ESTCP
Cost and Performance Report

(ER-0510)

Field Testing of Activated Carbon Mixing and In Situ Stabilization of PCBs in Sediment at Hunters Point Shipyard Parcel F, San Francisco Bay, California

August 2008

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT
Project: ER-0510

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ACRONYMS AND ABBREVIATIONS

AC	activated carbon
AEI	Aquatic Environments, Inc.
ANOVA	analysis of variance
BAF	Bioaccumulation Factor
BC	black carbon
BRAC	Base Realignment and Closure Act
C&P	Cost and Performance (Report)
CEI	Compass Environmental, Inc.
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DDT	dichlorodiphenyltrichloroethane
DoD	Department of Defense
ERDC	Engineering Research and Development Center
ESTCP	Environmental Security Technology Certification Program
FR	Final Report
FS	Feasibility Study
GAC	granular activated carbon
HOC	hydrophobic organic compounds
NAVFAC	Naval Facilities Engineering Command
NPL	National Priorities List
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PE	polyethylene
PI	Principal Investigator
RAB	Restoration Advisory Board
RAC	regenerated activated carbon
SARA	Superfund Amendments and Reauthorization Act
SD	standard deviation
SERDP	Strategic Environmental Research and Development Program
SPMD	semipermeable membrane device
TOC	total organic carbon

USACE	U. S. Army Corps of Engineers
USEPA	U. S. Environmental Protection Agency
VAC	virgin activated carbon

ACKNOWLEDGEMENTS

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1.0 EXECUTIVE SUMMARY

Prior laboratory studies and a preliminary field pilot-scale study showed that the addition of activated carbon (AC) to sediment contaminated with polychlorinated biphenyls (PCB) significantly reduced the chemical and biological availability of PCBs. Encouraged by those results, we recently completed a field-scale project (ER-0510) to demonstrate that AC sorbent mixed with sediment is a cost-effective, in situ, nonremoval, management strategy for reducing risk and the bioavailability of PCBs in offshore sediments at the Hunters Point Shipyard site. In order to achieve these goals, we identified three primary objectives for the scope of this project:

- Demonstrate and compare the effectiveness, in terms of AC application and ease of use, of two available large-scale mixing technologies
- Demonstrate that AC treatment reduces PCB bioaccumulation in field tests
- Demonstrate no significant sediment resuspension and PCB release after the large-scale mixing technologies are used.

Using two commercial equipment devices, AC was successfully incorporated into the test plots to a nominal 1 ft depth at a dose of 2 to 3%, depending on sampling locations. This was verified by the increases in total organic carbon contents and black carbon contents in AC-amended sediment. In situ 28-day semipermeable membrane device (SPMD) uptake studies showed 50-66% reductions in PCB uptakes in AC-amended test plots, depending on AC dose. In situ bioassays with the bent-nosed clam, *Macoma nasuta*, also showed the effectiveness of AC treatment, although the in situ bioassay results were sometimes confounded by field conditions resulting from newly deposited sediment, heat stress, and shallow burrowing depth. To overcome these factors, ex situ bioassays with *M. nasuta* were conducted with field sediment in the laboratory, which showed about 50% reduction in PCB bioaccumulation with a 2% AC dose.

Field-exposed AC retained a strong stabilization capability to reduce aqueous equilibrium PCB concentrations by as much as 95%, depending on AC dose, which supports the long-term effectiveness of AC in the field at least up to 18 months. This was demonstrated also in long-term SPMD exposure tests lasting more than seven months. The time series test results showed the AC continually reduced SPMD uptake of PCBs, achieving reductions ranging from 76% for tetrachloro PCBs to 42% for heptachloro PCBs. A strong AC-dose response effect was observed both for aqueous equilibrium PCB concentrations and *M. nasuta* PCB bioaccumulations. Neither PCB resuspension from the test plots nor adverse impacts to indigenous amphipods and benthic community were observed during the entire assessment period. Overall, the AC treatment did not impact macro-invertebrate benthic community composition, richness, or diversity.

Cost analysis showed that scalingup the AC treatment method would result in a total cost savings that may be 70 to 75% less than for dredging and disposal.

This project completes the first field demonstration of sorptive amendment to sediment to reduce PCB exposure and risk. Overall, this study indicates that if ongoing PCB contaminant sources are eliminated and freshly deposited sediments are clean, in situ AC amendment to contaminated sediments can provide a suitable, cost-effective method for reducing contaminant exposure to the water column and biota. Additional mixing during or after AC deployment, sequential AC deployment, or greater AC dose, or reducing AC particle size will improve overall effectiveness.

2.0 INTRODUCTION

2.1 BACKGROUND

Contaminated sediments pose challenging cleanup and management problems at many Department of Defense (DoD) sites. In the San Francisco Bay Area, for example, four major Naval Facilities undergoing base closure have contaminated sediments: Hunters Point Naval Shipyard, Alameda Naval Air Station, Moffett Field Naval Air Station, and Mare Island Naval Shipyard. Currently the standard approach to addressing contaminated marine "mud flat" sediments is the expensive ex situ process of dredging and disposal. Finding cost-effective in situ technologies for contaminated sediment management will significantly reduce expenditures on environmental restoration.

The technology demonstrated in this project is an in situ treatment for sediment contaminated with hydrophobic organic contaminants such as PCBs), pesticides, and polycyclic aromatic hydrocarbons (PAH). Generally, this technology involves mixing AC into the contaminated sediment, which strongly adsorbs the hydrophobic organic contaminants in the sediment. This strong sorption stabilizes and reduces the bioavailability of the contaminants in benthic organisms. The goals for this ESTCP project are intended to demonstrate that AC sorbent mixed with sediment is a cost-effective, in situ, nonremoval management strategy for reducing the bioavailability of PCBs in offshore sediments at the Hunters Point site in San Francisco Bay, CA.

Hunters Point Shipyard (HPS) is a former Navy installation located on a peninsula in the southeast corner of San Francisco, CA. From 1945 to 1974, the Navy used HPS predominantly for ship repair and maintenance. HPS was deactivated in 1974 and remained relatively unused until 1976, when it was leased to Triple A Machine Shop, a private ship repair company. In 1986, the Navy resumed occupancy of HPS. Three years later, HPS became a Superfund site, as it was placed on the National Priorities List (NPL) in 1989. The Navy then closed the Base in 1991 under the Defense Base Realignment and Closure Act (BRAC) of 1990. The base is in the process of conversion to nonmilitary use. Historically, the area comprising the HPS site consisted of about 928 acres, which have been divided into the six parcels: A - F. Parcel A has been recently transferred to the City of San Francisco, and the HPS site now comprises about 853 acres. Parcel F, which contains offshore sediment, comprises approximately 432 acres.

Historical site activities at HPS resulted in the release of chemicals to the environment, including offshore sediments in Parcel F. Environmental restoration activities are being conducted under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA).

2.2 OBJECTIVE OF THE DEMONSTRATION

This project was a field-scale demonstration of AC-induced in situ PCB stabilization in sediment. The demonstration evaluated the use of AC for remediation of PCB-contaminated sediment at Parcel F of Hunters Point Naval Shipyard. The project entailed a field pilot-scale operation over a 3-year period. The overarching goal of this project was to demonstrate that AC sorbent mixed with sediment was a cost-effective, in situ, nonremoval, management strategy for reducing the bioavailability of PCBs in offshore sediments at the HPS site. In order to achieve this goal, we identified three primary objectives for the scope of this project:

- Demonstrate and compare the effectiveness, in terms of AC application and ease of use, of two available large-scale mixing technologies
- Demonstrate that AC treatment reduces PCB bioaccumulation in field tests
- Demonstrate no significant sediment resuspension and PCB release after the large-scale mixing technologies are used.

These three primary objectives were further subdivided into the five primary performance objectives shown in Table 2. Secondary performance objectives, which support the primary performance objectives, can be also found in Table 2.

In addition to evaluating primary and secondary performance objectives, the demonstration project generated supporting cost and performance data for implementation of the novel sediment remediation technology at DoD sites with conditions similar to those at Hunters Point.

2.3 REGULATORY DRIVERS

Environmental restoration activities at the site are being conducted in accordance with the CERCLA, as amended by the SARA.

3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

We report on the addition of highlysorbent activated carbon (AC) to the upper sediment layer using available large-scale mixing technologies to manage sediment contamination by hydrophobic organic compounds (HOC). Conceptually, the approach builds on prior studies by others and us that describe the role of black carbon (BC), e.g., soot, chars, and soot-like materials such as coal, to affect the transport, uptake, and biomagnification of HOCs in sediments. Particle-scale analyses of sediment from the general study area showed that the majority of PCBs were associated with chars and, as such, were not as readily released to water. These observations from field sediments led to the study of AC as an in situ amendment in which AC would be mixed into the upper, biologicallyactive sediment layer to stabilize the PCBs and reduce their availability to the aqueous phase and biota (Figure 1). This would enhance significantly a process that was occurring naturally, albeit slowly. Laboratory results with field sediments from this and other sites were promising, and demonstrated that addition of AC to sediment reduced the availability of PCBs, PAHs, and dichlorodiphenyltrichloroethane (DDT) to water and uptake by organisms such as clams, amphipods, polychaetes, and mussels. A time line of the development of this technology is shown in Table 1.

