proving Ground, Maryland, where three AC delivery methods (SediMite™, AquaGate, AC slurry) were evaluated. With all delivery methods, reduced PCB bioavailability was observed and no significant phytotoxicity or impact to species abundance was shown.

Results from the Hunters Point, Lower Grasse River, and Upper Canal Creek Studies, as well as the other on-going pilot studies, provide valuable information about the long-term effectiveness and the physical stability of the AC and the chemical permanence of the remedy. According to Patmont et al. (2015), *in situ* treatment via AC has progressed from an innovative sediment remediation approach to a proven, reliable technology when applied correctly.

Despite these successes, there is an ongoing need to continue to build regulatory confidence and acceptance of AC amendments to remediate contaminated sediment sites, and to provide a reliable alternative to mass removal (dredging) or isolation capping. The efficiency of AC is known to be dependent on several factors including AC characteristics (particle size and pore geometry), concentration of AC applied, the steric properties of the sorbates (such as hydrophobicity, molar volume, and planarity of molecular conformation), sorption competition among different HOC, organic matter (OM) adsorbates (OM "fouling"), and mixing intensity (Kupryianchyk et al. 2015). *In situ* AC amendment of contaminated sediments has been demonstrated in depositional, low-energy environments, where the potential for erosion and transport of the carbon amendment after placement is low. Additional research on application to sites with varying characteristics is needed (Hilber and Bucheli 2010, Ghosh et al. 2011, Kupryianchyk et al. 2015).

Recent research through Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) projects addresses strategies to assess the ecological recovery after *in situ* sediment treatment by AC amendment. In a three-phase project at Hunters Point in San Francisco Bay, San Francisco, California, Luthy et al. (2011, 2013, and 2015) showed successful use of rapid assessment tools for measuring concentrations of PCBs in porewater, developed a biodynamic modelling approach to verify the benefit of AC treatment in sediments, and evaluated changes in risk related to loss or removal of AC after treatment.

Continued research is needed in several areas (SERDP/ESTCP 2004), including the development of novel amendments able to actively bind CoCs other than HOCs, developments of efficient and low-impact delivery methods for amendments in sediments, pilot-scale studies at various hydrodynamic and ecological environments to understand where the technology is best suited, additional tools for the assessment of ecosystem recovery, and additional full-scale demonstrations to extend knowledge gained from small-scale pilot studies (Ghosh et al 2011, SERDP/ESTCP 2004). Building on the previous successes of the projects discussed above, this project addressed several research needs, evaluated the application of the technology under new conditions, and assessed the ability to reduce bioavailable concentrations thereby reducing ecological and human health risks.

### 2.1.2 AquaGate Composite Aggregate Technology

The goal of the reactive amendment technology for *in situ* remediation of contaminated sediments at Pier 7 at PSNS & IMF was to reduce bioavailability by introducing a small amount of a chemical sorbent to the contaminated surface sediment. The composition of the sorbent was selected based on the nature of sediment contamination and the extent to which amendments are required to achieve specific remedial strategies.

Among the large number of amendments tested, AC has shown promising results in laboratory treatability studies and at pilot-scale for reducing the bioavailability of HOCs (such as PCBs) in sediment. However, all forms of AC (powdered and granular) have a very low specific gravity and bulk density, and readily float in fresh and saline waters. This property limits the ability for AC to be applied via direct placement in underwater environments because AC added directly to the water column may not settle to the sediment bed and instead is likely to remain floating or suspended in the water column, preventing reliable or uniform application in the target placement area.

A range of approaches for applying AC to underwater sediments have been developed and demonstrated at a pilot scale. For this project, it was desired that PAC be applied to take advantage of the performance benefit of PAC over granular forms of AC. One of the technologies considered to have significant potential for flexible, low-cost application of PAC was developed by AquaBlok, Ltd. (AquaBlok).

AquaBlok initially applied its composite particle technology to the delivery of a bentonite-based material to form a low-permeability layer over contaminated sediments. This technology has been successfully evaluated under the USEPA Superfund Innovative Technology Evaluation (SITE) program and installed at >100 sites to contain the migration of contamination in sediments or soils. In 2007, AquaBlok began working in Norway and the United States to adapt its technology for the delivery of PAC through the water. This product is called AquaGate®+PAC (AquaGate). A schematic representation of the composite particle approach employed by AquaBlok for PAC is presented in Figure 1 and Figure 2. The AquaGate composite particle is manufactured using a stone core coated with a combination of bentonite-based clay and PAC materials. The PAC particles used for this AquaGate application were ≤74 micrometers (µm) in diameter. This approach increases surface area of the thin PAC coating later (around the stone core) and provides uniform delivery/placement of a small amount of PAC over a larger area than if AC alone were utilized. Because the lighter powder coating materials are bound to an aggregate substrate to form the composite particle, the particle has a very high specific gravity (compared to the coating materials) and will sink rapidly through the water.

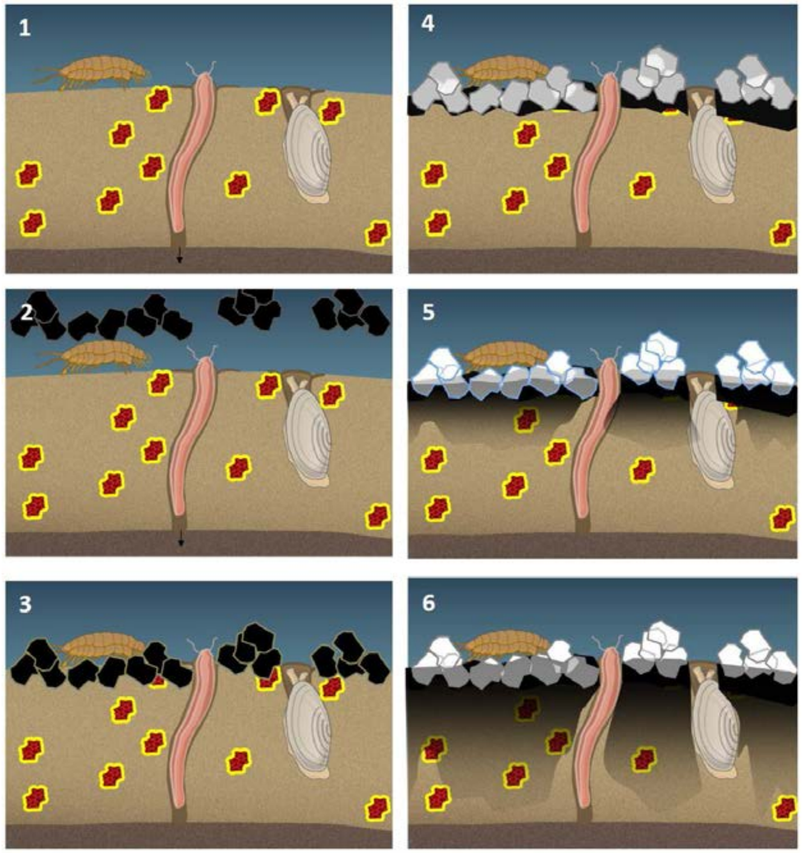


**Figure 2. AquaGate Delivery, AC Release, and Mixing in Surface Sediment Showing the Pre-installation Conditions.**

*(1) the gravitation descent of the amendment coated aggregate, (2) the layering of the aggregate on the sediment bed, (3) the release of the amendment to the sediment, and (4–6) the gradual burial and mixing of the amendment over time.*

After placement, the coating materials disaggregate from the stone core and become mixed with the underlying sediment (Figure 1, Figure 2). Natural mixing (bioturbation) is expected to help incorporate the PAC material into the surface sediment layer allowing it to adsorb target contaminants, providing reduction in bioavailability over time. Because bentonite-based clay minerals are used as a component of the coating material and this material is known to have a high cation exchange and binding capacity for metals, the amendment was also evaluated for mercury (Hg) sorption capability.

The AquaGate technology was considered to be in its development phase at the time of this project; a large-scale remedial application of the material had not yet taken place commercially. To date, AquaGate has been surface applied in a marsh setting under an existing ESTCP project (Menzie and Davis 2010). In addition, a form of AquaGate was applied in a deep water setting during a pilot project in Bergen, Norway, in early 2010. However, this delivery technology has not been used in the United States to place PAC in a deep-water, active shipyard setting.

Based on a number of research and demonstration projects supported by SERDP/ESTCP and industry, reactive sediment amendments—and specifically AC—has emerged as a well understood, innovative remediation alternative. Significant bench-scale testing of AC has demonstrated its applicability for binding contaminants into matrices that reduce aqueous-phase concentrations and bioavailability (Ghosh et al. 2000, Ghosh et al. 2003, Ghosh et al. 2009, Merritt et al. 2009, Millward et al. 2005, USEPA 2005, Zimmerman et al. 2004 and 2005). For hydrophobic organic contaminants, such as PCBs, AC has shown consistently positive results (Magar et al. 2003, Luthy et al. 2004). Other materials, such as bentonite, have shown a degree of effectiveness for binding metals, such as Hg.

## 2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The principal strategies used for managing contaminated sediment include dredging, *in situ* capping, MNR, and *in situ* treatment. Dredging removes contaminated sediment from a water body. Capping refers to the placement of a subaqueous covering—or cap—of clean material over contaminated sediment that remains in place as a means of isolation or stabilization. MNR is a remedy that typically uses ongoing, naturally occurring processes to contain, destroy, or reduce the bioavailability or toxicity of contaminants in sediment. *In situ* treatment is an approach that involves the biological, chemical, or physical amendment of contaminated sediment in place and includes sequestration (bioavailability reduction as is the case for AquaGate amendment technology). Each remedial strategy has its advantages and limitations. The selection of the most appropriate strategy, or combination of strategies, requires balancing several criteria for remedial selection, which includes long-term effectiveness, permanence, and cost as well as reduction of toxicity or mobility through treatment (USEPA 2005).

The DoD faces increasing demands to address contaminated sediment sites, particularly for active harbor areas and relatively deep waters. *In situ* treatment, such as sequestration (e.g., AquaGate) has been demonstrated to reduce the bioavailability of HOCs in place. AquaGate amendment has several key advantages over dredging as a remedial option in this setting due to its ability to remediate around piers and infrastructure (e.g., bridges, docks, bulkheads, or pilings), overhead restrictions, and narrow channel widths. The technology would be preferred as a remedy over capping due to constraints on water depths for berthing and navigational purposes. *In situ* treatment, compared to dredging or capping in general, also minimizes the impact on existing habitat, shortening the length of recovery (Gosh et al. 2011). This is of particular benefit in settings where it may not be possible to achieve sediment deposition at a rate that would increase the time to meet MNR recovery goals.

Another benefit of the technology is that it can be installed with conventional equipment, which most settings can accommodate due to ease of maneuverability and portability and the ability to deploy within an active Naval Shipyard. Site access and logistics would not be as large of an issue as is generally encountered during dredging. Unless low-cost, readily-available disposal is available, sequestration will be less expensive than dredging due to the absence of transport, staging, sediment treatment (where applicable), and disposal of dredging sediment. Furthermore, additional cost to treat effluent prior to discharge to an appropriate receiving water body from dewatered sediment is frequently encountered for dredging. There may be scenarios where dredging is less expensive, such as sites with shallow contamination (less volume of dredged material) and especially if low contaminant levels enable ocean disposal. Costs associated with capping are comparable to sequestration, although the capping material may be less expensive; generally, the volume of material placed is much larger.

Sequestration has the ability to reduce exposure to contaminants in a comparable time frame to capping and dredging (where dredging residuals are low) and would likely be a faster option to achieve a remedial action objective than MNR. Furthermore, sequestration treatments such as AquaGate have the benefit of being able to be applied in combination with other remedial alternatives such as capping or dredging, and also when armoring is needed.

There remains some uncertainty as to the long-term effectiveness of sequestration treatment in the field; further research is needed. Since the initiation of this project, the application of sequestration at full-scale has been performed successfully, but long-term monitoring data is not yet available. Because of public perception and predisposition by the regulatory community, dredging continues to be the most common and accepted means of sediment remediation.

Any remedy that leaves untreated contaminants in place, such as *in situ* sequestration, may have the potential for risk of re-exposure of the contaminants. A similar risk would be encountered for sites utilizing MNR, capping, or dredging with high concentrations in residuals left in place. However, the risk from potential effects of re-exposure may be less if low concentrations of contaminants remain in the sediment. Furthermore, sequestration may be limited in its ability to deliver needed amendments to deeply buried contamination, particularly in deep water environments where the bioturbation is the primary mechanism for mixing.

