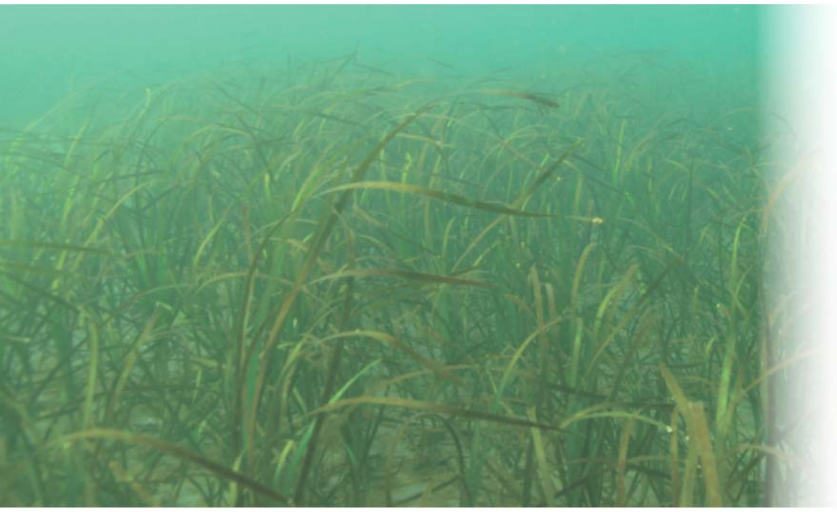

Custom Plywood Interim Action Thin Layer Capping Pilot Study Work Plan Anacortes, Washington

Prepared for
Washington State Department of Ecology

July 10, 2012
17800-05

HARTCROWSER

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Custom Plywood Interim Action
Thin Layer Capping Pilot Study Work Plan
Anacortes, Washington

Prepared for
Washington State Department of Ecology

July 10, 2012
17800-05

Prepared by
Hart Crowser, Inc.

Jason Stutes
Senior Project Marine Ecologist

Brad Helland, PE
Senior Associate Sediment Specialist

Allison Reak
Marine Permitting Specialist

120 Third Avenue South, Suite 110
Edmonds, Washington 98020-8411
Fax 425.778.9417
Tel 425.775.4682

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CONTENTS

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CUSTOM PLYWOOD INTERIM ACTION
THIN LAYER CAPPING PILOT STUDY WORK PLAN
ANACORTES, WASHINGTON

1.0 INTRODUCTION

Eelgrass is a native, perennial marine grass that is protected under several state and federal statutes and regulations because of its high value to the aquatic ecosystem, its sensitivity to disturbance, and its inability to thrive in altered environments (Phillips 1985). The governmental mandate to preserve eelgrass is challenged by the need to remediate contaminated sediment in areas where critical eelgrass beds are found. Restoration of large tracts of eelgrass is often not practicable because of (1) a general lack of area that would foster a successful transplanting effort and (2) a substantial relative cost. In general, eelgrass occurs in areas that are favorable for its growth and is usually limited by elevation, water quality, and water clarity. Because of the infeasibility of restoring eelgrass to large areas of dredged and/or thick-layer capped sediment (where resultant remediation actions are often not compatible with favorable growing conditions for eelgrass transplants), there is a need for a sediment remediation approach that balances the benefits of reducing exposure to contaminated sediments with allowing existing eelgrass—and its associated marine community—to survive in place with minimal alteration to its health and productivity over the long term. We propose a carbon-amended thin-layer sediment capping approach to optimize the benefits of both environmental protection and *in situ* eelgrass preservation.

This pilot study was previously authorized without the carbon amendment under the US Army Corps of Engineers (USACE) Nationwide Permit 18 (NWS-2010-288) and was contingent on implementation of the requirements and/or agreements set forth in the Biological Evaluation Eelgrass Remediation Thin Layer Cap Pilot Study Custom Plywood Interim Remedial Action dated August 5, 2011, and the special conditions specified in the USACE authorization letter dated October 18, 2011. Special conditions include an in-water work period of July 16 through January 31 and pre-construction forage fish spawning surveys.

Since the original permit was issued, a further need to increase cap effectiveness was desired due to new information gathered over the winter (2011/2012). In addition to this, all Nationwide Permits were reissued with new stipulations and conditions (corrected March 19, 2012). A reverification process was initiated June 29, 2012, to reauthorize these activities (including the additional carbon amendment activities) under the Nationwide Permit 18. This workplan will serve

to supplement to the previously generated documents detailing the activities to be performed for the pilot study.