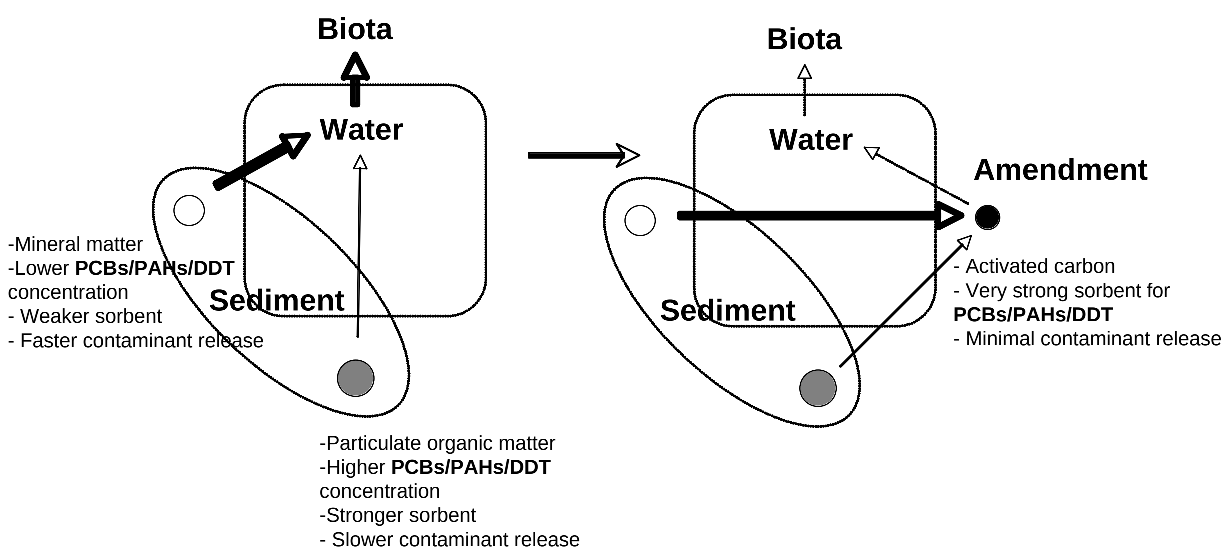

Figure 1. Schematic of AC amendment in reducing exposure and environmental risk.

Table 1. Technology development history.

Development Phase	Time Frame	Funding Agency	Publications
Discovery of the predominant role of coal and coke on strong sorption of PAHs in sediments	1998-1999	SERDP	6, 7
Discovery of low bioavailability of PAHs sorbed on coal and coke in sediments	1999-2000	SERDP, USACE ERDC	8, 9, 10
Discovery of the predominant role of coal-derived and char particles in the sorption of PCBs in Hunters Point and Milwaukee Harbor sediments	2001-2002	SERDP, Stanford University Graduate Fellowship	3, 11, 12
Demonstration of very low absorption efficiency for a radio-labeled PCB and a PAH on activated carbon in particle-feeding tests with clams	2001-2004	Stanford University Bio-X Research Program	3, 12, 21
Demonstration of reduced PCB aqueous availability from Hunters Point sediment treated with AC	2002-2004	SERDP	3, 4, 12

ERDC = Engineer Research and Development Center
USACE = U.S. Army Corps of Engineers

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Technology Advantages: This treatment technology for contaminated sediments is innovative as it is an in situ process, which would circumvent the need to do expensive sediment dredging and disposal. Many DoD facilities across the country are challenged with management of sediments contaminated with persistent organic contaminants such as PCBs, PAHs, and DDT. This work addresses the DoD need for cost-effective in situ remediation technologies for persistent organic contaminants in sediments. The development of this technology for contaminated sediment management offers the potential to significantly reduce expenditures on environmental restoration, as well as gain acceptance by regulators and communities since it does not involve dredging and habitat destruction. This treatment technology did not show noticeable adverse impacts on the health of the benthic community and did not impact sediment resuspension and PCB release into the water column over the treatment plots. Also, the potential of the treatment was retained throughout the project time span.

Technology Limitations: Our laboratory results suggest that we may achieve a factor of 10 or more reduction in the bioavailability (or effective concentration) of PCBs in the field. We define low-range PCB concentrations in sediment as <1 ppm, mid-range as 1-10 ppm, and high-range as >10 ppm. Therefore, if the final cleanup goal is to achieve sediments having an effective PCB concentration of <1 ppm, then sediment having a mid-range PCB concentration (1-10 ppm) would be an appropriate target for AC treatment. We recognize that the final cleanup goal for the Hunters Point site is still in development, yet anticipate that the application of this in situ technology would most likely be limited to sediment having a low- to mid-range contaminant concentration of total PCBs. In fact, this philosophy is embraced in the Final Feasibility Study (FS) for Parcel F sediments, which considers possible AC amendment for PCB stabilization throughout much of South Basin with some targeted removal of higher PCB levels. Dredging and disposal of hot spot areas with high-range contaminant concentrations would be appropriate, as reductions in effective PCB concentration through AC treatment may not be sufficient. The decision to use the AC in situ technology would be mediated by final cleanup goals for a particular site. This project revealed that over time, e.g., 18-24 months, newly deposited, contaminated sediment masked the effectiveness of the underlying AC amendment for benthic organisms that exhibit surficial deposit feeding strategies. If ongoing PCB contaminant sources are eliminated and freshly deposited sediments are clean, then in situ AC amendment of contaminated sediments can provide a suitable method for reducing contaminant release to the water column and uptake by biota for exposures resulting from within the sediment bed.

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4.0 PERFORMANCE OBJECTIVES

As explained in Section 2.2, each performance objective was categorized as either primary or secondary, considering the impact of its success or failure on other objectives. Performance objectives are summarized in Table 2.

Table 2. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
PRIMARY CRITERIA (Qualitative)			
Ease of use (comparison of mixing technologies)	Field demonstration experiences	• Two mixing technologies can be compared in terms of mobility, AC delivery, and the effectiveness of AC amendment.	• Rototiller system (Aquamog) showed better performance.
PRIMARY CRITERIA (Quantitative)			
PCB bioaccumulation in test organisms	*M. nasuta* tissue PCB concentrations from in situ and ex situ 28-day bioassays	• Significantly lower PCB tissue concentrations in test *M. nasuta* tissue that exposed AC-treated plots compared to control plots • Student t-test or analysis of variance (ANOVA) for statistical analysis	• 24 months post-treatment ex situ bioassay showed significantly reduced PCB biouptake into *M. nasuta* exposed to AC-amended plots (Plots D and F) compared to control plots (Plots C and E). • In situ bioassay results were confounded by field-specific conditions from incoming freshly deposited sediment occurring 18-24 months post treatment.
PCB bioaccumulation in indigenous organisms	Indigenous *Corophium spp.* amphipods tissue PCB concentrations at pre- and post-treatment assessments	• Significantly lower PCB tissue concentrations • No impact due to release of PCBs from mixing • Student t-test or ANOVA for statistical analysis	• No significant difference observed • PCB levels in indigenous amphipods responded to overlying water rather than under-lying sediment layer. • No enhanced PCB flux due to AC-sediment mixing

Table 2. Performance objectives. (continued)

Performance Objective	Data Requirements	Success Criteria	Results
PRIMARY CRITERIA (Quantitative)			
AC application	Averaged TOC contents of sediment cores from all test plots at pre- and post-treatment assessments	• Averaged TOC should be 3.8 ± 2.5 wt%, given an initial TOC of 1.0 wt%. • The SD was used to make a qualitative statement about the homogeneity of the mixing. • SD = 0.0 – 1.5 wt%, excellent mixing SD = 1.6 – 2.5 wt%, good mixing SD = 2.6 – 3.6 wt%, fair mixing SD > 3.6 wt%, poor mixing	• Averaged TOC of Plots D and F are 2-3 wt% depending on sampling locations, which were less than the target TOC 3.8% due to overmixing vertically or horizontally. • Plot D with rotovator mixing showed excellent mixing. • Plot F with injector mixing showed excellent~good mixing.
PCB resuspension	Aqueous and suspended particulate PCB concentrations above test plots	• No significant differences in the dissolved PCB concentrations and the particulate-associated PCB concentrations in the water column above Plots D and F after treatment when compared to controls	• No significant differences spatially (among test plots).
SECONDARY CRITERIA (Qualitative)			
Effects of AC treatment on indigenous benthic community	Aqueous and suspended particulate PCB concentrations above test plots	• No significant differences exist between metrics of benthic community (e.g., richness, abundance, diversity) in the test plots	• No significant differences among test plots (richness and diversity). • Effect of AC amendment, if any, was dominated by larger seasonal effects.
Versatility -AEI mixing device -CEI mixing device	Experience from demonstration operation	• Mixing devices will provide different yet adequate AC mixing into the sediments in Plots D and F	• Both mixing devices provided adequate AC mixing.
Scale-up constraints -Throughput -Combination of devices	Experience from demonstration operation	• Treatment of 370 ft^2 plots in one day for each mixing device	• Both mixing devices succeeded in accomplishing AC deployment into the test plots.