Effects to the benthic community have the potential to be observed from sequestration. Adverse effects have been observed in approximately 20% of the laboratory studies of individual species with 2–5% AC by weight (Rakowska et al. 2012, Janssen and Beckingham 2013). These adverse effects may be due to affinity of AC to sorb lipids, carbohydrates, proteins, and nutrients; impairment of digestion from amendment; or degradation of habitat quality. Field studies of benthic community health have found no or mild effects on diversity and abundance at low doses of AC amendments. The response of the benthic community is thought to be amendment-, community-, and site-dependent. However, it is also important to recognize dredging and capping as forms of remediation also have the potential to impact the benthic community, as these remedies remove or bury the existing benthic community, necessitating recolonization. In the case of capping, the cap material may influence a change in community composition.

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## 3.0 PERFORMANCE OBJECTIVES

Following a successful laboratory treatability study conducted with sediments from the site, the field demonstration was designed to provide baseline (2 months prior to amendment placement) and post-placement monitoring at 0.5, 3, 10, 21, and 33 months after placement of the reactive amendment. The POs for the project are provided in Table 1. The evaluation was based on data collected during the laboratory treatability study (PO 1, Kirtay et al. 2012) and data collected during pre- and post-placement monitoring events (PO 2–PO 7). Data collected in support of these POs provided multiple lines of evidence for assessing the effectiveness of amendment placement as an *in situ* strategy for reducing chemical bioavailability at contaminated sediment sites.

**Table 1. Project Performance Objectives (POs).**

| Performance Objective (PO) | Data Requirement | Success Criteria | Results |
|---|---|---|---|
| **Quantitative POs** | | | |
| (1.) * Verify amendment performance in the laboratory. | Bioaccumulation results for *Neanthes arenaceodentata* compared to control exposed to site sediment amended under a range of mixing conditions. | • Reduction in biouptake of target CoC (PCBs) in treatment compared to controls.<br>• Target >50% reduction in PCBs. | Met<br>(Met for 24-hr mix and 1-month mix, which were most similar to field conditions) |
| (2.) Demonstrate amendment associated reduction in contaminant bioavailability in the field. | SEA Ring deployments to measure *in situ*:<br>- Bioaccumulation in polychaete and bivalve tissues.<br>- Porewater concentrations with passive samplers. | • Significant reduction (>50%) in bioaccumulation of PCBs compared to baseline.<br>• Hg and MeHg measured for tracking purposes only. | Met<br>(Met for PCBs) |
| (3.) Demonstrate reduction in contaminant bioavailability is sustained over time. | SEA Ring deployments to measure *in situ*:<br>- Bioaccumulation in polychaete and bivalve tissues.<br>- Porewater concentrations with passive samplers. | • Reduction in bioaccumulation compared to baseline is sustained >2 years.<br>• Hg and MeHg measured for tracking. | Met<br>(Met for PCBs) |
| **Qualitative POs** | | | |
| (4.) * Demonstrate detectability of amendment using SPI visual monitoring methods in the laboratory. | Lab SPI images of control, no mix layer, and two mixed layers. | • Amendment was qualitatively distinguishable from native sediment in SPI images. | Met |
| (5.) Demonstrate uniform deep water placement to target area. | SPI images; TOC and BC analysis of sediment cores. | • Amendment evenly distributed at target thickness (~2±1 in).<br>• 2.1–4.1% increase in TOC and BC content in surface sediments.<br>• Within ~90% of the target area as indicated by SPI surveys. | Met<br>(Met for SPI, visual analysis of cores, diver survey, and TOC) |

**Table 1. Performance Objectives for the Project (Continued).**

| Performance Objective (PO) | Data Requirement | Success Criteria | Results |
|---|---|---|---|
| (6.) Demonstrate amendment physical stability over time. | SPI images; TOC and BC analysis of sediment cores. | • Amendment remains evenly distributed laterally while mixing vertically over time.<br>• Same success criteria as PO 5. | Met<br>(Met for SPI, visual analysis of cores, TOC in 10-, 21-, and 33-month events, BC in 3-, 10-, and 21-month events) |
| (7.) Evaluate benthic community changes in response to amendment. | Benthic community census data. | • No or minimal adverse impact in benthic community ecological health metrics. | Met |

*Objective performed as part of a laboratory study prior to field demonstration.

Note: The POs were demonstrated with monitoring tools including the Sediment Ecotoxicity Assessment Ring (SEA Ring), Sediment Profile Imaging (SPI) system, benthic community analysis, and measurements of total organic carbon (TOC), black carbon (BC), and CoC concentrations in sediments, tissues, and passive samplers.

# 4.0 SITE DESCRIPTION

## 4.1 SITE LOCATION

The site selected for the reactive amendment demonstration was adjacent to and under the southwest end of Pier 7 at PSNS & IMF inside the Bremerton Naval Complex (BNC) (Bremerton, Washington, Figure 3). The Pier 7 site was selected because it met the selection criteria for this project and provided a unique opportunity to evaluate the implementation of a reactive amendment at a moderately contaminated DoD sediment site on field scale within an active harbor. Vessel traffic during the study ranged from small recreational and commercial fishing vessels to occasional larger tug and Navy ship traffic, and regularly scheduled Washington State ferries arriving and leaving the Bremerton Ferry Terminal.

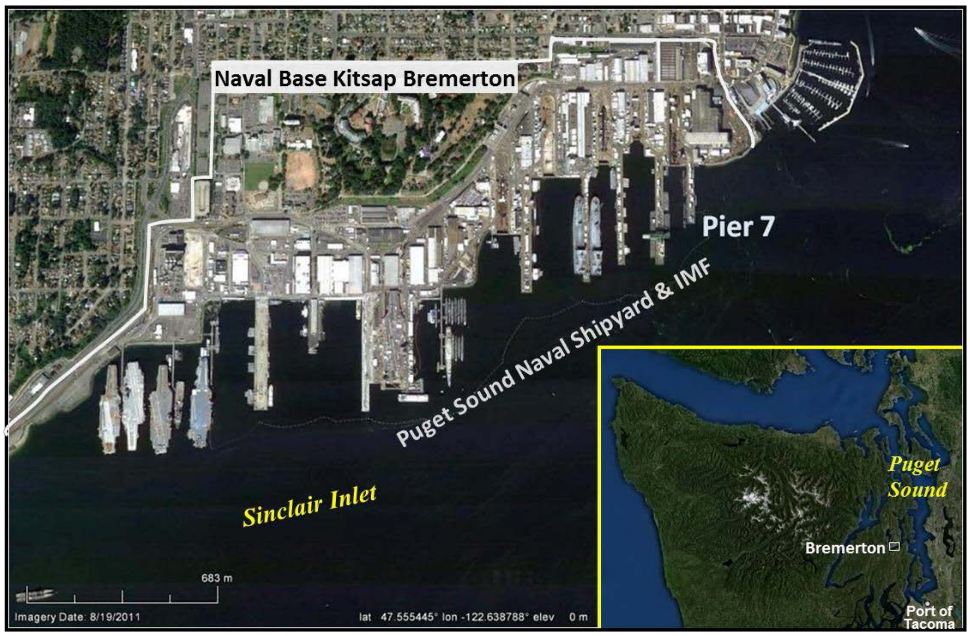



**Figure 3. Site Location – Pier 7 at PSNS & IMF in Sinclair Inlet near Bremerton, Washington.**

## 4.2 SITE GEOLOGY/HYDROGEOLOGY

The BNC shoreline has been greatly modified from its original condition. At present, the shoreline is comprised of an industrial waterfront armored with quay walls and riprap, and is developed with several large piers and six dry docks. Along the quay walls, water depth drops off more or less vertically to approximately 15–20 feet below mean lower low water (MLLW). In rip-rapped areas, depths at the immediate shoreline are commonly <5 feet MLLW, but drop off steeply beyond this. Recent bathymetric survey data at BNC reveal water depths generally ranging between 40 and 45 feet, except in dredged areas near piers and vessel berthing areas where depths increase to 45–50 feet. Offshore of the site, water depths are generally 40–45 feet. Depths increase to >120 feet at a bathymetric depression located southeast of BNC in the entrance channel to Sinclair Inlet (U.S. Navy 2008).

Nearshore sediments along the north shore of Sinclair Inlet and in the central inlet are dominated by silt and clay, while sand is primarily restricted to the mouth of the inlet where the currents are higher (McLaren 2011). The implications of the depositional nature of the inlet are that contaminated sediments remain resident in the inlet for long periods. Tidal currents and winds are the primary sources of water circulation in Sinclair Inlet. Weak tidal currents move water in and out of the inlet with a maximum velocity of 0.2–0.3 knots. Surface currents generally flow out of the inlet, although surface current flow into the inlet has been observed during summer months. Near-bottom currents primarily flow into the inlet, regardless of season. Currents are generally not capable of re-suspending bottom sediments.

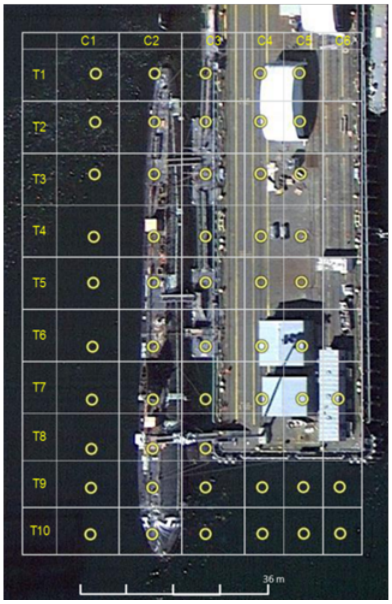
## 4.3 CONTAMINANT DISTRIBUTION

Pier 7 lies within an area known as OU B Marine, which was previously subject to a Superfund sediment cleanup (USEPA 2000a). Sediments near Pier 7 were sampled to document conditions in vicinity of the pier prior to replacement of fender piles associated with the pier. Both pre- and post-sampling was carried out to meet the requirement of state water quality certification for the project (U.S. Navy 2008, U.S. Navy 2010). The pre-construction sediment sampling involved collection and analysis of 11 sediment samples (0–10 centimeters [cm]) for PCB, TOC, and grain size. PCBs were detected in all samples. PCB concentrations (quantified as total Aroclors) ranged from 0.12–35 milligrams per kilogram (mg/kg) (2.0–1,100 mg/kg OC normalized).

In 2009, work commenced at Pier 7 to replace 325 timber creosote piles with 166 concrete pilings, and place a sand blanket and gravel armoring on the bottom covering about 15 feet either side of the piling line. Upon completion of this project, post-sampling was carried out at the same sampling locations, and additional samples were collected near the areas containing the highest PCB concentrations measured during the pre-construction sampling. PCBs were detected in all but two samples and ranged in concentration from 0.028–2.0 mg/kg (0.94–140 mg/kg OC normalized). In general, overall PCB concentrations were lower in the post-construction samples than were measured in the pre-construction samples.

Despite a determination that the Pier 7 construction activities would not have a direct impact on achieving the OU B Marine cleanup goals, the continual presence of elevated levels (above Washington State Sediment Quality Standards [SQS]) of PCBs (and Hg) in the Pier 7 area resulted in the desire to test alternative *in situ* treatment methods, such as reactive amendments, in this area.

In May 2010, a diver-assisted sediment survey was conducted around Pier 7 to more thoroughly delineate the nature and extent of contamination at the demonstration area. Ten transects perpendicular to the pier were established with 4-in surface cores taken about every 50 feet in the berthing area and every 30 feet under the pier, avoiding the recently disturbed area 15 feet on either side of the fender pilings (Figure 4). Rapid Sediment Characterization (RSC, Kirtay et al. 2001) methods were used to screen the samples using a portable X-ray Fluorescence (XRF) detector for metals (copper [Cu], zinc [Zn], and lead [Pb]) and Enzyme Linked Immuno-Sorbent Assays (ELISA) for PCBs (as Aroclor 1254, RaPID$^{TM}$ Assay, Strategic Diagnostics Inc., Newark, Delaware) and PAHs (as total PAHs, USEPA Method 4035). The results showed an isolated area of elevated contamination for PCBs and patchy locations of elevated total Hg.