2.0 OBJECTIVES

The objective of the pilot study is to determine whether the contaminated sediments underlying eelgrass can be remediated with thin layers of sand, some of which will be amended with activated carbon, without adverse impacts to existing marine habitat. This low-impact capping method is proposed to test the tolerance of eelgrass and its associated invertebrate community to placement of varied thicknesses of sediment capping materials.

Low-impact placement involves dispersed placement (pluviating) of sand particles through the water column onto the seabed, gradually building a layer of cap material. Cap material will be broadcast over the water surface using a spinning sand spreader, making multiple applications as necessary over time, rather than less controlled, more acute applications of capping material using a clamshell bucket or drop barge. In the areas where activated carbon will amend the thin layer of sand, the carbon will be applied in a thin layer (less than 1/4 inch) using a similar mechanical delivery system prior to placement of sand. The carbon amendment is formulated with activated carbon, clay, and sand in cylindrical pellets (typically measuring 4–5 millimeters [mm] in diameter by 10 mm in length) that are designed to sink to the sediment bed and become incorporated into the sediment matrix. The result is intended to place a thin layer of carbon pellets on the sediment bed covered by a thin layer of sand.

3.0 METHODOLOGY

The proposed pilot study will follow a five-step approach:

1. **Assessment of Pretreatment Conditions:** Survey reference and test plot areas to establish baseline metrics for eelgrass (area, density, shoot morphology and biomass), bulk sediment dioxin/furan (D/F) concentration, sediment porewater concentration (as measured by passive sampling devices [PSD]; see Appendix A), and clam tissue concentration. Capping will be preceded by a forage fish spawning survey targeting herring.

2. **Treatment:** In addition to an off-site reference plot, six plots measuring 18 feet x 18 feet will be established in eelgrass areas within the site. The presence of carbon amendment in capping material, and the depth of capping material will be tested in a factorial design (Table 1).

3. **Interim Assessment:** At a minimum of once during the pilot study, we will examine eelgrass growth, function, and response at reference and test plots, comparing both pre-treatment and reference plot indicators to test plot indicators to determine relative health. We will also collect bulk sediment, PSD, and (if possible) clam tissue data for comparison with references and to evaluate effects of carbon amendment. Sediment profile imaging may be employed to evaluate the distribution of carbon amendment in surface sediment.

4. **Final Assessment:** Examine eelgrass growth, function, and response at test and reference plots. Collect bulk sediment, PSD, and clam tissue data for comparison with references and to evaluate effects of carbon amendment. Sediment profile imaging may be employed to evaluate the distribution of carbon in surface sediment.

5. **Conclusion**: Analyze for project effects and determine which capping design provides optimal protectiveness and eelgrass preservation.

The pilot study will be implemented to cover approximately one calendar year for eelgrass response variables and two calendar years for remediation effectiveness (i.e., sediment dioxin and clam tissue dioxin concentrations), which will include portions of two growing seasons (eelgrass growing seasons are generally from February through October in Padilla Bay; Thom 1988). Table 2 summarizes the level of effort over the duration of the pilot study. The capping activity is authorized from July 16th through January 31 during any year that the Nationwide Permit is valid.

Details of sampling methods, equipment, and schedule are contained in Appendix A, Chemistry Sampling and Analysis Plan.

3.1 TEST PLOT DELINEATION

Reference and test plot areas will be delineated within the larger 13-acre area of eelgrass within the remediation area, considering 2011 macrovegetation survey data of moderately dense eelgrass and 2012 sediment chemistry data of moderate toxicity concentrations, plus sufficient depth for boat access. Plots will be delineated at locations within the same range of depths (i.e., between –4 and –6 ft mean lower low water [MLLW]), at least 20 ft from the edge of the existing bed, to avoid stressing parts of the bed that are more vulnerable to disturbance. Sheet 1 shows the approximate location of the test plots at the site and Sheet 2

shows their configuration. The total area of the test plots[1] will be limited to 1944 square feet (sf) with each of the six 18 foot x 18 foot test plots measuring 324 sf. The total cap area was derived from the 25 cubic yards (cy) fill limit (specified in Nationwide Permit 18) and will be divided between six test plots. A reference plot, which will receive no capping material, will also measure 18 feet x 18 feet (324 sf).

Test and reference plot areas will be marked in the field by divers using low-relief monuments, and coordinates will be recorded using a survey-grade Global Positioning System (GPS) unit. Monument placement will be temporary, for the duration of the study; after the final assessment, monuments will be removed.

3.2 SEDIMENT CAP MATERIAL AND PLACEMENT

Sediment cap material will consist of less than 25 cy of washed sand and carbon amendment. Sand grain size will be selected for the smallest particle size that can be applied by the spreader and remain in place on the seabed without being resuspended or transported by tidal or longshore currents. The material will be washed to remove any organic and silt fractions so that turbidity will not be generated during placement.