Table 2. Performance objectives. (continued)

Performance Objective	Data Requirements	Success Criteria	Results
SECONDARY CRITERIA (Qualitative)			
Factors affecting technology performance -Lab and field mixing differences -Ineffective AC homogenization	Comparison of lab and field bioaccumulation reduction results	• No significant changes in the PCB concentrations of tissues assessed for bioaccumulation.	• Sediment deposition occurring 18-24 months post treatment confounded field (in situ) biological measurements with *M. nasuta* to assess the effect of AC amendment.
SECONDARY CRITERIA (Quantitative)			
AC/sediment stability	6-month and 18-month averaged TOC values from Plots D and F	• No significant differences between the 6-month and 18-month TOC values measured in cross sections of sediment cores taken from Plots D and F.	• Not applicable due to heterogeneity of mixing and difference in sampling locations.
PCB uptake into SPMDs	6-month and 18-month PCB uptake into SPMDs	• Significantly lower PCB uptake into SPMDs for those deployed in Plots D and F after treatment compared to controls.	• 50-66 % less PCB uptake into SPMDs were observed in AC-treated plots (Plots D and F) compared to mixing control plot (Plot C).
Aqueous equilibrium PCB concentrations	Sediment core processing and analyses	• Significantly lower aqueous equilibrium PCB concentrations with sediment from Plots D and F after treatment when compared to aqueous equilibrium PCB concentrations with sediment in controls.	• Significantly lower aqueous equilibrium PCB concentrations were observed in AC-treated plots. • The extent of reduction depended on AC dose, with greater than 95% reduction for AC dose =3.65%. • The AC retained its capacity to sorb PCBs at 6- and 18-months post treatment.
PCB desorption rates	Desorption characteristics of field sediments	• Significantly lower PCB desorption rates with sediment from Plots D and F after treatment when compared to PCB desorption rates with sediment in controls	• ~50 % reduction in desorption rates was observed with the AC-treated plot samples.

AEI = Aquatic Environments, Inc.
CEI = Compass Environmental, Inc.
SD = standard deviation
SPMD = semi-permeable membrane device
TOC = total organic carbon

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5.0 SITE DESCRIPTION

We selected the test site to be the HPS Parcel F, Area X, tidal mudflat in South Basin for several reasons. First, PCBs have been identified as the major risk driver for HPS Parcel F Area X and most of the sediment in Area X of Parcel F has a mid-range PCB concentration. Second, the combined results of Sedflume experiments on HPS Parcel F sediment and comprehensive hydrodynamic modeling studies indicate that the South Basin area is a net depositional zone and comprised of cohesive sediments not subject to exceeding sediment critical shear stress in most storm events. Third, preliminary field tests indicate that when AC is mixed into the sediment it stays in place due to the cohesive nature of the sediment and the slightly depositional nature of the site. Last, the Navy site managers at Hunters Point have indicated that they hope to use this technology in their final remedial decisions; if they do, technology transfer to other DoD sites should be straightforward. As a result, this technology has been included as an alternative remedial option in the Navy's FS report.

5.1 SITE HISTORY AND CHARACTERISTICS

HPS is a former Navy installation located on a peninsula in the southeast corner of San Francisco, CA (Figure 2), which comprises about 928 acres, with approximately 432 acres of offshore sediment. The Navy used the site for maintaining and repairing ships between 1945 and 1974. The facility was deactivated from 1974 to 1976. A private ship repair company, Triple A Machine Shop, leased the facility for its business in 1976 until the Navy resumed occupancy in 1986. The site was closed in 1991 under the DoD BRAC program and the property is in the process of conversion to nonmilitary use. Historical site activities at HPS resulted in the release of chemicals to the environment, including offshore sediments. The cleanup of the chemicals is required for re-use of the site and cleanup of chemicals from the former landfill and other locations on shore has been completed.

The site was closed in 1991 under the DoD BRAC. Currently, there are no operations in the selected demonstration area. An FS has been completed for the offshore contaminated sediment.

Pictures of the demonstration area are presented in Figures 2 and 3. The demonstration area is at the HPS tidal mudflat in South Basin. The top 4 inches of the sediment in the demonstration area consists of small gravel, shells, and clay particles. Underneath this top layer, a more homogenous layer of clay, characteristic of bay mud, exists. The bulk density of the surface sediment (top 1 ft) is approximately 1.3 to 1.4 g/cm. The water depths are from 6 ft to less than 2 ft. Tidal currents are very weak. Because PCBs tend to adsorb to fine-grained sediment particles and organic matter, sediment resuspension and deposition are major contaminant transport pathways in South Basin. However, resuspension events due to storm winds are infrequent and only impact the surficial sediments. The basin is a net depositional environment with a net sedimentation rate of about 1 cm per year.

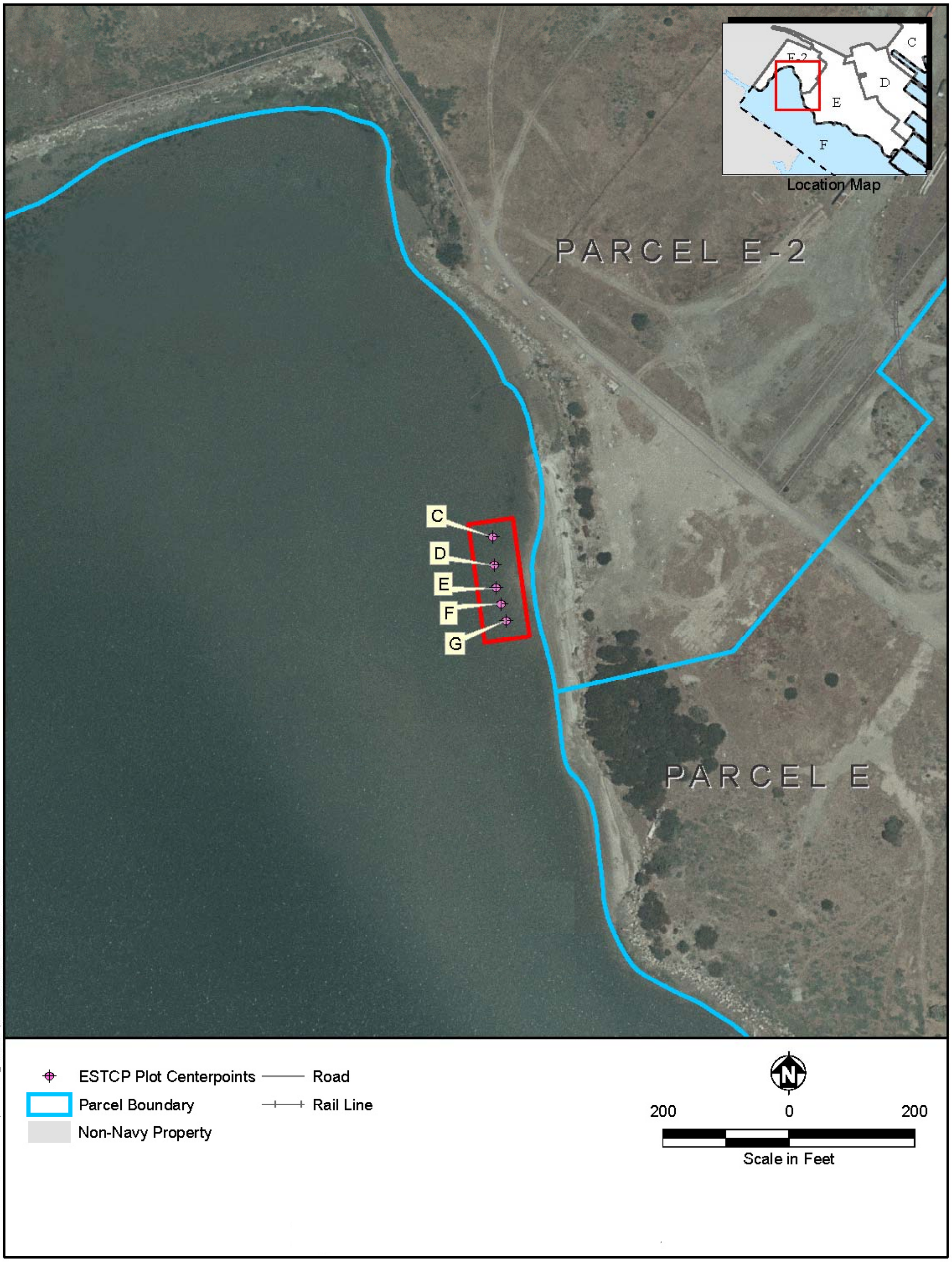

Figure 2. Demonstration area.