**$PCB_{RSC}$ ng/g**

| | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|
| T1 | 234 | 192 | 91 | 46 | 152 | |
| T2 | 176 | 151 | 28 | 261 | 58 | |
| T3 | 170 | 96 | 285 | 74 | 48 | |
| T4 | 341 | 140 | 113 | 133 | 11 | |
| T5 | 111 | 594 | 159 | 150 | 74 | |
| T6 | 243 | 262 | 6650 | 305 | 439 | |
| T7 | 224 | 261 | 129 | 655 | 193 | 105 |
| T8 | 227 | 129 | 163 | | | |
| T9 | 74 | 74 | 73 | 84 | 80 | |
| T10 | 161 | 24 | 126 | 92 | 134 | 115 |

**Hg ug/g**

| | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|
| T1 | | 0.64 | 0.40 | 0.24 | 0.62 | |
| T2 | 0.52 | 0.20 | | 0.70 | 0.17 | |
| T3 | 0.43 | 0.11 | 0.73 | 0.19 | | |
| T4 | 1.19 | 0.29 | 0.45 | 0.57 | 0.21 | |
| T5 | 0.21 | 0.83 | 0.69 | 0.44 | 0.49 | |
| T6 | 0.56 | 0.49 | 0.90 | 0.36 | 0.60 | |
| T7 | 0.33 | 0.85 | 0.14 | 0.69 | 0.34 | 0.26 |
| T8 | 0.12 | 0.17 | 0.28 | | | |
| T9 | 0.32 | 0.35 | 0.17 | 0.06 | 0.18 | 0.20 |
| T10 | 0.67 | 0.06 | 0.44 | 0.81 | 0.92 | 1.00 |

**Figure 4. Locations of Sediment Samples and Corresponding Concentrations of PCBs and Hg.**

*Locations of sediment sampling transects (left figure), concentrations of PCBs (ELISA, nanograms per gram [ng/g], middle figure), and Hg (cold vapor atomic absorption [CVAA], micrograms per gram [µg/g], right figure) in surface sediment samples collected from Pier 7 to characterize the site and identify sediments for use in the laboratory treatability study.*

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# 5.0 TEST DESIGN

## 5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Prior to the field-scale demonstration, a laboratory treatability study was performed to evaluate the site-specific effectiveness of the reactive amendment using sediments collected from the vicinity of the Pier 7 site. For this project, a field-scale demonstration of the effectiveness of reactive amendment was performed. Baseline conditions were characterized prior to amendment placement and surface sediments were monitored for three years after amendment placement at several intervals. Physical, chemical, and biological parameters were monitored as follows to evaluate the POs:

- Physical parameters were used to demonstrate uniform deep water placement in the target area by assessment of the distribution and coverage, uniformity, and thicknesses of the amendment immediately after placement and to evaluate changes due to natural sedimentation, benthic mixing, and ship or tug activity. Physical parameters included: (1) Images of the profile of the sediment, (2) measurement of TOC in sediment, (3) measurement of BC in sediment, and (4) visual assessment of cores.
- Chemical parameters were used to measure the magnitude the reactive amendment reduced contaminant bioavailability and sustainability of bioavailability reductions over time. Chemical parameters included: (1) Measurement of concentrations of PCBs, Hg, and MeHg in tissue; (2) measurement of concentrations of PCBs in sediment porewater; and (3) measurement of concentrations of PCBs, Hg, and MeHg in bulk sediment.
- Biological parameters were used to evaluate potential changes in the benthic community in response to amendment placement. Biological parameters included: (1) Benthic community census and (2) images of the profile of the sediment.

## 5.2 BASELINE CHARACTERIZATION

Baseline characterization occurred in August 2012 (two months prior to amendment placement), to establish pre-remedial baseline bioavailability and ecological conditions for the site. Baseline characterization included the following:

- Benthic community census
- Bioavailable concentrations in tissue *(in situ* SEA Ring bioaccumulation)
- Bioavailable concentrations in sediment porewater (*in situ* solid phase microextraction [SPME] passive sampling)
- Concentrations in sediment
- Amendment placement (for future comparison), stability, and mixing (SPI)
- Amendment placement (for future comparison), stability, and mixing (TOC, BC, and visual analysis of cores)

These activities are discussed further in 5.4 (Field Testing). The results of the baseline characterization are given in Section 5.6 (Sampling Results).

## 5.3 TREATABILITY OR LABORATORY STUDY RESULTS

In 2011, Space and Naval Warfare Systems Command (SPAWAR) Systems Center Pacific (SSC Pacific) carried out laboratory treatability studies by mixing commercially available PAC reactive amendment AquaGate with PCB- and Hg-contaminated sediments obtained from the contaminated area adjacent to Pier 7 at PSNS & IMF. Components of the treatability study included pre-screening the site to delineate the nature and extent of contamination, conducting laboratory studies to verify the effectiveness of the amendment in terms of reducing contaminant bioavailability, and testing the SPI system (Germano and Associates 2012) for its ability to distinguish the amendment from native site sediment to support monitoring the placement, stability, and mixing of the amendment after installation.

The results from the treatability study demonstrated that amending the contaminated sediment collected from the Pier 7 site with AC (in the form of AquaGate in this study) effectively reduced the bioavailability of PCBs to the marine polychaete, *Neanthes arenaceodentata*. Increasing AquaGate contact time with the Pier 7 sediment resulted in progressively lower biouptake with up to 94% reduction of total PCBs for the one month mixed treatment. Additionally, the results from testing the SPI camera as a placement/stability verification monitoring tool also yielded promising results as the tool was able to distinguish the amendment from the native sediment. Results from the laboratory treatability study were used to support the design of the pilot-scale demonstration at PSNS & IMF (Kirtay et al. 2013).

## 5.4 FIELD TESTING

The project occurred over three years. Baseline characterization samples were obtained in August 2012 (two months prior to amendment placement), to establish pre-remedial baseline bioavailability and ecological conditions for the site. From October 16–19, 2012, AquaGate was placed in the target area. Post-placement monitoring events occurred at 0.5, 3, 10, 21, and 33 months post-amendment placement. Post-placement characterization documented the extent to which the amendment material mixes with underlying sediment, surface layer contaminant bioavailability changes, and ecological health is potentially changed. The activities completed during each phase are shown in Table 2.

**Table 2. Baseline and Post-construction Monitoring Event Schedule and Activities.**

| Activity | Baseline (August 2012) | 0.5 Month Monitoring Event (October 2012) | 3 Month Monitoring Event (January 2013) | 10 Month Monitoring Event (August 2013) | 21 Month Monitoring Event (July 2014) | 33 Month Monitoring Event (July 2015) | Performance Objective (PO) Addressed* |
|---|---|---|---|---|---|---|---|
| Benthic Community Census | X | | | X | X | X | 7 |
| Bioavailable concentrations of PCBs, Hg, and MeHg in tissue | X | | | X | X | X | 2, 3 |
| Bioavailable concentrations of PCBs in sediment porewater | X | | | X | X | X | 2, 3 |
| Concentrations of PCBs, Hg, and MeHg in Sediment (also grain size) | X | | | X | X | X | 2, 3 |
| Amendment placement, stability, and mixing; Benthic recovery (SPI) | X | X | | X | X | X | 5, 6, 7 |
| Amendment placement, stability, and mixing (TOC, BC, and visual analysis) | X | X | X | X | X | X | 5, 6 |

*POs are enumerated in Table 1.

The sampling locations included the following:

- Ten multi-metric stations (Figure 5) placed on the target amendment placement area (amended stations). The following observations were made at multi-metric sampling locations: (1) SEA Ring *in situ* benthic invertebrate bioaccumulation, (2) core sampling to provide visual confirmation as well as sectioning of cores for measurements of TOC and BC analysis to confirm stability and mixing of AC, (3) core sampling to provide surface sediment sampling of chemical (PCBs, Hg, and MeHg) and physical parameters (grain size), (4) *in situ* passive sampler (SPME) measurement of PCBs in sediment porewater, and (5) benthic sediment grab for benthic invertebrate census.
- Four benthic community census reference stations were located off of the target amendment area (unamended stations).

- 42 SPI stations were spatially distributed within and adjacent to the amendment area to provide information about sediment physical characteristics, benthic invertebrate community ecological health, and amendment presence, depth, and mixing. During the 10-month monitoring event, 8 additional sampling locations were added to the existing 42 SPI stations for a total of 50 stations. For the 33-month event, 1 additional SPI station was added for a total of 51 stations.

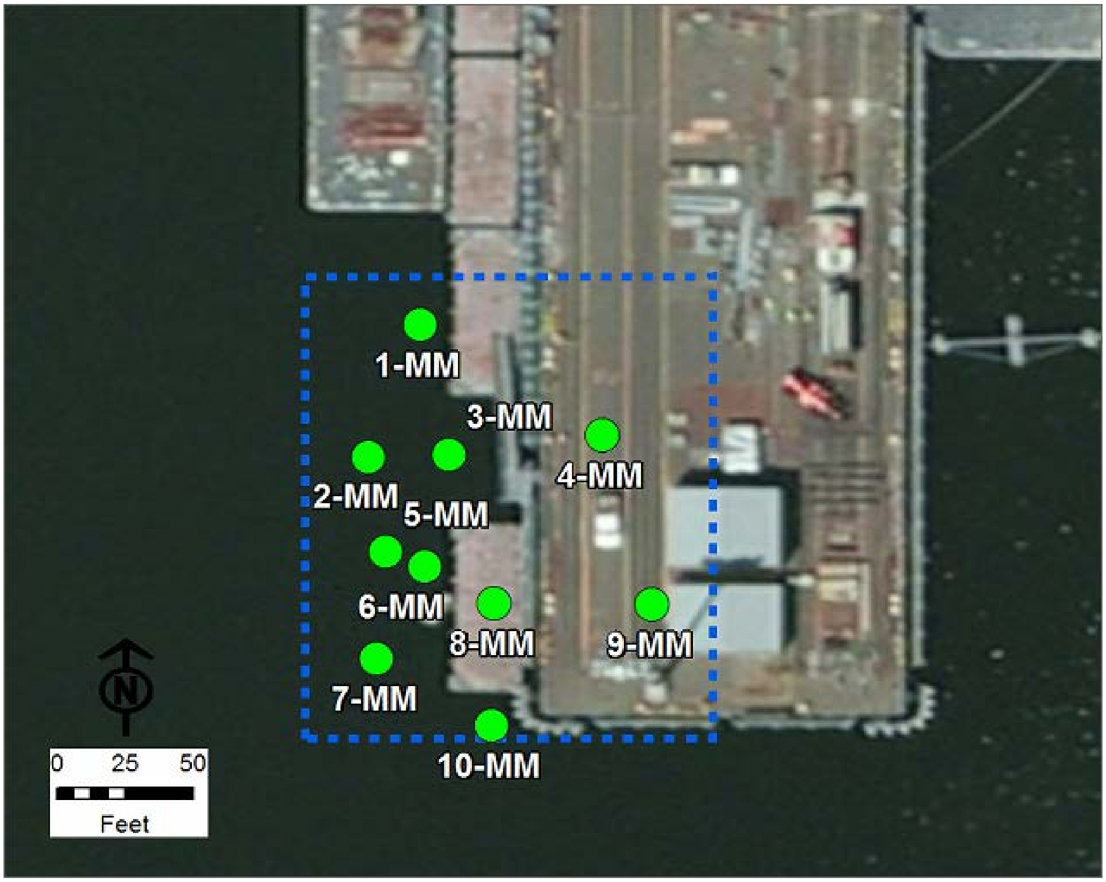


**Figure 5. Multi-metric Sampling Locations.**

## 5.5 SAMPLING METHODS

### 5.5.1 Benthic Community Census and Infaunal Succession

A benthic community census was conducted for the baseline characterization (2 months prior to the amendment placement) and the monitoring events 10, 21, and 33 months post-remedy deployment at 10 multi-metric and 4 reference locations. Macrobenthic invertebrates in the samples were identified to the lowest possible taxonomic level and the following six biological indices were used to evaluate the data: total abundance, taxa richness, species diversity, species evenness, species dominance, and dominance of the five most abundant taxa.