Cap material will be applied to the test plots using a boat-mounted spreading device described below. The boat will be positioned using GPS coordinates and controlled by a 3-point anchoring system, using three helical (screw-type) anchors. The 3-point system will allow a single placement of each anchor for the duration of the project. Helical anchors have a small footprint (about 8 inches diameter) and will be used to minimize disturbance to the substrate and eelgrass. After the study, the anchors will either be removed or screwed deeper into the substrate until the tops are at least 6 inches below grade.

Cap material will be broadcast from the boat over the test plots as the boat moves slowly over the test plot areas, using the three-point anchor system to maintain an accurate and repeatable track. Cap thickness will be verified via installation of sediment stakes and sediment traps. Divers will verify cap thickness immediately after pluviation and between sampling intervals.

[1] An off-site reference plot is not included in these measurements.

3.3 PRE-TREATMENT MONITORING AND ASSESSMENT

The reference and test plots will be surveyed for eelgrass growth and function by assessing the following biological parameters:

- Shoot morphology, including surface area (i.e., shoot length and diameter plus leaf blade numbers, lengths, and widths);
- Biomass dry weight;
- Shoot density;
- Areal extent of eelgrass within each plot; and
- Epibenthic community indicator species (density, diversity, and dominance).

For the purpose of this study, a shoot is defined as the primary green vegetation (including leaf blades) extending from the sub-surface sections of the rhizome(s).

Divers will assess each test and reference plot for total area, using presence/absence notations along transects within each bed. Divers will count shoot density within a minimum of ten, randomly placed, 0.25-square-meter (m^2) (50 centimeter [cm] x 50 cm) quadrats in each test and reference plot, and photograph each quadrat. Divers will collect five shoots from each test and reference plot for laboratory assessment of epibenthic indicator species. A mesh bag (250 micrometer [µm] mesh size) will be placed over the shoots while the diver cuts each shoot at the base. Shoots and epibiota will be sealed in the bag for later processing for assessment indicators.

Bulk sediment samples will be taken from each plot and from the off-site reference area for D/F analysis. Three randomly located surface sediment grab samples within each plot will be composited for a single D/F analysis (along with conventional parameters like grain size and TOC). See Appendix A for further details.

Porewater samples will be collected using passive sampling devices as described further in Appendix A. The use of such samplers is intended to monitor porewater concentrations *in situ* rather than *ex situ* as a better surrogate measurement of tissue bioaccumulation.

Clam tissue from organisms placed at each test plot will be collected for D/F tissue analysis, as discussed in Appendix A. This initial assessment will provide a baseline for D/F bioaccumulation.

3.4 CAP PLACEMENT VERIFICATION

Cap thickness at each test plot will be measured by using graduated stakes for assessing long term trends and monitoring cap placement. Four stakes marked in 0.5-in increments will be placed in each of the six test plots and the reference plot. The location of the stakes will be recorded by GPS using temporary surface marker buoys pulled taut, and the pre-treatment substrate elevation at each stake will be recorded by divers. Before and after capping material placement, substrate elevations will be recorded by divers to measure cap thickness. In addition, a sediment trap with a retrieval line and float will be placed within each test plot to monitor cap sand thickness during placement. The buckets can be retrieved at any time during placement to confirm cap thickness.

3.5 INTERIM MONITORING AND ASSESSMENT

Divers will survey all test and reference plots for the eelgrass growth parameters described above (excluding epibenthic indicators). Quadrat samples will be photographed as a secondary, qualitative evaluation tool. Survey data will be promptly evaluated to determine eelgrass mortality, survival, and growth by comparing reference plot eelgrass metrics to test plot eelgrass metrics. If any test plot shows statistically significant increased numbers of dead, dying, or severely stressed eelgrass (compared to reference plots), then that capping scenario will be removed from possible consideration for the larger capping effort.

Divers will also assess substrate elevations at each survey marker (test and reference plots), note any anomalies in the test plots (e.g., substrate scour, debris, etc.) and replace any missing stakes. If significant changes to eelgrass health are noted, changes to the study design will be initiated through adaptive management discussions with concerned resource agencies.

3.6 POST-TREATMENT MONITORING AND ASSESSMENT

One full year after the final placement of cap material, reference and test plots will be monitored by divers for the same physical and biological parameters used to assess pre-treatment conditions.