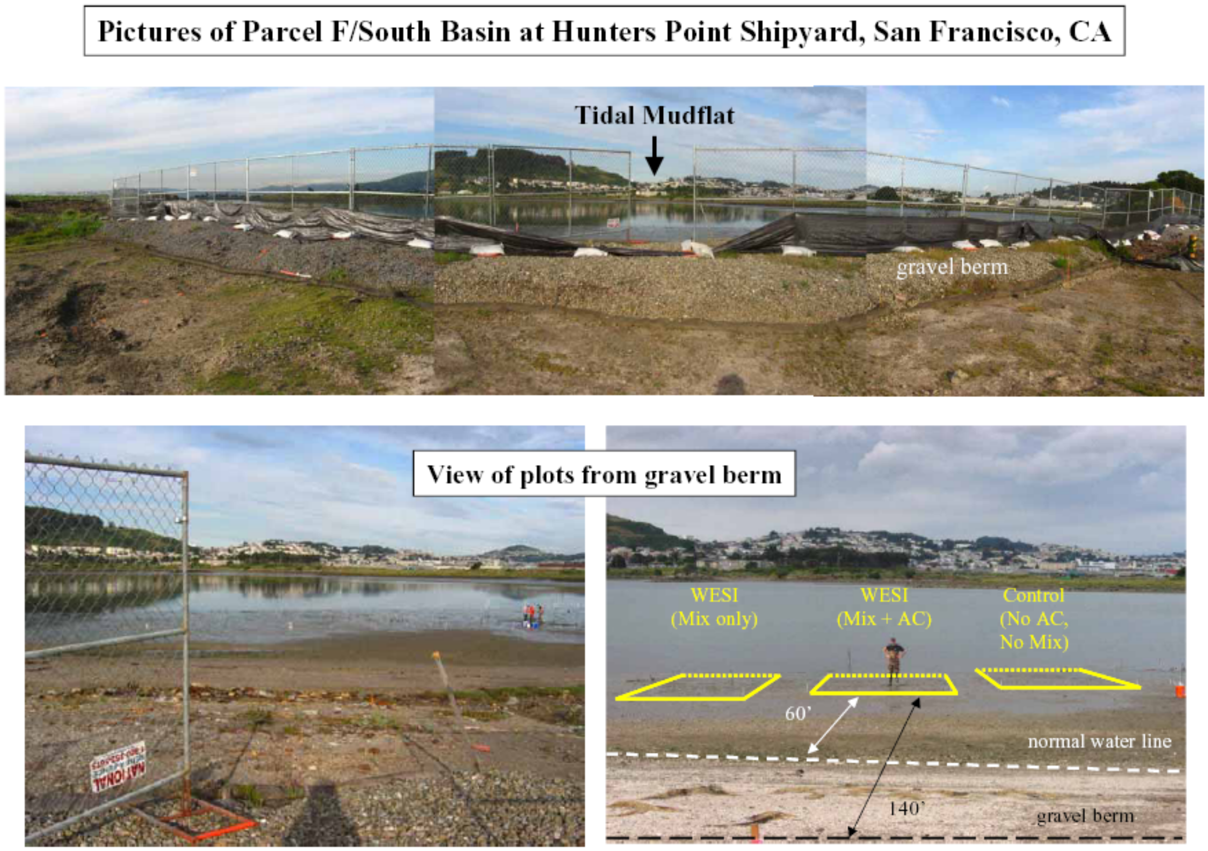

Figure 3. Demonstration and plot locations.

5.2 CONTAMINANT DISTRIBUTION

The site characterization was conducted in 1991 to evaluate the presence of contaminants in offshore areas of the HPS. The area (Figure 2) that has been selected for demonstrating the in situ treatment technology has a PCB concentration of approximately 2 ppm for 0-12 inch depth.

To collect baseline PCB distribution data for the test plots, pretreatment assessments were conducted in December 2005, one month before AC deployments. PCB concentrations for the top 6-inch sediment layer in four test plots were measured using five sediment cores collected from each plot. Sediment core sampling was based on a stratified random sampling strategy. Sediment PCB concentrations for the test plots were similar to each other in the range of 1 to 2 ppm. Other sediment characteristics (TOC and BC) were also assessed and further discussed in Section 6.2.

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6.0 TEST DESIGN

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

This project is designed to compare the effectiveness of two available large-scale mixing technologies, demonstrate that AC treatment reduces PCB release and bioaccumulation in field tests, and demonstrate that no significant sediment resuspension and PCB release occurs after the large-scale mixing technologies are employed. Four test plots of 370 ft^2 area were used in the field study. Two test plots were amended with AC using two different mixing devices respectively; one test plot served as a mixing control, and the other served as a non-mixing control. The four plots were analyzed using a combination of statistical tests, once before and thrice after treatment. The primary performance criteria that were used to demonstrate success of this innovative AC treatment technology are listed in Table 2.

6.2 BASELINE CHARACTERIZATION

Baseline characterization was conducted one month before mixing the AC into the contaminated sediment. Various physicochemical and biological background properties of four test plots were assessed. Collectively, all four plots showed similar physicochemical and biological properties. Baseline sediment PCB concentrations in all four plots were similar (~1.1 ppm), and TOC values and BC values in the four plots were similar (~0.5 wt% TOC, ~0.002 g/g BC). Baseline PCB uptake for SPMDs, clam tissue samples, and amphipod tissue samples were similar across the four plots as well.

6.3 TREATABILITY OR LABORATORY STUDY RESULTS

The effectiveness of AC amendment to reduce the chemical and biological availability of PCBs in sediment was demonstrated in various laboratory studies, and in a preliminary field study. We concluded from laboratory tests with benthic organisms that the efficacy of treatment depends on factors affecting the rate and extent of mass transfer of PCBs from sediment to the AC, notably: the AC dose, the AC particle size, the extent and duration of AC mixing, and the contact time between AC and sediment.

As a part of this project, laboratory physicochemical (aqueous equilibrium and SPMD) and biological tests on Hunters Point sediment amended with regenerated activated carbon (RAC) were completed to compare RAC's effectiveness (PCB stabilization) and toxicity to that for a virgin activated carbon (VAC) amendment. RAC performed as well as, or better, than the VAC (Figure 4) to reduce PCB bioaccumulation for Neanthes arenaceodentata worms, aqueous equilibrium PCB concentrations, and SPMD PCB uptake.

Based on the results of this study, we had decided to use RAC instead of VAC in the field treatments to save the treatment cost. Although RAC was not utilized in this project because of an unique site-specific condition applicable to sediments in South Basin, the use of RAC would have reduced the cost of AC by about 30% or more.

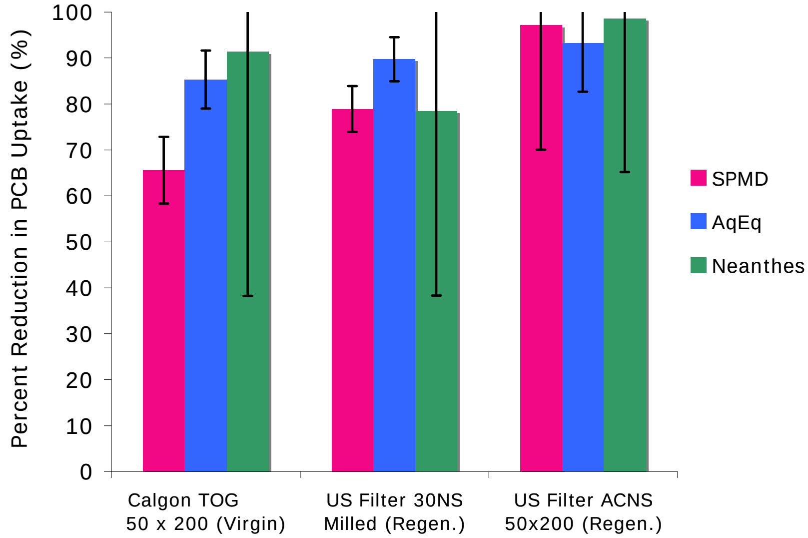

Figure 4. Laboratory results comparing VAC and RAC treatments.