SPI camera images were used as a measure of benthic infaunal succession with observations for the baseline characterization and 0.5-, 10-, 21-, and 33-month post-remedy monitoring events.

Infaunal successional stages were recognized in SPI images by the presence of dense assemblages of near-surface polychaetes or the presence of subsurface feeding voids; both may have been present in the same image. The successional stages were based on the theory that organism-sediment interactions in fine-grained sediments follow a predictable sequence after a major seafloor perturbation (Germano and Associates 2013a).

### 5.5.2 Bioavailable Concentrations of PCBs, Hg, and MeHg in Tissue

Concentrations of PCBs, Hg, and MeHg in *Nephtys caecoides* polychaete worms and *Macoma nasuta* bent-nose clam tissue were analyzed following an *in situ* 14-day exposure using SEA Ring technology (Burton et al. 2013, Rosen et al. 2012). For all surveys except the 33-month event, intact cores were collected for exposure in the laboratory (Ramboll Environ, Port Gamble, Washington) under Project #ER-201130 as a means of comparing the *in situ* exposure results with those obtained under similar conditions in the laboratory.

### 5.5.3 Bioavailable Concentrations of PCBs in Sediment Porewater

SPME passive samplers were deployed for 14 days at each of the 10 multi-metric stations to provide a measurement of freely dissolved PCBs present in porewater of the surface sediment layer. The concentrations of total PCBs in sediment porewater were expressed by summing detected tetra-, penta-, and hexachlorobiphenyl congeners (congeners from other homolog groups were not detected).

### 5.5.4 Concentrations of PCBs, Hg, and MeHg in Sediment and Grain Size

Core samples were obtained during the baseline characterization, 10-, 21-, and 33-month post amendment placement monitoring events for analysis of surface sediment samples (0–15 cm below the sediment-water interface). Samples were collected and processed in general accordance with ASTM 1391 (ASTM International 2008). The analytical laboratory determined the percent debris in the samples by wet sieving (#10 [2 millimeters (mm)]) to remove debris such as shell hash, aggregate, and cobble. Concentrations of PCB congeners were then corrected for debris content.

### 5.5.5 Sediment Profile Image (SPI) Survey

The SPI survey was used to monitor amendment thickness and mixing, and provide information on sediment characteristics including buried organic-rich horizons, baseline depth, extent of biological mixing, and large-scale variations in sediment grain size that may indicate significant variations in energy regime and successional stage. SPI surveys were conducted from a boat using a frame-mounted camera or by hand using divers (under pier) at 42–51 locations within and adjacent to the target area.

### 5.5.6 Core Collection for TOC, BC, and Visual Analysis

Core samples for TOC, BC, and visual analysis were obtained in the baseline characterization, 0.5, 3-, 10-, 21-, and 33-month post amendment placement monitoring events for analysis of surface sediment samples (0–15 cm below the sediment-water interface). Samples were collected in general accordance with ASTM 1391 (ASTM 2008). The cores were sectioned into three 5-cm intervals (0–5 cm, 5–10 cm, and 10–15 cm below sediment-water interface) for visual analysis as well as TOC and BC analyses. The cores were visually examined to evaluate reactive amendment presence, depth, and mixing.

## 5.6 SAMPLING RESULTS

Sampling results are summarized below by PO.

### 5.6.1 POs 2 and 3: Demonstrate Amendment Associated Reduction in Contaminant Bioavailability in the Field, and Reductions Are Sustained Over Time

Concentrations of total PCBs on a lipid weight (lw) basis in *Macoma nasuta* tissue significantly decreased from the baseline characterization to the 21- and 33-month monitoring events (an average of 82% and 88% for lw basis, respectively) as shown in Figure 6. Concentrations of total PCBs on a lw basis in *Nephtys caecoides* tissue significantly decreased from the baseline characterization to the 10-, 21-, and 33-month monitoring events (an average of 87%, 89%, and 97% on a lw basis, respectively) as shown in Figure 6.

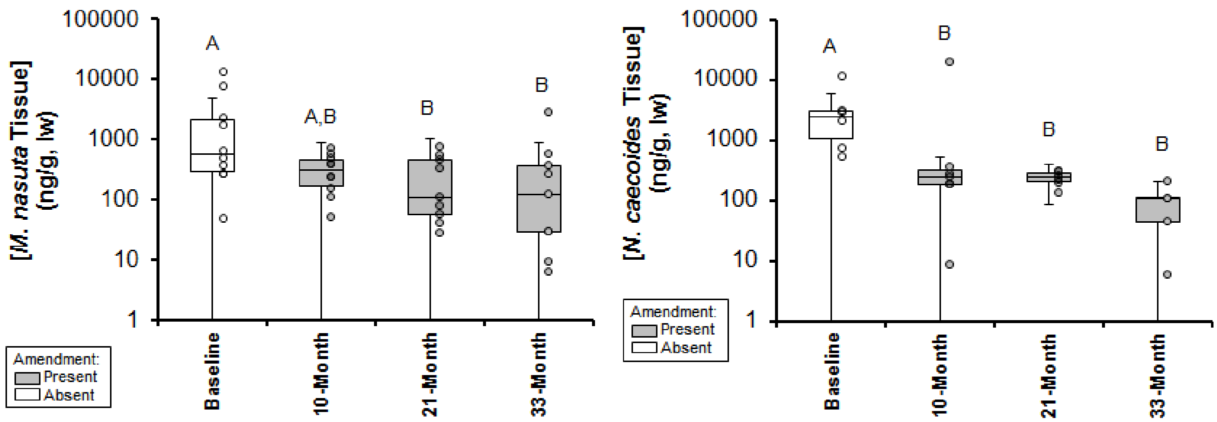


**Figure 6. Concentrations of Total PCBs in *Macoma nasuta* (left) and *Nephtys caecoides* (right) Tissue (ng/g, lw).**

*Events not connected by the same letter are significantly different ($p \leq 0.05$). Results are plotted as the median (horizontal bar), interquartile range (IQR) (limits of boxes are 25$^{th}$ and 75$^{th}$ percentiles), and error bars are 1.5 times the IQR. Data points are plotted as circle symbols.*

Concentrations of total PCBs freely dissolved in porewater were significantly decreased from the baseline characterization to the 10-, 21-, and 33-month monitoring events (an average of 75%, 86%, and 81% decreases were observed, respectively) as shown in Figure 7. Concentrations of total PCBs in bulk sediment in the 33-month event were not significantly different than concentrations in the baseline (average decrease of 56%). However, concentrations of total PCBs in bulk were significantly lower in the 10- and 21-month events than the baseline (average of 80% and 71%, respectively). The reason for the initial decrease of PCB concentrations observed for the 10-month event is not fully understood. The reduction could have been caused by inhomogeneity of sediments at the site, dilution from the amendment, or the difficulty in extracting PCBs bound to sediments treated with the AC due to irreversible binding of PCBs to the carbon particles as was observed during the treatability study and reported by other studies (Kupryianchyk et al. 2013).

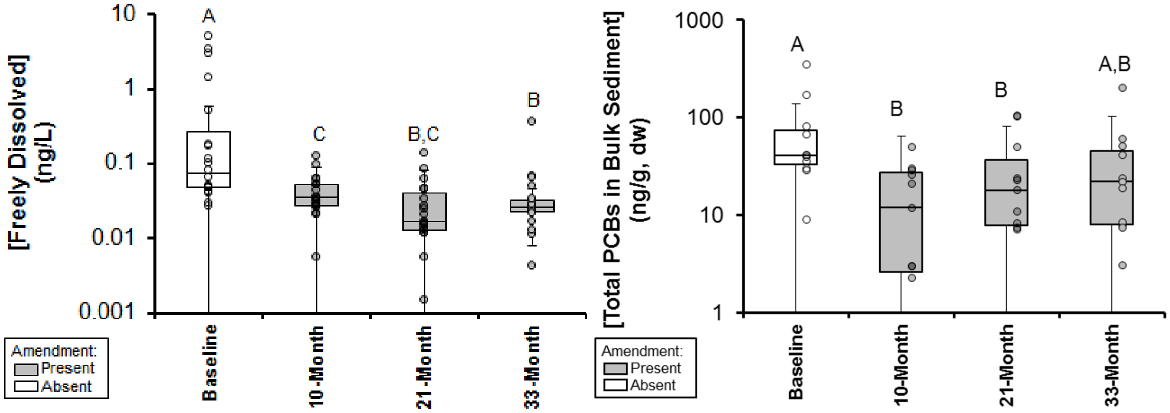


**Figure 7. Concentrations of Total PCBs Freely Dissolved in Porewater (left, nanograms per liter [ng/L]) and Total PCBs in Bulk Sediment (right, ng/g, dry weight [dw]).**

*Events not connected by the same letter are significantly different (p ≤0.05). Results are plotted as the median (horizontal bar), IQR (limits of boxes are 25th and 75th percentiles), and error bars are 1.5 times the IQR. Data points are plotted as circle symbols.*

The concentrations of total Hg in bulk sediment (unsieved) in the 10- and 21-month events were significantly lower than the baseline (81% and 80% on average, respectively, Figure 8). The reason for the initial decrease of total Hg concentrations observed for the 10- and 21-month events is not fully understood. The reduction could have been caused by inhomogeneity of sediments at the site, dilution from the amendment, and differences in the sample processing and analytical methods used during the study. No significant difference was observed from the baseline to the 33-month event (average 51% lower).

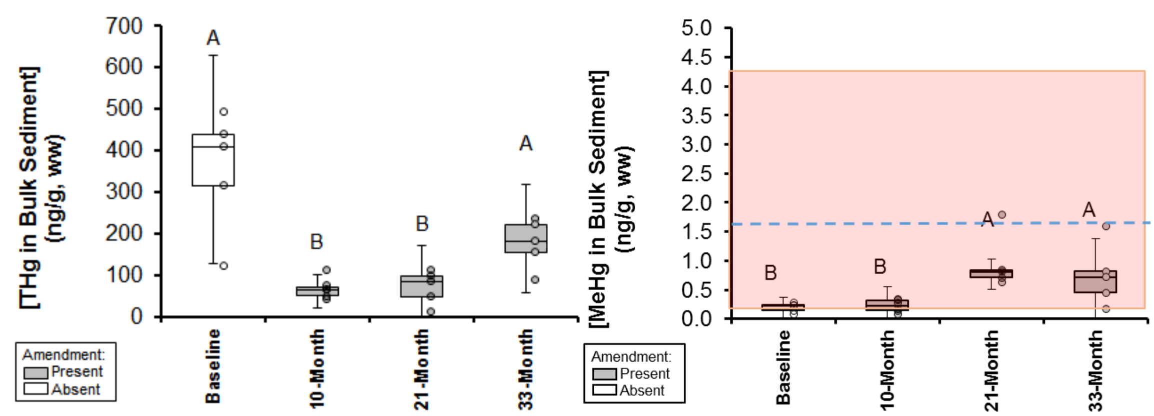


**Figure 8. Concentrations of Total Hg (left) and MeHg (right) in Bulk Sediment (ng/g, wet weight [ww]).**

*Events not connected by the same letter are significantly different (p ≤0.05). Results are plotted as the median (horizontal bar), IQR (limits of boxes are 25th and 75th percentiles), and error bars are 1.5 times the IQR. Data points are plotted as circle symbols. The range of MeHg observed for OU B Marine and Sinclair Inlet during long-term monitoring (shaded area) and average MeHg concentrations reported for reference areas of Puget Sound (dashed line).*

The concentrations of MeHg in bulk sediment, conversely to the total Hg, increased from the baseline to the 10-, 21-, and 33-month events by 15%, 398%, and 290%, respectively (Figure 8). The differences in sediment MeHg concentrations observed may be due to seasonal methylation processes that varied between the sampling events. The MeHg concentrations measured in samples from Pier 7 during this study were lower than the average sediment MeHg concentrations reported for sediment monitoring within OU B Marine of 1.52 ng/g ww (0.2–3.1 ng/g ww) and Sinclair Inlet of 1.96 ng/g ww (0.4–4.3 ng/g ww) (U.S. Navy 2015b) and Puget Sound reference areas (average 1.54 ng/g ww) (Moran et al. 2013).