Additional post-treatment monitoring may be conducted the following year (i.e., 2013), to assess continuing site recovery and, if necessary, to implement an eelgrass recovery contingency plan. In general, an eelgrass recovery

contingency plan would be triggered should eelgrass indicators measure significantly lower in the test area compared to reference area measures for three of the four parameters:

- Areal coverage;
- Shoot density;
- Shoot morphology (leaf length, width, number per shoot, and biomass dry weight); and
- Epibenthic indicator species diversity/abundance.

Additional sediment, porewater/PSD, and tissue sampling may be conducted to assess bioaccumulation effects over longer periods.

3.7 EQUIPMENT DESIGN AND CALIBRATION

Capping material will be broadcast over the eelgrass using a medium-duty-vehicle material spreader powered by an internal gas engine (e.g., Swenson MDV #0002-585-00 or similar). The spreader consists of a V-shaped vibrating hopper with a 4.0-cy capacity that will be loaded with capping material sand. An internal conveyor moves sand from the hopper through a feedgate onto a spinner assembly. The spinner discharges the sand in a circular pattern. The spreader is small enough to be mounted on either a small barge or large boat.

The volume and thickness of capping material placed on the eelgrass bed depends on three variables: feedgate opening, spinner speed, and vehicle speed. The size of the feedgate opening controls the volume of sand that falls onto the spinner and the spinner speed controls the broadcast diameter. Broadcast diameter can be set between 4 and 40 feet. The speed of the delivery vehicle across the application area affects cap thickness.

A land-based calibration of the spreader will determine the operational settings (spinner speed, gate opening size, and operating speed) that deliver the desired cap area and thickness. The spreader will be mounted on a truck and operated at a controlled upland location (greater than 200 feet from the marine shoreline) while the delivery variables are adjusted to meet the pilot study design. Sand thickness may vary by up to one inch, with thicker deposition occurring along the center of the application area and thinner deposition around the outer edge. Spreader settings may be adjusted during in-water placement, based on observations made during land-based calibration and in-water application.

3.8 DECONTAMINATION PROTOCOLS

Field equipment that comes into contact with aquatic substrate (e.g., transect lines, plot measurement stakes, anchors, sample bags) will be decontaminated with seawater wash and triple rinse, on site, before transportation from the site. Divers will enter and exit the sampling area by boat, in the water column, to avoid contact with the substrate. Diving gear that contacts the sediment (e.g., gloves, booties, fins) will be decontaminated on site before it is removed from the site. These practices will be covered in greater detail in the Health and Safety Plan (HASP).

3.9 EELGRASS HABITAT ASSESSMENT CRITERIA

Eelgrass habitat will be analyzed and evaluated according to the following criteria:

1. For each cap thickness, test plot eelgrass spatial area (percent coverage) must be statistically unchanged when compared to pre-treatment estimates (when standardized to changes in reference plot coverage).

2. For each cap thickness, test plot eelgrass densities must be statistically unchanged when compared to pre-treatment estimates (when standardized to changes in reference plot coverage).

3. For each cap thickness, test plot eelgrass shoot biomass must be statistically unchanged when compared to pre-treatment estimates (when standardized to changes in reference plot coverage).

Both interim and final measurements of eelgrass growth indicators, shoot density, and spatial coverage will be used to assess eelgrass tolerance to various capping approaches. A reduction of at least 30 percent in eelgrass shoot aerial biomass, density, and/or coverage (two of the three) for a particular capping scheme (i.e., thickness) would trigger no further capping at the interim stage. A post-treatment reduction of at least 30 percent in eelgrass shoot biomass, density, aerial coverage, and/or epibenthic community function within a capping scheme would trigger a longer recovery period and the use of adaptive actions with interested resource managers.

The pilot study summary report will include relevant raw data and basic statistics as appendices, including details of sampling and subsampling procedures used, diver observations, taxonomic sorting and identification records, and relevant

field and laboratory notes. Simple graphical presentations will be used, where possible, to summarize data trends.

3.9.1 Eelgrass Data Collection, Processing, and Analysis

Survey documentation will include the date and time of the survey, names of surveyors and their affiliation, turbidity/visibility measurements, presence of invertebrate and vertebrate species, and anecdotal observations pertinent to habitat characterization of the project site (e.g., presence of debris, substrate disturbance, propeller scour, etc.).

Survey protocols will generally follow WDFW's 2008 Eelgrass/Macroalgae Habitat Interim Survey Guidelines.

3.9.2 Eelgrass Area

Two parallel transects will be established through each plot, at 2.5 and 7.5 feet from the longest edge, extending at least 5 feet beyond the plot margins. Divers will swim along each transect, recording the distances at which contiguous eelgrass begins/ends, and estimating the lateral extent of coverage every 2 feet along the five-foot-wide swath of the transect. The area of coverage will be calculated by summation and divided by the total plot area (324 sf) to yield a percent cover for each plot.