6.4 FIELD TESTING

The demonstration was a 3-year project. The schedule of the project is summarized in Table 3. The schedule of milestones is provided in Table 4. The field activities started in December 2005.

Table 3. Schedule of plot sampling and analysis.

Months Since Treatment (t)	Sampling Description
	Pre-Treatment Sampling
t = -1.5	• Collect overlying water samples, sediment cores, quartrats, amphipod samples • Deploy clams, SPMDs, and polyethylenes (PEs)
t = -0.5	• Retrieve clams, SPMDs, and PEs
	Mixing and AC Treatments
t = 0	• Deploy AC and mechanical mixing or mechanical mixing only to three of the four plots
	Post-Treatment Samplings
t = 0.05	• Collect overlying water samples
t = 5.5	• Collect overlying water samples, sediment cores, quartrats, amphipod samples • Deploy clams, SPMDs, and PEs
t = 6.5	• Retrieve clams, SPMDs, and PEs
t = 17.5	• Collect overlying water samples, sediment cores, quartrats, amphipod samples • Deploy clams, SPMDs, and PEs
t = 18.5	• Retrieve clams, SPMDs, and PEs
t = 24	• Collect surface sediment samples for various characterizations • Correct 6 inch deep sediment for laboratory bioassay and various characterizations

Table 4. Demonstration schedule (updated from the Demonstration Plan).

TASK		2005			2006				2007				2008				2009
	Quarter (1=Jan-Mar, 2=Apr-Jun, etc)	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1
1	Preparation of draft Demonstration Plan																
2	Review and approval of final Demonstration Plan																
3	Deployment of carbon treatments in the field																
4	Assessment of sediment and PCB resuspension																
5	Biological monitoring of treatment units																
6	Physicochemical monitoring of treatment units																
7	Financial and Progress reporting to ESTCP																
8	Technology cost assessment and transition pentia																
9	Preparation of draft Final Report (FR) and Cost and Performance (C&P) Report																
10	Review and approval of final FR and C&P Report																

6.5 SAMPLING METHODS

This project was designed to compare the effectiveness of two available large-scale mixing technologies, demonstrate that AC treatment reduces PCB release to pore water and PCB bioaccumulation in field tests, and evaluate sediment resuspension and PCB release to overlying water. To achieve these objectives, four test plots of 370 ft^2 area were used in the field study and analyzed once before and thrice after treatments were applied. Various treatments were applied to three of the four plots, as shown in Figure 5, leaving one plot (Plot E) to serve as a reference plot (a non-mixed control). Plot C was treated by mixing the sediment with the Aquamog rotovator but without applying AC. Plots D and F were treated by applying an approximate 3.4 wt% AC and mixing it into the sediment with the Aquamog and CEI slurry injector system, respectively. The AC dose was applied to an approximate depth of one foot, corresponding to a nominal depth including the biologically active zone. A variety of samples were taken once before and thrice after treatments were applied, as outlined in the schedule in Table 3. The pretreatment samples were used to obtain baseline data.

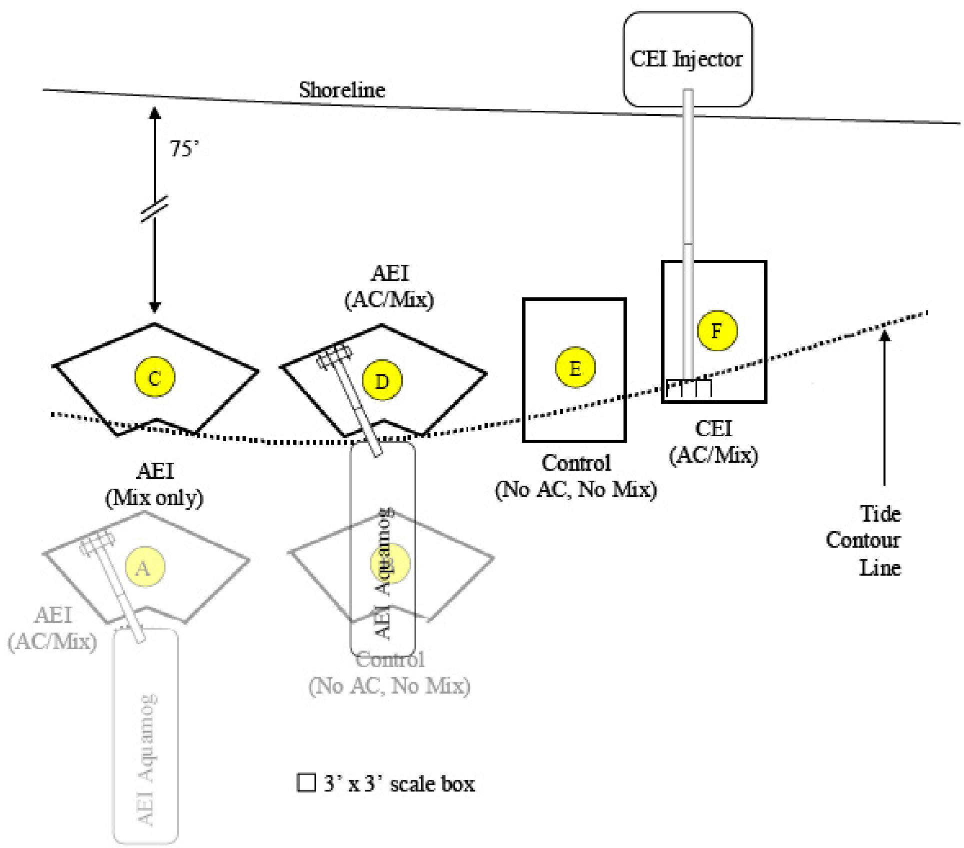

Figure 5. Schematic of ESTCP plots and mixing equipments.

In each of the four plots, five sampling locations had been selected using a stratified random sampling strategy. Sampling locations at each post-treatment sampling event were differently selected to avoid sampling in obviously disturbed locations. The types of samples obtained from each plot at each sampling time point is illustrated in Figures 6 and 7.

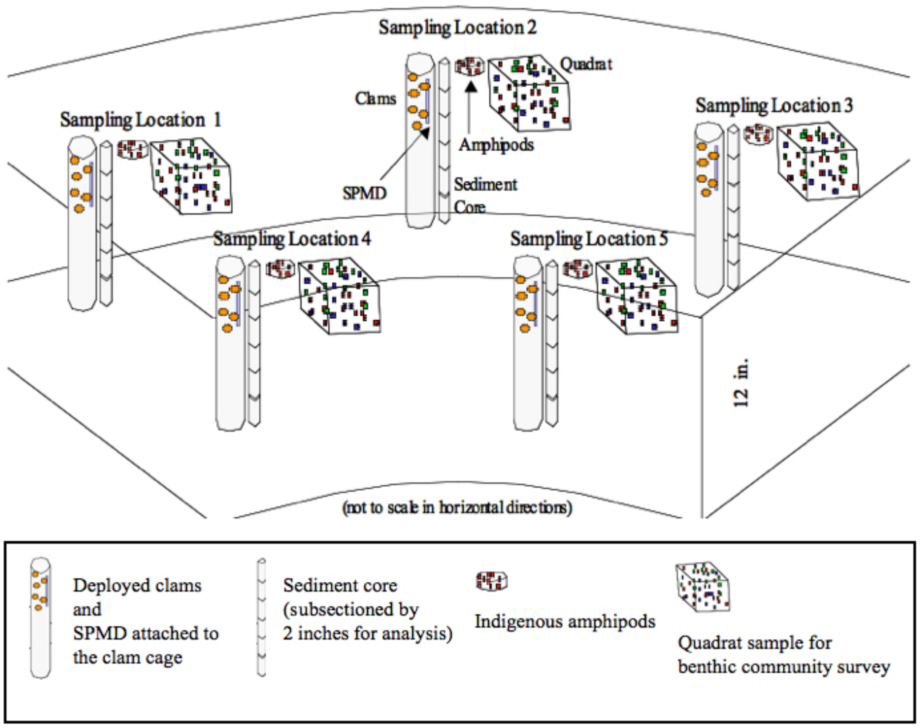

Figure 6. Schematic of samples to be taken from each plot at sampling time points.
(t = -1-month pretreatment, and 6- and 18-months post-treatment)

Figure 7. Field samples.
(clams, amphipods, sediment cores, overlying water, SPMDs, and quadrats)

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7.0 PERFORMANCE ASSESSMENT

This 3-year project successfully demonstrated that the top layer of sediments in a PCB-contaminated tidal mudflat could be amended with AC using large-scale commercial equipment (Figures 8 and 9). This is the first field demonstration anywhere of in situ sorptive sequestration of PCBs in contaminated sediments. We showed that the field-scale AC-amendment reduced the availability of PCBs to water and biota without adversely impacting the natural benthic community of macroinvertebrates nor releasing PCBs into overlying water. We also identified two field factors that affected performance of the AC amendment: the deposition of fresh, incoming contaminated sediment, and slow, diffusion-limited PCB mass transfer under quiescent field conditions. Further, we demonstrated that the sequestration potential of AC was evident during the entire project period.