### 5.6.2 POs 5 and 6: Demonstrate Uniform Deep Water Placement to Target Footprint and Physical Stability Over Time

Following placement of the amendment, an SPI survey was performed to evaluate the placement to the target footprint and stability over time (Figure 9). Table 3 summarizes the thickness of the amendment within the target amendment area. Although the SPI survey was conducted only two weeks (0.5 months) after the material had been placed, the covering of AC particles had already released from the underlying carrier granules. By 10 months, it appeared that the AC was worked into the underlying sediment by the burrowing activities of resident infauna and other mixing processes. Visual evidence of the reactive amendment being re-worked into the bottom sediments by bioturbation was clearly evident. By the 21- and 33-month sampling events, the AC was observed deeper in the sediment profile with a small layer of deposited sediment at the surface.

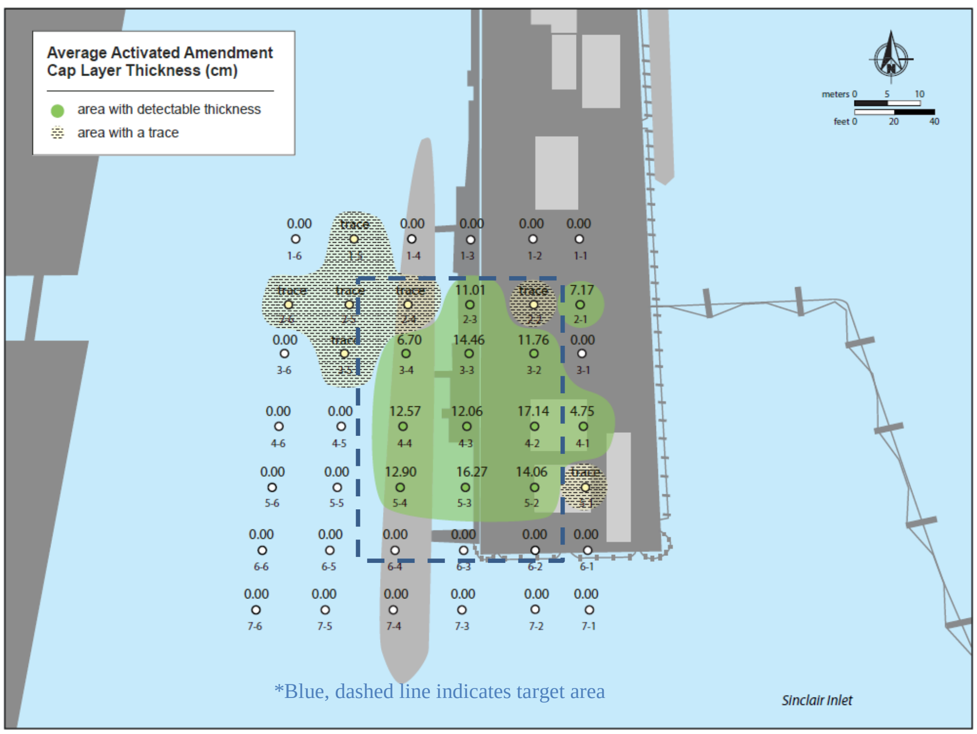


**Figure 9. AC Amendment Thickness during the 0.5-month Post-placement SPI Survey (Germano and Associates 2013b).**

**Table 3. Thickness of the Amendment within the Target Area.**

| Event | Number of Stations with Deposits of AquaGate | Number of Stations Sampled* | Percent of Stations with Deposits of AquaGate | Amendment Thickness** (cm) |
|---|---|---|---|---|
| 0.5-Month | 12 | 15 | 80% | 11 ±5.6 (0.1–17) |
| 10-Month | 18 | 22 | 82% | 6.9 ±5.4 (0.1–18) |
| 21-Month | 14 | 21 | 67% | 11 ±5.2 (2.3–19) |
| 33-Month | 16 | 22 | 73% | 8.8 ±5.3 (0.1–17) |

* Indeterminate stations were not included

** Shown as Average ± Standard Deviation (SD) (Minimum – Maximum)

### 5.6.3 TOC and BC Contents in Surface Sediment

In the 0-5 cm interval below the sediment-water interface, there was a significant increase in TOC from the baseline to the 0.5- and 10-month events (increases of 103% and 133% on average, respectively). No significant difference in TOC contents from baseline to the 3-, 21-, and 33-month events were observed (average increases of 22%, 76%, and 14%, respectively. In the 5–10 cm interval below the sediment-water interface, no significant difference in TOC was observed from the baseline to all subsequent monitoring events, with the exception of the 10-month event, which had a 137% average increase. The 0.5- and 10-month events had average decreases of 10% and 64%, respectively. The 21- and 33-month events had increases of 35% and 34%. In the 10–15 cm interval below the sediment-water interface, no significant difference was observed from the baseline to all subsequent events (on average increases ranging from 11–97%, with the exception of the 0.5-month event, which had a 21% decrease). The changes to the analytical method used for TOC occurred in the 3-month event. All events utilized Lloyd Kahn method except the 3-month event, which used SW-846 9060; this may have influenced differences in content from the baseline to the 3-month.

In the 0–5 cm depth interval below the sediment-water interface, no significant difference in BC content was observed from baseline to the subsequent monitoring events. In all subsequent events, there was an average increase, ranging from 10–51%, with the exception of an average 61% decrease in the 33-month event. In the 5–10 cm and 10–15 cm intervals, there was no significant difference from baseline to the subsequent monitoring events with the exception of significant increases in the 10-month event (average increases of 185% and 227%, respectively). In the 5–10 cm interval, there were decreases in the 0.5-, 3-, and 33-month events (average of 50%, 26%, and 51%, respectively) and an increase in the 21-month event (average 34%). In the 10–15 cm interval, there were decreases in the 0.5- and 33-month events (average of 22% and 37%, respectively) and an increase in the 3- and 21-month event (average 107% and 75%).

TOC and BC contents were highly variable among stations, there was heterogeneity within the stations, and sample processing was complicated by widely varying amounts of shell hash, cobble, and aggregate that could have biased the results obtained.

### 5.6.4 PO 7: Evaluate Benthic Community Changes in Response to Amendment

The infaunal successional stage was evaluated in the sediment profile images obtained in each SPI survey (reports from Germano and Associates provided in Appendix C of the Final Technical Report). Results are presented in Table 4. The percent of stations with Stage 3 taxa evident within the target area is comparable to the stations outside the target area for the baseline survey. In the 0.5-month survey, the percentage is somewhat lower within the target area compared to outside the target area. In the 10- and 21-month surveys, the percent of stations with Stage 3 taxa is comparable within and outside the target area. In the 33-month survey, the percent of stations with Stage 3 taxa is reduced in the target amendment area, specifically the berthing area where Stage 1 taxa was observed to be present at several stations. The cause of this change is unclear; however, it was likely caused by physical disturbance from vessel movement near the pier. It would be informative to observe the benthic community for additional monitoring events to understand the duration of this apparent disturbance. While there is variability in successional stage over the 0.5-, 10-, 21-, and 33-month post-placement surveys, it appears that the benthic community was not adversely affected as a result of the amendment placement.

**Table 4. Number of Stations with Stage 3 Taxa.**

| | Within Target Area | | | Outside Target Area | | |
|---|---|---|---|---|---|---|
| Survey | Number of Stations with Stage 3 Taxa | Total Number of Stations * | Percent of Stations with Stage 3 Taxa | Number of Stations with Stage 3 Taxa | Total Number of Stations * | Percent of Stations with Stage 3 Taxa |
| Baseline | 8 | 10 | 80% | 18 | 26 | 69% |
| 0.5-Month | 3 | 6 | 50% | 16 | 20 | 80% |
| 10-Month | 7 | 16 | 44% | 13 | 26 | 50% |
| 21-Month | 15 | 17 | 88% | 20 | 24 | 83% |
| 33-Month | 8 | 20 | 40% | 16 | 24 | 67% |

*Excludes stations at which infaunal successional status could not be determined.

Results of the benthic survey are presented in Figure 10. Total abundance was observed to have no significant difference from the baseline characterization to all monitoring events at the amended stations (multi-metric stations). Species diversity was not significantly different from the baseline to 10- and 21-month monitoring events for the amended stations with an average 9% and 0.3% decrease, respectively. Species diversity was significantly lower in the 33-month event compared to the baseline, with an average 26% decrease at the amended stations. Taxa richness was not significantly different from the baseline to the 10- and 21-month events at the amended stations (average decrease of 8% and 4%, respectively). There was a significant decrease from the baseline to the 33-month event (average 32% decrease). Pielou's evenness was not significantly different from baseline to all monitoring events for the amended and unamended stations. Swartz's Dominance Index (SDI) was not significantly different from the baseline to all monitoring events for both amended and unamended stations. The percent abundance of the five most abundant taxa was not significantly different from the baseline to the 10-, 21-, and 33-month events at the amended stations and unamended stations. Overall, there were generally no significant differences between amended and unamended stations across post-remedy sampling events for the six evaluated metrics. Therefore, there is no evidence that benthic communities were adversely affected by the amendment placement.

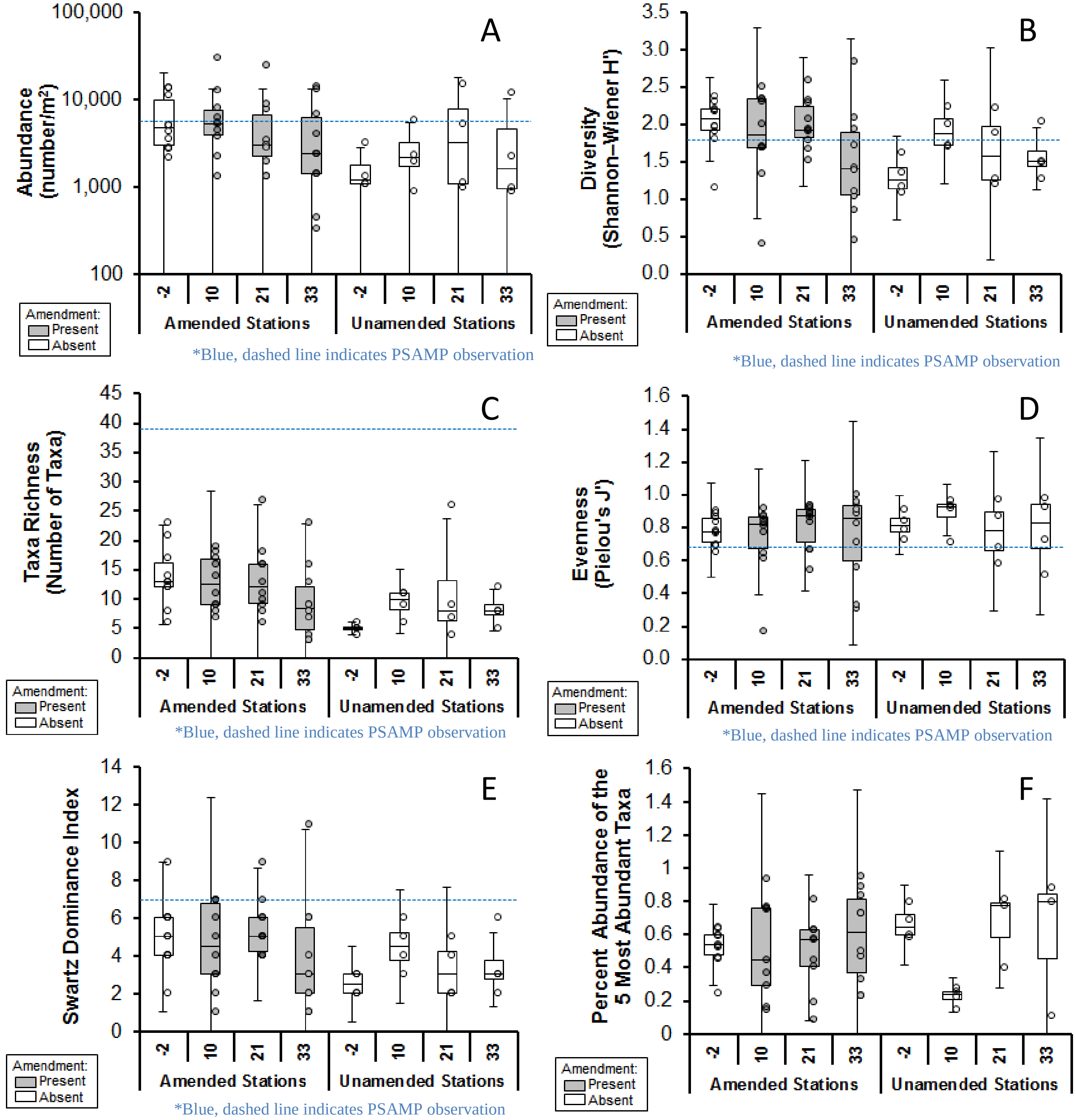


**Figure 10. Summary of Benthic Community Results for (A) Abundance, (B) Diversity, (C) Taxa Richness, (D) Evenness, (E) Dominance, and (F) Percent Abundance.**

*Results are plotted as the median (horizontal bar), IQR (limits of boxes are 25th and 75th percentiles), and error bars are 1.5 times the IQR. Data points are plotted as circle symbols.*

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## 6.0 PERFORMANCE ASSESSMENT

A performance assessment for each of the POs is presented below, along with whether each objective was met, and the data supporting these conclusions.