Pre-treatment, interim, and post-treatment eelgrass area will be compared for each plot. Treated plot areas will also be compared to reference plot areas to determine if large-scale, non-project conditions might be affecting the site's eelgrass.

Change in percent cover for each plot may be determined using an ANOVA (or Mann-Whitney U test, should assumptions not be met). The statistical analysis will use the parameters recommended by WDFW 2008 (i.e., $\alpha = 0.10$, power $(1 - \beta) = 0.90$, and the effects threshold of a mean eelgrass area difference >20 percent).

3.9.3 Eelgrass Density

Counts for density will be haphazardly placed within the bounds of the test/reference plots. Density counts will consist of all shoots emerging from the substrate within a 0.25-m^2 quadrat. Counts will be collected from each plot until appropriate statistical robustness is achieved (WDFW 2008), up to 30 counts.

Density sample data will be combined within each plot to yield a mean density per square meter. For each cap thickness, the three mean density replicates will be averaged and compared to an average of the three reference plot mean densities to determine statistically significant differences.

Changes in average density for each plot and for combined replicate plots may be determined using an ANOVA (or Mann-Whitney U test, should assumptions not be met). The choice of statistical test will depend on the variances between samples, normality of the data, and additively of effects. The statistical analysis will use the parametrics recommended by WDFW 2008 (i.e., $\alpha = 0.10$, power $(1 - \beta) = 0.90$, and the effects threshold of mean eelgrass area difference > 20 percent).

3.9.4 Eelgrass Shoot Morphology and Biomass

Eelgrass shoot samples will be collected haphazardly at the same time as density samples. Shoot samples will be collected randomly from within the plot. To avoid disturbing the epibenthic community, divers will grasp the eelgrass shoots just below the sediment-water interface, place a labeled one-liter (nominal) plastic self-sealing bag over the shoot, and cut the shoot from inside the bag. The diver will seal the bag without squeezing out excess water, so that the sample will consist of a undisturbed eelgrass shoot plus about one liter of surrounding seawater. Sample bags will be transferred to the boat and stored in a cooler on ice until they can be processed for analysis.

Processing will involve pouring the water and eelgrass from each sample into a larger (e.g., one gallon) self-sealing bag and thoroughly rinsing the one-liter bag into the larger bag with enough buffered-formalin seawater to achieve a 5- to 10-percent preserved solution (about 52 to 106 milliliters [ml] per bag). The eelgrass shoot will be processed for leaf morphology and biomass. (The epibenthic species from the shoots and surrounding liquid will be processed for epibenthic indicator species.)

Biomass dry weight and leaf morphology metrics (length, width, and total area) will be averaged within each plot for statistical comparison to replicates and reference plot averages. Comparisons of each metric for each plot and for combined replicate plots may be determined using an ANOVA (or Mann-Whitney U test, should assumptions not be met).

3.9.5 Epibenthic Processing and Analysis

Epibenthic samples will be processed by qualified biologists trained in regional taxonomy, and sample data will be analyzed using the statistical methods discussed below.

3.9.5.1 Laboratory Methods

A lab technician will transfer the contents of each sample bag onto a 250-µm sieve. Each sample bag and eelgrass shoot will be thoroughly rinsed through the same 250-µm sieve to collect any organisms adhering to those surfaces. Epibenthos will then be sorted and identified to the lowest practicable taxonomic level by a qualified biologist. A technician will transfer the results of the sorting and identification data sheets to a computerized database. Data will be QA/QC'd at each step (identification, sorting sheet transfer, and database entry) by a second, similarly-trained biologist. Each QA/QC event will be tracked in a standard sample log database.

Chemical samples and analyses will follow the QA/QC scheme outline in Appendix A and cross reference the database codes used in the eelgrass database.

3.9.5.2 Analytical Methods

Epibenthic sample data will be evaluated for taxa abundance and diversity using nearshore salmonid prey functional groups developed in conjunction with US Fish and Wildlife and WDFW in 1990 and updated by information contained in Hass et al. 2002. Functional groups of key salmonid prey species will likely consist of:

Group 1: Harpacticoida (e.g., *Harpacticus* spp., *Tisbe* spp., *Zaus* spp., et al.);

Group 2: Amphipoda (e.g., *Corophium* spp., *Aorides* spp., *Allorchestes angusta, Gammaropsis* spp., et al.);

Group 3: Isopoda, Tanaidacea, and Cumacea (e.g., *Gnorimosphaeroma* spp., *Leptochelia* spp., *Cumella* spp., et al.); and

Group 4: Diptera (e.g., Chironomidaea fly larvae).