Using a one-time, approximate 30-minute mixing event, AC amendment was able to reduce PCB bioaccumulation in marine clams (*M. nasuta*) by 30-50% (Figure 10), reduce available PCB in sediment pore water by 50 to 70% for continuous passive sampler exposures lasting 7 months (Figure 11), and reduce PCB desorption rates from sediment. With additional mixing in the laboratory, AC-amended field sediment showed more than 95% reduced partitioning into the aqueous phase depending on AC dose (Figure 12), which confirms that the potency of AC was retained.

Furthermore, we demonstrated the strong effects of AC dose and mixing regime on reductions in PCB bioaccumulation through the comparison of data collected for sediment-AC contact under well-mixed, homogeneous conditions in the laboratory and data collected for sediment-AC contact under a one-time, brief mixing event in the field (Figure 13). The lower reductions in PCB bioaccumulation observed in the field calls for predictive models to assess long-term trends in changes in PCB-pore water concentrations under field conditions with slow mass transfer and heterogeneous distribution of AC. We expect that comprehensive understanding of PCB mass transfer under field conditions will provide a foundation for performance modeling and allow improved predictive assessments for this in situ remediation technology.

To enhance the immediate effect of AC amendment in the field and maximize the overall treatment effect by AC, improvements of AC-sediment contact will be essential. Additional mechanical mixing, sequential deployment of AC, increasing AC dose, or adjusting AC particle sizes are possible solutions for this issue. If ongoing sources are eliminated and freshly deposited sediments are clean, AC amendment to contaminated sediments can provide a suitable in situ method for reducing risk and contaminant exposures to the water column and biota for those contaminants originating from within the sediment.

Figure 8. AEI aguamog with rototiller arm.
[(A) mobilization, (B) positioning on the test plot at hight tide, (C) manually deployed AC on the top of the test plot, (D) AC-sediment mixing]

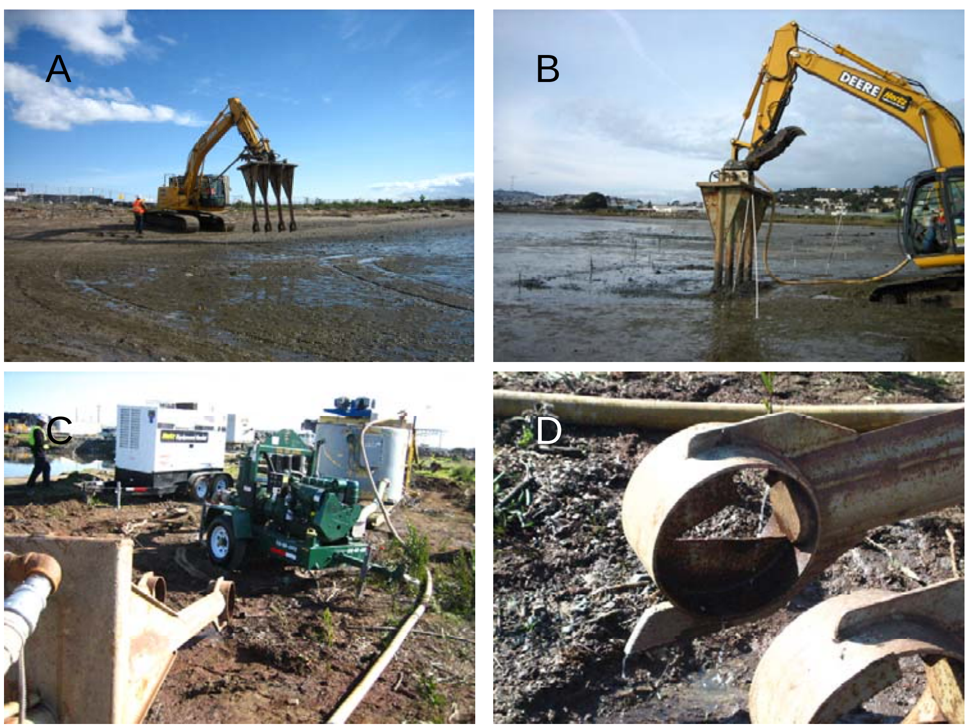

Figure 9. CEI injector system.
[(A) mobilization of the injector device, (B) AC-sediment mixing, (C) AC slurry tank, (d) tip of injector showing slurry discharge port]

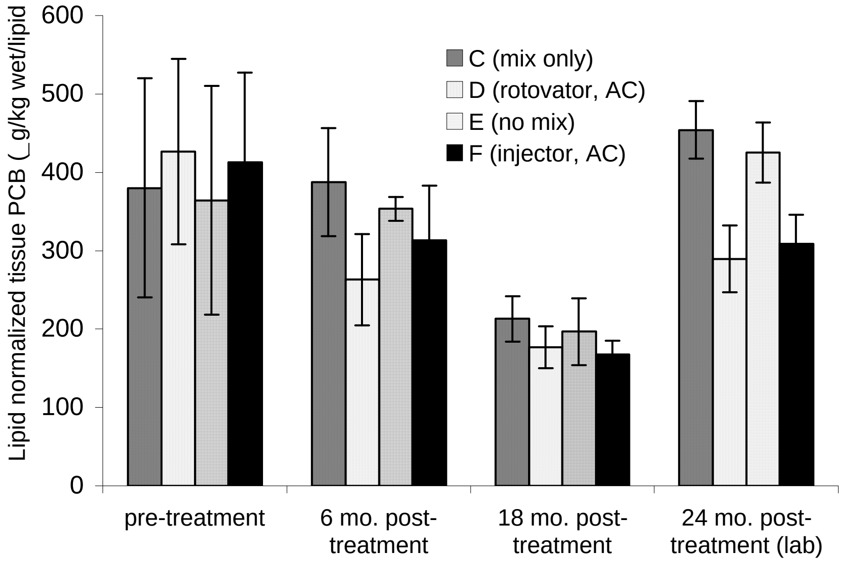

Figure 10. Lipid-normalized tissue PCB concentrations (wet weight) for *M. nasuta* exposed to the four test plots for 28 days.
Each column and error bar represents the mean and one standard deviation (n=3-5). The 18-month, post-treatment response of clams to AC amendment and PCB uptake is confounded by the deposition of fresh, incoming PCB-containing sediment.

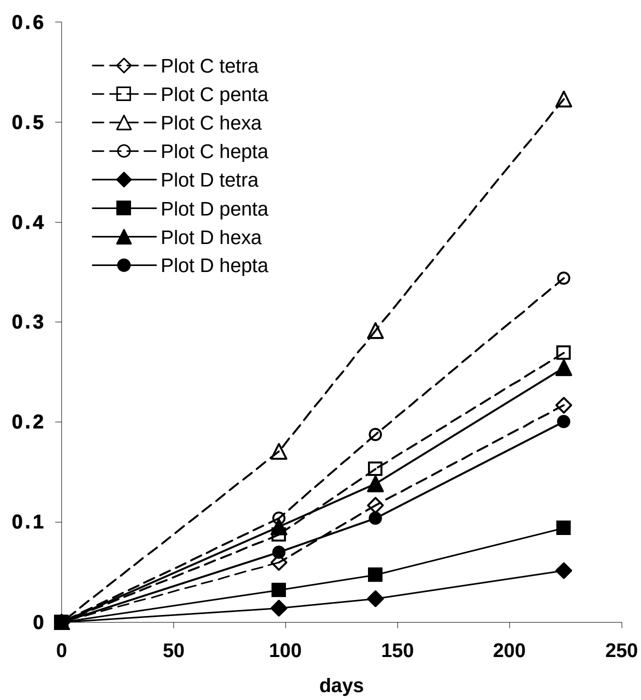

Figure 11. Time series PCB uptakes into SPMDs from plots C (mixing control) and D (AC mix, rotovator) (n=1-2). The time series began 13 months after AC treatment.

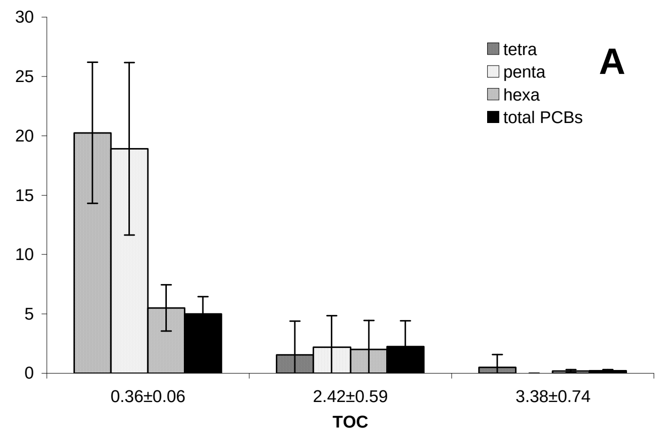

Figure 12. AC dose-response relationship for aqueous equilibrium PCB concentrations normalized by sediment concentrations (Plot D). Each column and error bar represents the mean and one standard deviation (n=5).