**PO 1 – Verify amendment performance in the laboratory.** This was evaluated with *ex situ* bioaccumulation testing with the polychaete worm *Neanthes arenaceodentata* and sediments from Pier 7. Concentrations of total PCB in tissue from the control sediment (unamended) were compared to amended site sediment under a range of mixing conditions (no mix, 24-hour mix, and 1-month mix). The PO was met if concentrations of total PCBs in tissue exposed to amended sediment were reduced at least 50% and statistically significantly less than the concentrations in tissue exposed to the control. The PO was met for the 24-hour and 1-month mix amendments, which are most similar to conditions observed in the field.

**PO 2 – Demonstrate amendment associated reduction in contaminant bioavailability in the field.** This was evaluated with *in situ* bioaccumulation testing to obtain tissue concentrations and passive sampling to obtain concentrations in sediment porewater. The bioaccumulation testing utilized SEA Ring technology with the polychaete worm *Nephtys caecoides* and bent-nose clam *Macoma nasuta*. *In situ* passive sampling was conducted with SPME to provide a chemical measure of PCBs in sediment porewater. The PO was considered met if concentrations of total PCBs in the 10-, 21-, and 33-month monitoring events were significantly reduced (at least 50% reduction) from concentrations in the baseline. This PO was met for total PCBs (Figure 11), with biological and porewater results generally indicating an average decrease in bioavailability of 84% from the baseline. Concentrations of total PCBs in *M. nasuta* tissue were reduced 68%, 82%, and 88% on average in the 10-, 21-, and 33-month events compared to the baseline, respectively. Concentrations of total PCBs in *N. caecoides* tissue in the 10-, 21-, and 33-month events were reduced 87%, 89%, and 97% on average compared to the baseline, respectively. Concentrations of total PCBs in sediment porewater from baseline to 10-, 21-, and 33-month events were reduced 75%, 86%, and 81% on average compared to the baseline, respectively. Total Hg and MeHg were tracked for informational purposes only, but results were unclear regarding the efficacy of the amendment to reduce Hg or MeHg bioavailability. Concentrations of total Hg and MeHg in *M. nasuta* and *N. caecoides* were below risk-based thresholds and generally consistent with ambient/natural levels. Overall, there was a general lack of consistent differences among the monitoring events, indicating the amendment did not have a detectable effect on bioavailability. This does not necessarily indicate AC would be ineffectual in reducing Hg or MeHg bioavailability in sediments, because it is possible reductions in bioavailability would be more measureable if baseline levels were greatly elevated above ambient/natural levels.

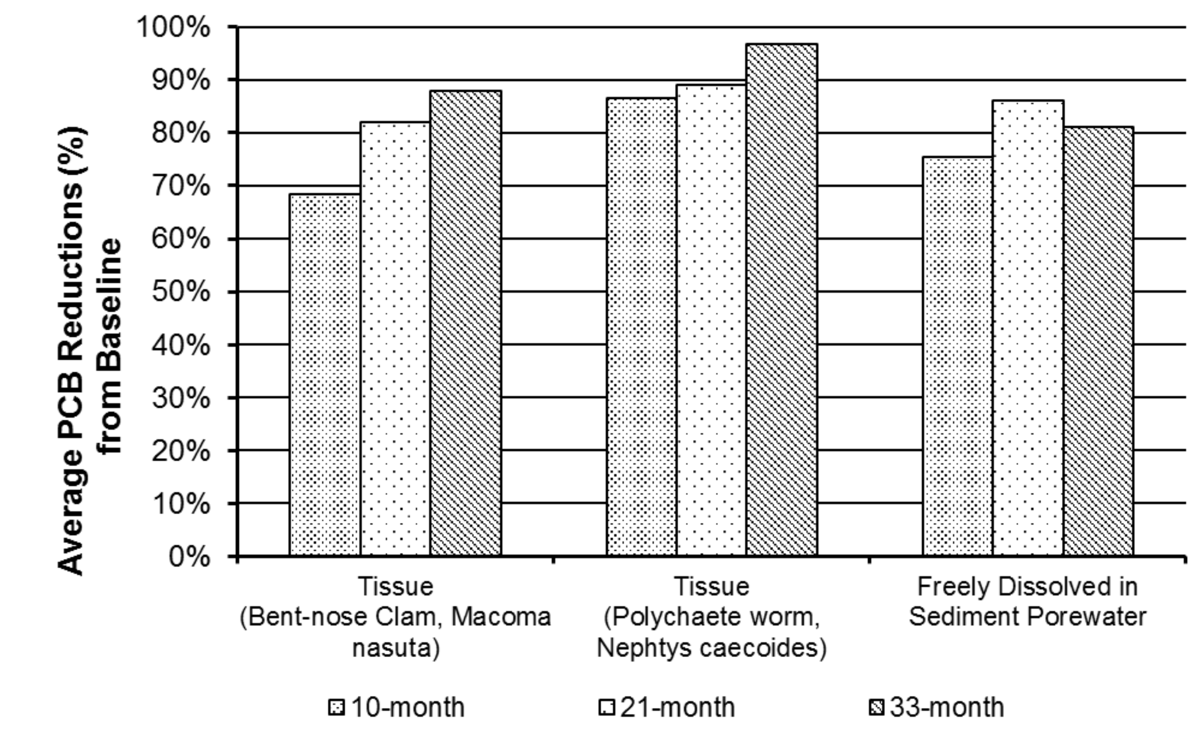


**Figure 11. Summary of Average Percent Reductions of Total PCBs in Tissue and Sediment Porewater.**

**PO 3 – Demonstrate reduction in contaminant bioavailability is sustained over time.** This was evaluated with the same analyses as discussed for PO 2, but is focused on the 33-month event. The PO was considered met if concentrations of total PCBs in the 33-month event were significantly reduced (at least 50%) from concentrations in the baseline. This PO was met for total PCBs. The reduction in concentrations of total PCBs in *Macoma nasuta* tissue from baseline to 33-month event was 88% on average. The reduction in concentrations of total PCBs in *Nephtys caecoides* tissue from baseline to the 33-month event was 97% on average. The reduction in concentrations of total PCBs in sediment porewater from baseline to 33-month event was 81% on average. These results are presented on a percent basis in Figure 11 and a concentration basis in Figure 12. Total Hg and MeHg were tracked for informational purposes only as discussed in PO 2.

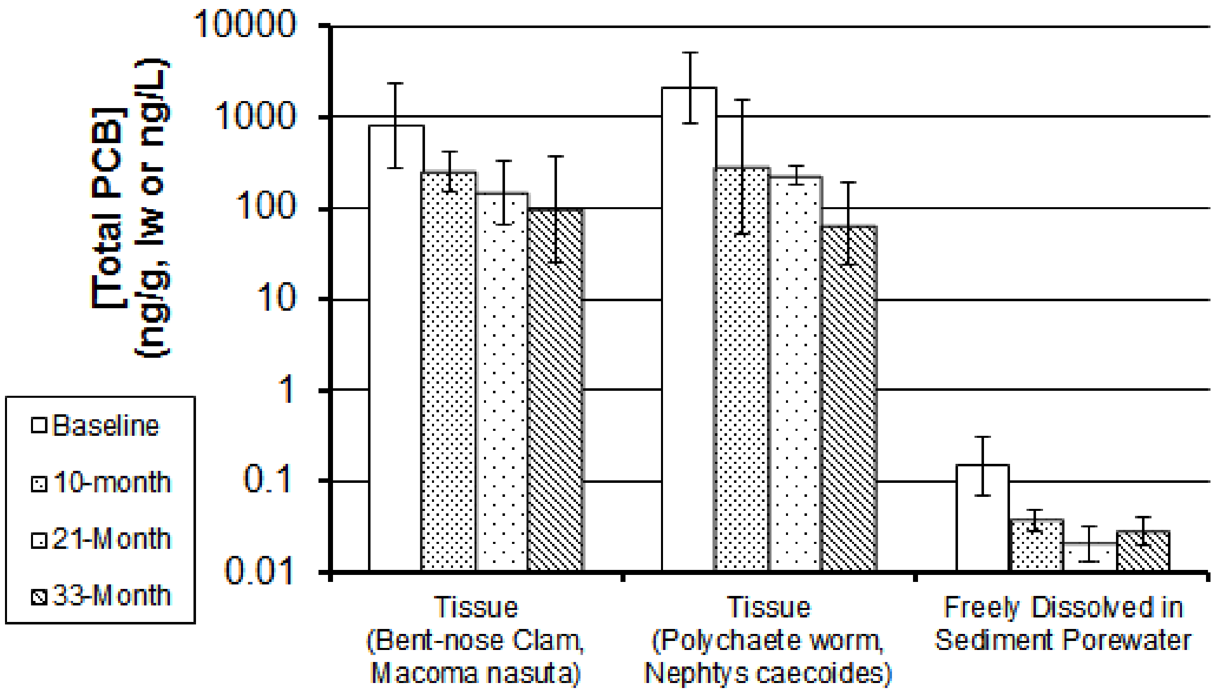


**Figure 12. Summary of Reduction in Concentrations of Total PCBs in Tissue and Sediment Porewater.**

*Results are shown as mean ± 95% confidence level (CL).*

**PO 4 – Demonstrate detectability of amendment using SPI visual monitoring methods in the laboratory.** This was evaluated by obtaining SPI images in sediment for control and the three mixing conditions (no mix, 24-hour, and 1-month). The PO was met if the amendment was qualitatively distinguishable from native sediment. This PO was met.

**PO 5 – Demonstrate uniform deep water placement to target area.** This was evaluated with the SPI camera system as well as TOC and BC content analysis in sediment cores at three intervals (0–5 cm, 5–10 cm, and 10–15 cm below the sediment-water interface). Observations in the baseline characterization were compared to the 0.5-month monitoring event. The PO was met if the following occurred:

1) The amendment was evenly distributed with an approximate target thickness of 2±1 inches (observed with images from the SPI survey).

2) The amendment was present in approximately 90% of the target amendment placement area (observed with images from the SPI survey).

3) An increase in TOC and BC content in surface sediments (0–10 cm below sediment-water interface) (not observed).

This PO was met for the approximate thickness (the average thickness was >4 in) and met for the presence within the target area (80% of the target area received measurable or trace deposits of AquaGate). Diver survey provided further confirmation the amendment was placed within the target area and the PAC coating was no longer on the aggregate core. An increase in TOC content in surface sediment (0–10 cm below sediment-water interface, as the average of the 0–5 cm and 5–10 cm intervals) was an average of 50% greater than in the baseline. Based on BC content, placement did not meet the PO, as BC content decreased an average of 3% in the surface sediments (0–10 cm below sediment water interface), potentially due to analytical issues with the measurement of BC content and high presence of shell hash in many samples.

**PO 6 – Demonstrate amendment physical stability over time.** This was evaluated with the same analyses and success criteria as discussed in PO 5 with comparison of observations in the 3- (TOC/BC content only), 10-, 21-, and 33-months and the baseline characterization. Based on SPI surveys, approximately 75%, 65%, and 65% of the target area retained measurable or trace deposits of the amendment with average thicknesses of 6.9 cm, 11 cm, and 8.8 cm, respectively. This PO was met for the approximate thickness and for the presence within the target area (80% of the target area received measurable or trace deposits of AquaGate). This PO was met for TOC content in surface sediments (0–10 cm below the sediment-water interface as an average of the 0–5 cm and 10–15 cm intervals) for the 10-, 21-, and 33-month events with increases of 124%, 52%, and 20% on average from the baseline, respectively; however, in the 3-month event, an average decrease in TOC content of 2% was observed. This PO was met for BC content in the surface sediment (0–10 cm below sediment-water interface). In the 3-, 10-, and 21-month events, average increases of 7%, 91%, and 18% from the baseline were observed, respectively; however, an average decrease of 55% was found in the 33-month event.