Epibenthic taxa abundance data will be transformed to numbers per standardized surface area and analyzed for statistically significant differences in

taxonomic group densities between reference plots and test plots before and after each treatment. The null hypothesis to be tested for each data set is:

$$H_0: \mu_{pre\text{-}treatment} = \mu_{post\text{-}treatment}$$

$$H_\alpha: \mu_{pre\text{-}treatment} = \mu_{post\text{-}treatment}$$

$$\alpha = 0.10$$

If test plot epibenthic groups show a significant decrease in abundance and/or diversity compared to reference plot groups, then the pilot study schedule may be extended to include an additional round of epibenthic sampling the following spring to assess whether capping effects on eelgrass persist.

Statistical tests will consist of single- and two-factor Analysis of Variance (ANOVA; Zar 1999) with Tukey's (Zar 1999) post-hoc tests where appropriate. Statistical tests will be completed in SPSS® using the General Linear Model data analysis tool. Unless noted otherwise, for all tests α=0.05 (significant results if $p < 0.05$). Tests will be run for three summary variables (total epibenthos density per m^2, total juvenile salmon prey [JSP] density per m^2, and taxa richness per sample). Principle components analysis will be used (data permitting) to determine overall replicate/test plot similarity across multiple metrics (diversity, abundance, dominance) to determine if various capping schemes are affecting the epibenthic community as a whole.

4.0 ADAPTIVE MANAGEMENT

The pilot study is designed to allow the gradual, episodic placement of cap material within living eelgrass to achieve sediment remediation goals without significant eelgrass mortality or functional loss of the associated epibenthic invertebrate community. Eelgrass research throughout the country indicates that the test plot eelgrass should respond with vigorous growth to quickly reach spatial and functional equilibrium with adjacent, untreated eelgrass; however, actual growth and recovery factors are highly variable and closely linked to local weather conditions, including daily solar radiation, temperature, rainfall (i.e., stormwater runoff and quality), wind (i.e., energy affecting waves and currents), and the duration of the growing season. The local eelgrass growing season extends from late February through October, with peak shoot density and leaf length from June to August. Because the July 16 to January 15 in-water work period will restrict study implementation to the last half of the growing season, efforts will be made to apply the first cap layer as early in the season as possible

(e.g., July 16) and maximize the recovery period following application of the cap layer.

The length of post-treatment recovery will also be determined by an evaluation of the eelgrass growth indicators (i.e., eelgrass area, density, and epibenthic community functional indicators) within each plot. If a reduction in productivity for any parameter is observed, then another round of sampling for function and productivity will be conducted to determine recovery during that growing season. If final analyses indicate that the test plots exhibit a significant decrease in eelgrass area or density, then alternative actions to address eelgrass recovery will be discussed with USACE, USFWS, NOAA Fisheries, DNR, and WDFW.

5.0 LITERATURE CITED

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TABLES

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Table 1 – Conditions for Thin Layer Capping Pilot Test

Sand Thin Layer Capping Thickness (in)	Carbon + Sand Plots	Sand Only Plots	Volume of Fill (yd^3)[a]
0	Carbon only – no sand	Control plot – no sand	0.26[b]
4	1/3 ft sand on top of carbon	1/3 ft sand only	8.0
8	2/3 ft sand on top of carbon	2/3 ft sand only	16.0
		Total Fill Volume (yd^3)	24.3

17800-05 Custom Plywood BE\Pilot Study 7-10-2012\Tables\Table 1.doc

Notes:

a) Calculated based on six plots each 18 ft x 18 ft.

b) Carbon pellets only; volume = 1/4 in x 18 ft x 18 ft = 0.26 yd^3

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Table 2 – Dioxin Sampling Schedule

Month	2012					2013					2014				
			Clam Tissue Sample				Clam Tissue Sample						Clam Tissue Sample		
			Short Term Exposure				Short Term Exposure						Short Term Exposure		
Placement Month	Eelgrass Assessment	Sediment Sample	PSD[1]	28-d Exposure	Cumulative Exposure[2]	Eelgrass Assessment	Sediment Sample	PSD[1]	28-d Exposure	Cumulative Exposure[2]	Eelgrass Assessment	Sediment Sample	PSD[1]	28-d Exposure	Cumulative Exposure[2]
Jan							7			Secondary Clam Placement					
Feb								7	7	3 (210)					
Mar															
Apr						7					optional	7			
May													7	7	
Jun															
Jul	7[3]	7			Initial Clam Placement	7[5]	7				optional				
Aug			7	7				7	7	3 (210)					
Sep	7[4]				3 (60)	7									
Oct		7			3 (90)										
Nov			7	7	3 (120)										
Dec															

Notes:

1780005 Custom Plywood BE\Pilot Study 7-10-2012\Table 2.xls

[1] Passive Sampling Device

[2] Clam tissue sampling for cumulative exposure will be conducted for 60, 90, 120, 210, and 2nd 210 days and placed into cages at the times indicated.
Note: The numbers in the table indicate the number of cages placed during the month indicated. Numbers in paretheses indicate exposure duration of cumulative exposure.