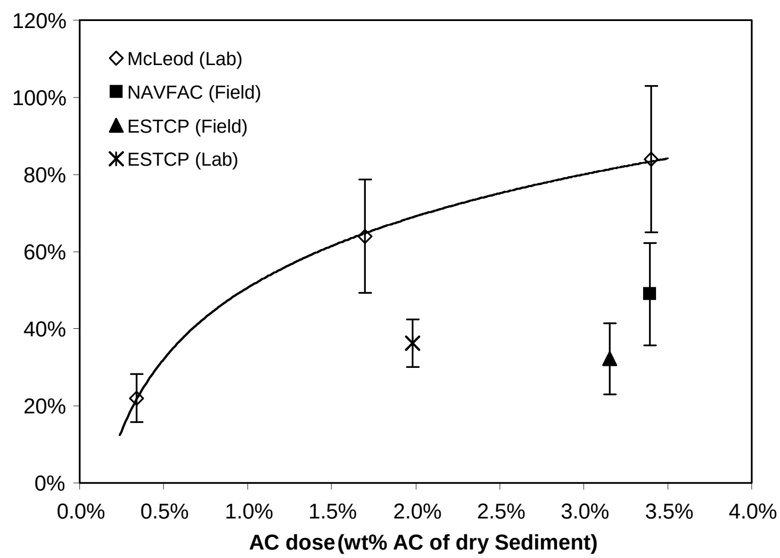

Figure 13. Activated carbon dose-response relationship for clam PCB bioaccumulation.

◇McLeod et al. (2007 and 2008) Laboratory studies that employed AC-sediment contact on a roller for 1 month (n= 3-4).

■ Prior NAVFAC field study 19 and rotovator mixing for about half an hour total on the test plot (% difference of lipid normalized Bioaccumulation Factor (BAF) compared to control plot) (n=3).

▲This ESTCP field study with rotovator mixing for about half an hour total on the test plot (% difference of lipid normalized tissue PCB residue compared to the mixing control plot) (n=3-5).

∗This ESTCP study based on rotovator mixing of field sediment and laboratory bioassay with additional mixing of collected field samples through sieving and 5-minute homogenizing (% difference of lipid normalized PCB tissue residue compared to the mixing control plot (n=5). Each point and error bar represents the mean and one standard deviation.

8.0 COST ASSESSMENT

8.1 COST MODEL

Table 5. Cost model for in situ stabilization by activated carbon mixing.

Cost Element	Data Tracked during the Demonstration	Costs	
Treatability study	• Detailed assessment required • Personnel required and associated labor • Materials • Analytical laboratory costs	Lab technician, 80 h	$2000
		Materials	$3000
		Analytical laboratory	$7200
Baseline characterization	• For 20 monitoring locations • Detailed field/laboratory assessments required • Field assessment costs • Analytical laboratory costs • Personnel required and associated labor • Materials	Field technician, 5*20 h Lab technician, 3*160 h	$2500 $12,000
		Materials	$18,000
		Analytical laboratory	$26,400
Site preparation	• No cost tracking	NA	
Activated carbon amendment	• For 700 ft^2 treatment by one of mixing options • Activated carbon • Mobilization/demobilization of AEI Aquamog • Mobilization/demobilization of CEI injector system • Personnel required and associated labor	Field technician, 5*20 h	$2500
		Materials	$3000
		Activated carbon (TOG), 350 lb / 100 ft^2	$ 7000
		AEI Aquamog Labor & rental, 2 days	$10,000
		CEI Injector Labor & rental, 2 days	$10,000
Operation and maintenance costs (periodic monitoring)	• For 20 monitoring locations • Detailed field/laboratory assessments required • Field assessment costs • Analytical laboratory costs • Personnel required and associated labor • Materials	Field technician, 5*20 h Lab technician, 3*320 h	$2500 $24,000
		Materials	$18,000
		Analytical laboratory	$26,400
		Reporting (per year)	$10,000
Decontamination and residual waste management	• Standard practice, no cost tracking	NA	
Public education program	• No cost tracking	NA	
Operation and maintenance costs	• No unique requirements recorded	NA	
Long-term monitoring	• No cost tracking	NA	

8.2 COST DRIVERS

The primary cost driver for this in situ AC amendment is the capital cost of AC amendment and site preparation. Although the two large-scale mixing devices showed adequate performance to the relatively small test area, their full-scale application or subtidal area application would be questioned due to their minimal mobility and production rate. Therefore an engineering task is to develop a better mixing technology. Appropriate site preparation (e.g., dewatering) would facilitate the application of AC amendment for the subtidal area, for example, by installing a coffer dam and using conventional soil tilling and mixing equipment.

The cost of activated carbon is also the cost driver. For the cost model from this study, the cost of AC was set as $2.9/lb, but this can be significantly lowered using regenerated carbon instead of virgin carbon. In a preliminary treatability test, we demonstrated that regenerated carbon showed equal or even better performance than virgin carbon. Also, bulk delivery of other types of VAC may be in range of about $1/lb, e.g., Calgon Carbsorb at about $1/lb, and RAC is even less costly.

The experience of performing the pilot-scale study through the ESTCP effort and analyzing the FS report shows that more effort is needed to explore efficient engineering options for the delivery and mixing of activated carbon into sediments for a full-scale application. An example of more efficient activated carbon delivery and mixing is discussed in Section 8.3.2.

8.3 COST ANALYSIS

A comparison of remedial alternatives and cost estimates is presented in the 2008 Final FS report for Parcel F at Hunters Point Navy Shipyard (Appendix D). In this section, the results from the cost analysis presented in the FS are summarized along with modified cost estimates for an alternate remediation option.

8.3.1 Remedial Alternatives for Cost Analysis

Seven remedial alternatives were analyzed in detail in the FS report. The present value cost estimates for these alternatives are presented in Figure 14 and range from $2-30 million. Based on the cost calculations presented in the FS, scaling up of the activated carbon application method used in the present ESTCP study (using an Aquamog) would result in a total cost that is about half the cost of dredging and disposal. The other alternatives of focused dredging and activated carbon amendment have costs that are higher than activated carbon amendment alone, but less than dredging.

A more cost effective approach of application over a large area may be achieved by installing a cofferdam and dewatering the South Basin like Alternative 5 and using standard earth moving and landscaping equipment to apply and amend the carbon as described below.

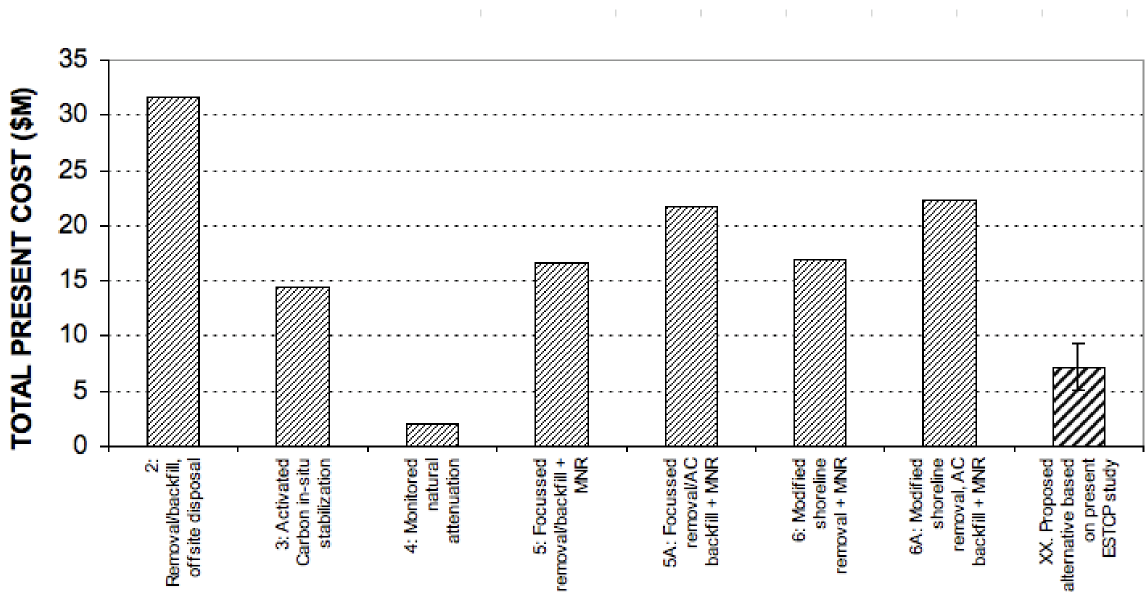

Figure 14. Present value cost comparison of different remedial alternatives for Hunters Point Navy Shipyard South Basin area (Area IX/X). (Source: 2008 Final Feasibility Study Report for Parcel F)

8.3.2 Proposed Application

This proposed application is similar to Alternative 5A described in the FS with two main differences: 1) sediments are not dredged and disposed before application of activated carbon, and 2) activated carbon is mixed into the top 1 ft of native sediment and not mixed in with clean backfill material brought from off site. The cost estimate assumptions were summarized below (quoted or rephrased from the Final FS Report for Parcel F12).