**PO 7 – Evaluate benthic community changes in response to amendment.** A comparison of benthic community to census results obtained in the baseline characterization and reference stations was made to the 10-, 21-, and 33-month monitoring events. This PO was met if there was no observed adverse impact to the benthic community as evaluated with six indices: total abundance, species diversity, taxa richness, Pielou’s evenness (J’), SDI, and percent abundance of the five most abundant taxa. This PO was met.

The SPI surveys found no difference in the percent of stations with evidence of Stage 3 taxa in the baseline, 10-month, and 21-month surveys; however, the percent of stations with Stage 3 taxa within the target area were lower in the 0.5- and 33-month surveys. The cause of the apparent retrograde of successional stage at the berthing area in the 33-month is unknown. Further monitoring of the site would help understand if the retrograde was due to a temporary condition at the site (such as temporary organic enrichment or physical disturbance) or will be sustained for a longer duration.

# 7.0 COST ASSESSMENT

The overall objective of this project was to demonstrate and validate placement, stability, performance, and persistence of reactive amendments for treatment of contaminated sediments in active DoD harbor settings. As part of the evaluation of performance, a cost evaluation and comparison to alternative contaminated sediment treatment methods, such as dredging, capping, and MNR, is provided.

## 7.1 COST MODEL

### 7.1.1 Cost Model for Demonstration of AquaGate Amendment

The area of demonstration at Pier 7 is 21,850 square feet (sq. ft.) (0.5 acres) and includes placement of AquaGate under the pier around pilings and in berthing area adjacent to the pier. The costs associated with placement of the AC amendment include placement and monitoring costs for the demonstration project (Table 5). It should be noted shipment costs in Table 5 are from Ohio to Washington (approximately $300/ton for freight shipment) and are more expensive than typical shipment costs. Typical costs for shipment are approximately $100/ton ($2,500/truck load), for 141 tons of AquaGate; a total shipment cost of $14,100 would be incurred under a typical shipment scenario. Field work costs do not include management, oversight, and coordination. Uncertainties in applying this cost estimate for AquaGate include variability in shipping costs depending on site location and complexity of placement.

**Table 5. Cost Model for Demonstration of the AquaGate Amendment.**

| Cost Element | Costs | |
|---|---|---|
| Baseline Characterization | Field Work | $97,000 |
| | Dive Support | $27,000 |
| | Laboratory Analysis | $59,000 |
| | Baseline SPI survey | 34,000 |
| | Reporting | $40,000 |
| | **Total** | **$257,000** |
| Placement | AquaGate<br>$2.90/sq. ft. (based on $450/ton and areal amendment density of 12.9 lbs/sq. ft.) | $63,000 |
| | Shipment<br>(from Ohio to Washington) | $42,000 |
| | Staging and placement of amendment | $140,000 |
| | Verification of placement<br>(SPI survey) | $34,000 |
| | **Total** | **$279,000** |
| | **Total per sq. ft.** | **$12.77** |
| Monitoring<br>(3 Events) | Field Work | $97,000 |
| | Dive Support | $27,000 |
| | Laboratory Analysis | $59,000 |
| | Monitoring SPI survey | $34,000 |
| | Reporting | $40,000 |
| | **Total per Event** | **$257,000** |
| | **Total** | **$771,000** |
| | **Demonstration Total** | **$1,307,000** |

### 7.1.2 Cost Model for Implementation of AquaGate Amendment

Implementation of the technology as a full-scale remedy would require less rigorous monitoring methods as efficacy of the amendment as a remedy would be established. For implementation, it is assumed that contaminant reduction would be measured with *ex situ* bioaccumulation bioassays. Also, the sediments would be monitored by bulk sediment chemistry and TOC and BC analysis. A cost model for implementation of AquaGate to other projects is presented in Table 6.

These costs are an estimate and may be lower or higher when specific site considerations are taken into account. For example, for a 5-acre site AC application, Patmont et al. (2015) estimated field placement to be up to $3.72/sq. ft. compared to $9.29/sq. ft. estimated here, and $0.93/sq. ft. for long-term monitoring compared to $13.73/sq. ft. estimated here. It is important to note, costs will vary based on site- and project-specific needs. While recent information from the AquaGate vendor indicates that placement costs at larger sites are considerably lower than for the demonstration (in the range of $5.89/sq. ft.). To be conservative, the $9.29/sq. ft. estimate was applied throughout, with the caveat that this is likely an overestimate especially at larger sites.

**Table 6. Cost Model for Implementation of AquaGate Amendment.**

| Cost Element | Costs | |
|---|---|---|
| Baseline Characterization | Field Work | $50,000 |
| | Bioassay and Chemistry Analysis | $30,000 |
| | Reporting | $20,000 |
| | **Total** | **$100,000** |
| Placement | AquaGate<br>$2.90/sq. ft. (based on $450/ton and areal amendment density of 12.9 lbs/sq. ft.) | $63,000 |
| | Shipment* | $0 |
| | Staging and placement of amendment | $140,000 |
| | **Total** | **$203,000** |
| | **Total per sq. ft.** | **$9.29** |
| Monitoring (6 Events) | Field Work | $45,000 |
| | Bioassay and Chemistry Analysis | $15,000 |
| | Reporting | $15,000 |
| | **Total per Event** | **$75,000** |
| | **Total** | **$450,000** |
| | **Implementation Total** | **$753,000** |

* For full-scale implementation, it is assumed larger quantities of AquaGate would be either produced or supplied near or onsite to eliminate freight costs.

## 7.2 COST DRIVERS

Cost drivers to consider in selecting this technology include the following:

- **Shipment** of material will vary in cost by amount required and the location of the project relative to product distribution centers. In addition, for most full-scale projects, near or onsite production of AquaGate can be performed, which would minimize or eliminate shipment costs.

- **Placement** costs can vary significantly based on the complexity of the site including considerations for bathymetry, currents, infrastructure, as well as site access and logistical considerations. In addition, most full-scale projects will benefit from improvements in efficiency of material handling and placement, potentially providing significant cost per square foot reductions.
- **Monitoring** is needed to ensure performance has met remedial action objectives and includes field sampling and laboratory analysis. The monitoring requirements would vary based on site-specific needs, and selection of methods to monitor the site could be influenced by factors such as water depths, currents, and site access.

## 7.3 COST ANALYSIS

To evaluate and compare the costs of AC amendment with alternative remedies, three hypothetical sites are considered. In all cases, long-term monitoring at the site is expected to be required to ensure remedy effectiveness. These costs are driven by labor, equipment, laboratory analyses, supplies, and transportation costs, but would not vary significantly among remedy selection for dredging, capping, and AC amendment ($75,000/event). However, MNR typically incurs more expensive monitoring ($100,000/event). For dredging, one monitoring event is assumed to take place to ensure post-construction targets are met, and a second event at year five to insure long-term remedy effectiveness. For capping and AC amendment, it is assumed that 1 post-construction monitoring event would take place, followed by 2 performance monitoring events in the first 5 years, and 1 event every 5 years following, out to 20 years. For MNR, a baseline event is assumed to establish current conditions followed by 1 event every 5 years out to 30 years. Dredging costs do not consider additional sediment volumes for bulking and overdredge allowance. All costs discussed below are estimates. There is still significant uncertainty as to the monitoring requirements associated with AC amendments due to the lack of long-term data on performance.

### 7.3.1 Site 1

Site 1 represents a large (5 acre) contaminated sediment site within deep waters of a harbor complex. Remedy selection must consider the presence of high levels of refuse (must be removed prior to dredging), infrastructure (such as piers and pilings) in the area of remedy, and dredged materials that must be managed as hazardous wastes. The sediments are contaminated from the sediment bed surface to 1 foot below the sediment-water interface. The site is potentially subject to scour from ship movement and currents. A comparison of costs for remedies at Site 1 is summarized in Table 7.

**Table 7. Cost Comparison for Remedies at Site 1.**

| Remedy | Cost Element | Costs | Total Cost |
|---|---|---|---|
| AquaGate AC | Placement costs<br>(product, shipping, staging, and placement)<br><br>Monitoring costs<br>(Post Construction + 5 events) | Based on implementation placement cost of $9.29/sq. ft.<br><br>$75,000/event | $2,473,000 |
| Dredging | Traditional dredging in open water, diver operated suction dredge under piers, removal of debris from the dredge area, management of material as hazardous waste, and includes all mobilization, demobilization, and transportation costs<br><br>Monitoring costs<br>(Post Construction + year 5) | Estimated at $400/cubic yard (cy)<br><br>$75,000/event | $3,380,000 |

#### *7.3.1.1 AquaGate AC Amendment*

Based on the costs determined to be $9.29/sq. ft., the placement cost for this site would be $2,023,000, with monitoring costs ($75,000/event for six events) increasing costs by $450,000, for a total placement cost of $2,473,000.

#### *7.3.1.2 Dredging*

Based on the nature of this site—specifically the infrastructure and pier pilings that would require diver support with a portable dredge and the cost of management as hazardous waste—costs associated with dredging would be $400/cubic yard (cy). This cost is based on traditional dredging in open water, diver-operated suction dredge under piers, removal of debris from the dredge area, management of material as hazardous waste, and includes all mobilization, demobilization, and transportation costs. Note that dredging costs do not include post-dredge cover materials to control residuals from resuspension of dredge material, if required. Based on the size of the site and dredging to 1 foot below the sediment-water interface, 8,070 cy would be dredged for an estimated cost of $3,230,000. Monitoring costs ($75,000/event for two events) would increase costs by $150,000, for total dredging costs of $3,380,000.

#### *7.3.1.3 Capping*

Due to the nature of the site, capping is not a feasible option. Ship traffic would likely disturb cap material and the required water depth for navigation prevents adding sufficient cap and armoring.

#### *7.3.1.4 Monitored Natural Recovery (MNR)*

Due to the nature of the site, MNR is not a feasible option. The area is not depositional due to ship traffic; therefore, the material would not be kept in place over the time frame needed for MNR to occur.

### 7.3.2 Site 2

Site 2 represents a medium-sized (3 acre) contaminated sediment site in a developed, coastal marine environment. Remedy selection must consider the steep slopes along the shore, high tidal flows and dredging disposal as subject to upland management (non-hazardous), and infrastructure in the area of remedy. Sediment contamination extends down to 1 foot below the sediment-water interface. There is little to no refuse present. A comparison of costs for remedies at Site 2 is summarized in Table 8.

**Table 8. Cost Comparison for Remedies at Site 2.**

| Remedy | Cost Element | Costs | Total Cost |
|---|---|---|---|
| AquaGate AC | Placement costs (product, shipping, staging, and placement)<br><br>Monitoring costs<br>(Post construction + 5 events) | Based on demonstration placement cost of $9.29/sq. ft.<br><br>$75,000/event | $1,664,000 |
| Dredging | Traditional dredging in open water, diver operated suction near infrastructure, upland management of dredged material, and includes all mobilization, demobilization, and transportation costs.<br><br>Monitoring costs<br>(Post Construction + year 5) | Based on best professional judgement, estimated at<br>$300/cy<br><br>$75,000/event | $1,600,000 |
| Capping | Placement (sand cap and significant armoring)<br><br>Monitoring costs<br>(Post construction + 5 events) | Based on best professional judgement, estimated at<br>$500,000/acre<br><br>$75,000/event | $1,950,000 |

#### *7.3.2.1 AquaGate AC Amendment*

Based on the costs as determined by the demonstration project of $9.29/sq. ft., the placement cost for this site would be $1,214,000, with monitoring ($75,000/event for six events) increasing costs by $450,000, for a total placement cost of $1,664,000.

#### *7.3.2.2 Dredging*

Based on the nature of this site—specifically the lack of refuse for removal and the upland management of dredged material—this site would have a moderate cost of $300/cy. Based on the area of the site and depth sediment contamination, 4,840 cy would be dredged for a cost of $1,450,000. Monitoring costs ($75,000/event for two events) would increase costs by $150,000, for total dredging costs of $1,600,000.