[3] Pretreatment assessment

[4] Interim assessment

[5] Final assessment

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SHEETS

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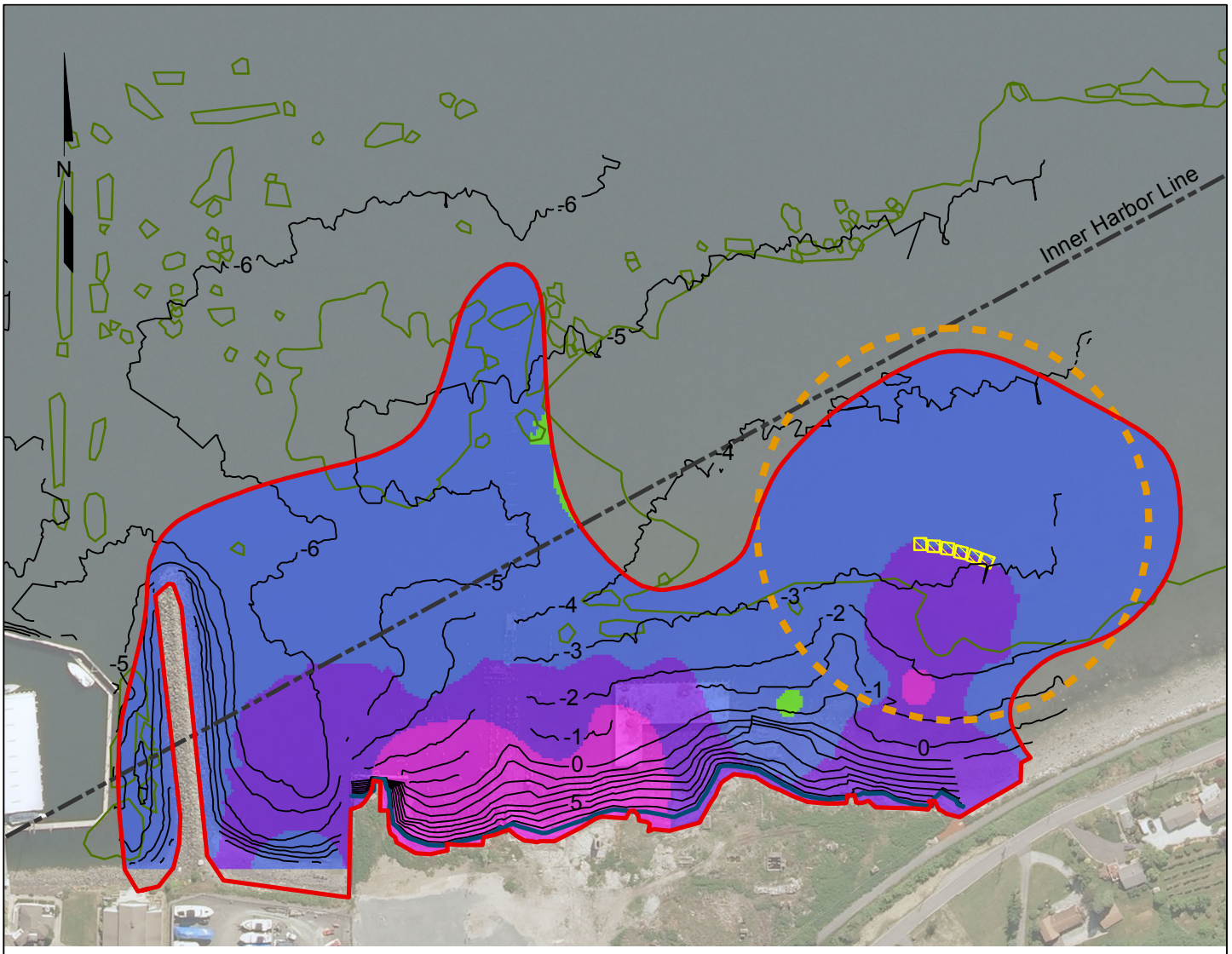

Test Plot (Approximate Location)

Approximate Extent of Eelgrass Beds

Interim Remedial Action Boundary

Action Area

MHHW Line

Dioxin/Furan Concentration in ppt

5 to 10 ppt

10 to 25 ppt

25 to 50 ppt

>50 ppt

Note: Area-weighted mean Dioxin/Furan Concentration: 24.5 ppt. Calculation completed using the inverse distance weighted (IDW) techinique.