- The remediation area is accessible, and no specialized equipment or services (aside from those described in this report) would be necessary to gain access to the site.
- All activities would be performed using modified U.S. Environmental Protection Agency (USEPA) Level D personal protective equipment.
- The cost for decontamination facilities, residual waste management, and dewatering facilities are similar to Alternative 2 (Excavation/Backfill and Off-Site Disposal).
- Engineering (design, permitting, and manifesting) and professional management costs are calculated as a percent of the total direct labor cost (12%).
- Sediment contaminated with PCBs would be stabilized by addition of 4% activated carbon to the top 1 foot of sediments.
- The area would be dewatered using cofferdams and centrifugal pumps before the treatment.

- Approximately 57,850 cubic yards would be treated, requiring approximately 1,610,000 lb of activated carbon.
- The cost of activated carbon is $1.04/lb, which is based on the quote for Calgon Carbsorb 50x200 for the Grasse River, NY, study.
- Activated carbon would be applied over the PCB-contaminated sediment area using a tractor spreader similar to Alternative 5A (Focused Removal and Activated Backfill).
- Ten crane mats would be on site for loading the carbon onto the bulldozer.
- The carbon will be mixed into the top 1 ft of native sediment using a bulldozer with tiller attachment similar to that described in Alternative 5A.
- The application and mixing of the carbon is performed in two increments to allow a more homogeneous application.
- Annual monitoring would be conducted for the same parameters for the first 5 years, followed by monitoring every 5 years for years 25 through 30, and reported in 5-year review documents.

As described in Table 6, the cost of activated carbon application into sediment after dewatering the South Basin area is $9.1 million, which is 30% of the cost of Alternative 2 (dredging/disposal). Activated carbon material cost is about half the total remediation cost. Significant cost reduction (about 25%) is possible by using a less expensive RAC, which is half as expensive as VAC.

The estimated costs follow the cost estimate for full-scale application that was presented in the Final Report of the preceding SERDP-funded study (ER-1207), but with consideration of greater volume of sediment for treatment and a higher activated carbon dose. Shown in Table 7 are the same cost calculations after accounting for the larger treatment volume of 57,850 cubic yards delineated in the FS and a higher dose (4%) of activated carbon. The revised cost based on the larger sediment volume is $7.5 million, which is close to the estimate provided in Table 6 for application after installing a cofferdam and draining South Basin.

Based on the cost comparisons presented above, a recommendation from the present ESTCP study is to explore the application of activated carbon into the top 1 ft of native sediment without sediment removal after installing a cofferdam across the narrow inlet and draining South Basin. An activated carbon dose of about 4% is recommended to overcome effects of spatial heterogeneity of application and potential losses from deeper mixing.

Table 6. Application of activated carbon into native sediment after installing a cofferdam and dewatering South Basin at HPS.

Cofferdam installation and pumping (South Basin, 2000 ft)		$343,272
Cofferdam installation and pumping (Yosemeti Creek, 150 ft)		$57,488
Thin layer backfill of AC only, no excavation, with tiller mixing		$4,694,777
Activated carbon cost	$4,670,300	
Broadcast carbon twice using tractor spreader (2 x 33 acre; $105/acre)	$6968	
Soil tilling twice using D3 doser with tiller attachment (2 x 40 hr @ $200/hr)	$15,960	
Decontamination	$1100	
Spare bulldoser with tiller	$449	
Confirmation sampling		$29,540
Residual waste management		$22,250
Professional labor management (@ 33% of capital costs, similar to Alt 5A)		$1,681,527
Design cost (@ 12% of capital costs, similar to Alt 5A)		$611,464
LONG-TERM MONITORING		
Annual monitoring first 4 years		$543,402
Monitoring every 5 years and 5-year review for years 5-30		$1,088,770
TOTAL		**$9,072,491**

Table 7. Cost calculation for activated carbon addition to sediment at Hunters Point South Basin.

(Cost estimate presented earlier in the Final Report of CC-1207 using typical cost of dredging operations) **(Revised sediment volume of 57,850 cubic yards, based on 2007 Feasibility Study)**		
SEDIMENT HANDLING COSTS		
Capital costs		
Site preparation		$20,000
Mobilization—equipment and silt curtain		285,000
Cost of fresh carbon (at $2.2/kg)		4,670,300
Carbon application and mixing		525,840
(approximation using typical cost for auger dredging, no disposal cost)		
Water quality monitoring during operations		50,000
Site restoration		5000
Direct Capital		$5,556,140
Engineering, procurement & construction management (12% of direct capital)		666,737
Contractor overhead/profit (15%)		833,421
Total capital cost		$7,056,298
INSTITUTIONAL CONTROLS		
Capital Items:		
Public education program		50,000
O&M plans		10,000
Deed restrictions		2500
Engineering, procurement and construction management (12% of direct capital)		7500
Present worth of longer term operating costs (assuming interest rate of 8%)		
Long term monitoring (40 years at $10,000/year)		119,246
Public education program (40 years at $15,000/year)		178,869
Maintaining O&M plans (40 years at $400/year)		4770
Reporting (40 years at $10,000/year)		119,246
TOTAL COSTS (using fresh granular activated carbon [GAC])		**$7,548,429**
TOTAL COST (using regenerated GAC)		$5,000,992
Material Handling and Cost Assumptions:		
Sediment volume to be treated in cubic yards from Parcel F FS report	57,850	
Volume of sediment to be treated in cubic meters (top 1 ft)	44,226	
Weight of dry sediment in kg (assuming dry bulk density of sediment = 1200 kg/cum)	53,071,590	
Weight of carbon needed in kg (4% of sediment dry weight; 2.5% + safety factor of 1.5%)	2,122,864	
Cost of carbon (assuming $2.2/kg for fresh GAC)	4,670,300	
Cost of carbon (assuming $1.0/kg for regenerated carbon)	2,122,864	

9.0 IMPLEMENTATION ISSUES

9.1 ENVIRONMENTAL CHECKLIST

The potential regulations that may apply to the demonstration are CERCLA and SARA. No hazardous emissions and residuals were produced by this in situ treatment technology during the demonstration.

9.2 OTHER REGULATORY ISSUES

The regulatory agencies for this demonstration project are area regulatory agencies such as USEPA Region 9, California Department of Toxic Substances Control, San Francisco Regional Water Quality Control Board, San Francisco Public Utility Commission and Department of Public Health, and National Oceanic and Atmospheric Administration. The Demonstration Plan was reviewed by these and other regulatory agencies before implementation.

The PI and the team attended the Bayview Hunters Point Restoration Advisory Board (RAB) meeting. A presentation on the technology was given to the RAB group on two occasions. A presentation was also given to the USEPA Biological Technical Assistant Group and to a national meeting of USEPA Regional Risk Assessors.

The Hunters Point site offers the opportunity to assess several strategies for activated carbon deployment, including mixing activated carbon with sediment or focused sediment removal and activated carbon-amended backfill.

9.3 END-USER ISSUES

The Navy site managers at Hunters Point have indicated that they hope to use the technology in their final remedial decisions; if they do, technology transfer to other DoD sites should be straightforward. We have discussed this work with the Hunters Point Base Closure Team on several occasions and received favorable comments. Consequently, this AC-amendment technology and modified treatment method were included as alternatives in the Navy's Final FS Report. Knowledge gained from this field demonstration project will be disseminated to Navy Remedial Project Managers, DoD personnel, and other interested parties through the Navy's Sediments Subgroup of the Risk Assessment Workgroup, the Navy's Alternative Restoration Technology Team committee, the Interstate Technology Regulatory Cooperation Sediments Workgroup, the Remediation Technology Development Forum Sediments Action Team, and the Tri-Service Environmental Centers Coordinating Committee and Symposium. Since this project represents the first demonstration anywhere of in situ treatment for sorptive stabilization of PCBs in sediment, the project technical papers published in the peer-reviewed literature should command considerable attention.

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APPENDIX A

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