#### *7.3.2.3 Capping*

Capping is generally estimated to cost $9.00–$15/sq. ft., or $350,000–$700,000/acre. This cost is driven by the cost of material, the level of armoring needed, and the ability to place cap material with relative ease. A level of uncertainty in cap longevity and effectiveness exists due to the tidal nature of the site. Considering the high tidal flows in this area and the steep slopes, it is estimated a significant level of armoring would be required and a cost of $500,000/acres is assumed. The cost of capping placement would be $1,500,000, with monitoring ($75,000/event for six events) increasing costs by $450,000, for a total placement cost of $1,950,000.

#### *7.3.2.4 Monitored Natural Recovery (MNR)*

Due to the nature of the site, MNR is not a feasible option. The area is not depositional due to tidal flows; therefore, deposition of clean sediments is unlikely to occur to a sufficient degree.

### 7.3.3 Site 3

Site 3 represents a small (1 acre) site along a flat bottom of a quiescent environment. Remedy selection must consider the highly depositional environment, dredged material upland disposal with minimal pretreatment, and contamination in sediments from the surface to 1 foot below the sediment-water interface. A comparison of costs for remedies at Site 3 is summarized in Table 9.

**Table 9. Cost Comparison for Remedies at Site 3.**

| Remedy | Cost Element | Costs | Total Cost |
|---|---|---|---|
| AquaGate AC | Placement costs<br>(product, shipping*, staging, and placement)<br><br>Monitoring costs<br>(Post construction + 5 events) | Based on demonstration placement cost of $11.21/sq. ft.<br><br>$75,000/event | $938,000 |
| Dredging | Traditional dredging in open water, upland disposal of dredged material (minimal pretreatment) includes all mobilization, demobilization and transportation costs<br><br>Monitoring costs<br>(Post construction + year 5) | Based on best professional judgement, estimated at $150/cy<br><br>$75,000/event | $392,000 |
| Capping | Placement costs<br>(sand cap and minimal armoring)<br><br>Monitoring costs<br>(Post construction + 5 events) | Based on best professional judgement, estimated at $350,000/acre<br><br>$75,000/event | $800,000 |
| MNR | Baseline monitoring, followed by monitoring every 5 years out to 30 years | $100,000/event | $600,000 |

*Shipping for small sites is assumed since material would not likely be produced onsite.

#### *7.3.3.1 AquaGate AC Amendment*

Based on the costs as determined by the demonstration project of $11.21/sq. ft., the placement cost for this site would be $488,000, with monitoring ($75,000/event for 4 years) increasing costs by $450,000, for a total cost of $938,000.

#### *7.3.3.2 Dredging*

Based on the nature of this site—specifically the lack of debris for removal, and the upland disposal of dredged material assuming minimal pre-treatment (dewatering not needed due to nearby disposal facility)—this site would be expected to have a lower cost at $150/cy. Based on the surface area and depth of contamination, 1,610 cy of dredged material is estimated for a cost of $242,000. Monitoring costs ($75,000/event for 2 events) would increase costs by $150,000, for a total cost of $392,000.

#### *7.3.3.3 Capping*

As noted above, capping is generally estimated at $9.00–$15.00/sq. ft., or $350,000–$700,000/acre. As this is not an erosional environment and the material has a low level of contamination, little armoring would be required, and the cost is estimated at $350,000 for the one acre site. Monitoring costs ($75,000/event for 6 events) would increase costs by $450,000, for a total cost of $800,000.

#### *7.3.3.4 Monitored Natural Recovery (MNR)*

As this is a highly depositional environment, MNR is a feasible option. Largely, costs associated with MNR are the long-term monitoring costs. Long-term monitoring would be required under any remedy scenario; however, monitoring would likely be more expensive, more frequent, and for a longer time frame with MNR. For the purposes of this assessment, it is assumed that monitoring would include a baseline event followed by 5 additional events, once every 5 years out to 30 years, for a total of 6 events. Assuming a cost of $100,000/event, the total cost would be $600,000. The frequency and length of monitoring can be highly variable and site-specific, adding uncertainty to this assessment.

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# 8.0 IMPLEMENTATION ISSUES

*In situ* remediation of HOC-impacted sediments with AC has been demonstrated to meet placement objectives for target area and thickness in deep waters as well as stability to remain in place over three years in an active shipyard. In this demonstration, AquaGate has been shown to reduce concentrations of PCBs in tissue and sediment porewater in the third year following placement in surface sediment by 81–97%. Most benthic invertebrate bioaccumulation studies of AC have shown reductions in concentrations of HOCs in tissue ranging from 70–90% compared to untreated control sediment (Ghosh et al. 2011). AC amendment as a contaminated sediment remedy is of great interest to the research community as there have been 25 field studies of AC *in situ* treatment of contaminated sediments in the past ten years (Patmont et al. 2015). *In situ* reactive amendment with AquaGate is well suited to be implemented in a variety of environmental conditions from shallow, quiescent, flat-bottom settings to deep water, variable, or sloping water depths, and tidal environments with active vessel traffic and infrastructure.

This technology would be of great interest as a remedy to HOC-impacted (e.g., PCBs, PAHs, and pesticides) surface sediments in association with Superfund sites and sites implementing remediation in response to equivalent state and local regulations associated with contaminated surface sediments. *In situ* treatment technology may be limited to sites with contamination to depths within the site-specific bioturbation mixing zone (generally 10–20 cm below sediment-water interface) unless it is determined that there is little or no advective transport of contaminant from depths below the bioturbation mixing zone.

AquaGate has an advantage in the ability to place amendments around infrastructure (e.g., piers and bulkheads) where dredging may be found to be more expensive or infeasible. Another advantage of AquaGate is the ability to place the amendment in navigational channels and berthing areas where capping may be infeasible due to water depth requirements. Costs of implementing AquaGate are competitive with alternative remedial methods; however, as with selection of any remedy, cost is dependent on site-specific conditions and complexity. Additionally, AquaGate has an advantage as a green remediation strategy, which is of interest to the USEPA to minimize environmental footprints after cleanup.

Placement of *in situ* reactive amendment to sediments at Pier 7 presented significant challenges associated with amendment placement in active harbors including security access, scheduling, deep water placement, working near and under waterfront structures, complex bathymetry and dredge cuts in berthing areas, strong and variable tidal currents, and possible disturbance from ship movement and other harbor activities. Also, as with any pilot project, the small size of the area limited the ability of the operator to gain efficiency or improve the potential uniformity or coverage within the placement area. In total, 141 tons of AquaGate were placed on surface sediments at Pier 7 within 4 days from the arrival of the tugs to the verification of the placement by U.S. Navy divers. There are improvements that could be made to placement, such as achieving placement within the entire target area and avoiding placement in areas outside the target area. Additionally, the evenness of the amendment thickness could be improved to place a more uniform distribution. Monitoring at Pier 7 was limited by diver assistance for deployment and retrieval of the SEA Rings and passive samplers. Also, measurements of TOC and BC content in sediment with presence of shell hash presented further challenges.

Although AC has been shown for decades to be effective in treating air, water, and wastewater, there remains some uncertainty as to the long-term effectiveness of sequestration treatment in the field.

Because of public perception and predisposition by the regulatory community, dredging continues to be the most common and accepted means of sediment remediation. Any remedy that leaves untreated contaminants in place, such as *in situ* sequestration, may have the potential for risk of re-exposure of the contaminants. A similar risk would be encountered for sites utilizing MNR, capping, or dredging when high concentrations in residuals are left in place. However, the risk from potential effects of re-exposure may be less if low concentrations of contaminants remain in the sediment.

Since the initiation of this project, the application of *in situ* sequestration at full-scale has been performed successfully. Long-term monitoring of these sites will be required to further support the expanded application of this technology. Further research is required to continue to understand, improve, and gain broader acceptance for the technology. Some considerations for further research are summarized below.

Research on the effectiveness of AC has focused primarily on PCBs, with some applications to other persistent HOCs such as pesticides and PAHs. Limited research has also been conducted on metals such as Hg. However, most sediment sites are characterized by mixtures of contaminants spanning many classes of chemicals. Further research on the effectiveness of amendments on a broader range of contaminants would be helpful. While previous research has evaluated a range of different amendments as well as multi-amendment strategies, these methods generally have not moved as far into pilot-scale demonstrations and full-scale applications.

In general, the effectiveness of amendments relies on their ability to reduce bioavailability rather than reduction in mass. However, most regulatory and risk-based frameworks are still based around total concentration or organic carbon normalized concentration reductions. As this report shows, amendments do not necessarily change whole sediment concentrations. More regulatory input is needed to better understand how remediation using amendments can lead to site closure, and how performance will be measured when bioavailability is reduced while whole sediment concentrations remain relatively unchanged. Focused research and demonstrations that strive to bridge this gap would help to further promote acceptance and broader application at sites. In particular, methods that would demonstrate the incorporation of bioavailability-based preliminary remediation goals and remedial action limits could help to address these gaps. In addition, strategies for spatial averaging of bioavailability-based exposure levels and remediation goals would help to put these measures in the same context as currently adopted surface-weighted average concentrations for bulk concentrations.

Within this study and other previous studies, bulk concentrations of PCBs have sometimes shown considerable reduction (beyond dilution) following the application of AC. One explanation for these reductions is that the extractability of the PCBs is reduced through the carbon addition and thus—although the mass is still present—it is not measured using standard extraction methods. An alternative explanation could be that the microenvironments created by the carbon could potentially enhance biodegradation. More detailed evaluation of this under controlled conditions would be of interest. If the AC reduces extractability using traditional extraction methods, then perhaps these reductions could serve as a proxy for reductions in bioavailability. If the carbon additions somehow enhance degradation, that would clearly be of interest as well.

A key area of uncertainty that remains for amendments is their persistence under a range of environmental conditions in the field. Because there are many forms of amendments and many different conditions across the types of sites where they may be applied, further research is needed to better guide under what site conditions the amendments will have long-term effectiveness, and what forms of amendment will have the best characteristics to achieve this. These are key considerations from an implementation and cost perspective. In addition, this could lead to a better understanding of potential maintenance requirements that would help in the selection and design phases of the remedy process. As part of this research, consideration should be given to more effective ways of tracking the carbon over time. Current methods including TOC, BC, and visual techniques are relatively effective over the short-run, but are subject to methodological complications, high levels of variability, and tend to have less and less certainty as time goes by.

Another potential area where additional research could help is in optimizing the application and monitoring methods for amendments. Most of the work to date has focused on demonstrating that the amendments work. However, the remedy is still relatively expensive, and optimization of the methods for applying the amendment and the amount and types of monitoring could significantly reduce costs in the future. Because amendment technologies do not necessarily reduce bulk sediment concentrations and instead aim to reduce contaminant bioavailability, monitoring remedy performance requires measuring changes to contaminant bioavailability. This can be accomplished using biological samples (e.g., clams or worms, like those used in this project) or by directly measuring chemical concentrations in sediment porewater using passive sampler techniques. Both methods are relatively costly and complex when compared to traditional bulk sediment monitoring. Furthermore, while both methods have proven effective to demonstrate technology performance at relatively small, pilot-scale conditions, scaling up these technologies to full-scale where tens or hundreds of acres may be remediated remains unaddressed.

A key research topic for monitoring would be to resolve potential advantages and pitfalls of *in situ* versus *ex situ* techniques for both passive samplers and bioaccumulation studies. Because amendments tend to become more effective with more mixing, there is uncertainty about the extent to which *ex situ* methods that involve substantial handling, compositing, and disturbance can lead to unrealistic results. From this standpoint, *in situ* methods have some advantages, but the cost and complexity of conducting *in situ* methods, along with the potential for loss of equipment and samples, often weighs against these advantages. Recent methods utilizing collection of intact cores for laboratory exposures provide a possible solution, but have not been fully developed. Further exploration of these approaches specific to the use of amendments would be useful.

Finally, there is still room for research related to risk of remedy in different habitats. While many studies have shown that amendments can be effective without significantly impacting benthic communities and habitats, there are other studies that have found the opposite. In addition, there are many sensitive habitat areas such as coral reef areas where the potential impact of amendments should be considered more carefully, and there is a general lack of understanding of how amendments might behave in relation to these types of habitats.

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