0 125 250 500 Feet

PURPOSE: EELGRASS SEDIMENT REMEDIATION
THIN LAYER CAP
PILOT STUDY

DATUM: MLLW = 0.0

ADJACENT PROPERTY OWNERS:
1. WDNR
2. GBH INVESTMENTS
3. CITY OF ANACORTES

FIGURE "SUPPLEMENTAL"

TEST PLOT AREA PLAN

USACE REF. NO. NWS-2010-288

WASH. DEPT. ECOLOGY TOXICS CONTROL PROGRAM

P.O. BOX 47600

OLYMPIA, WA 98504-7600

IN: FIDALGO BAY

NEAR: ANACORTES

COUNTY OF: SKAGIT

STATE OF: WASHINGTON

APPLICATION BY: DEPT. OF ECOLOGY

DATE: JUNE 29, 2012

SHEET 1 of 2

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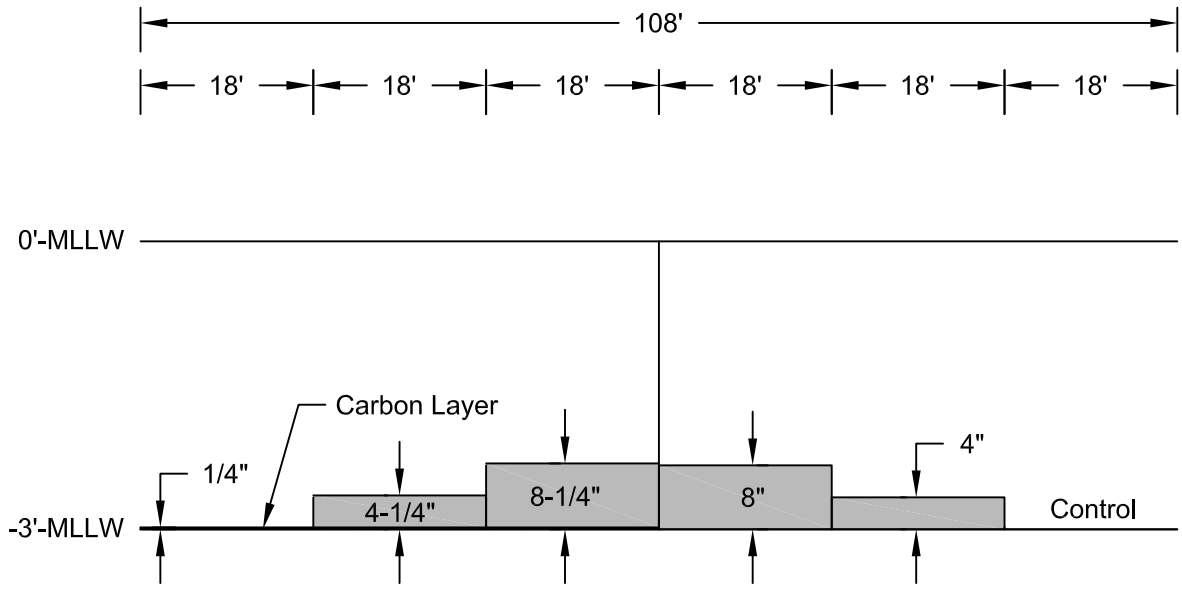

Horizontal Scale in Feet
0 20 40
0 2 4
Vertical Scale in Feet
Vertical Exaggeration x 10

PURPOSE: EELGRASS SEDIMENT REMEDIATION THIN LAYER CAP PILOT STUDY	FIGURE "SUPPLEMENTAL"	IN: FIDALGO BAY
	TEST PLOT AREA CROSS SECTION	NEAR: ANACORTES
DATUM: MLLW = 0.0	USACE REF. NO. NWS-2010-288	COUNTY OF: SKAGIT
ADJACENT PROPERTY OWNERS: 1. WDNR 2. GBH INVESTMENTS 3. CITY OF ANACORTES	WASH. DEPT. ECOLOGY TOXICS CONTROL PROGRAM	STATE OF: WASHINGTON
	P.O. BOX 47600	APPLICATION BY: DEPT. OF ECOLOGY
	OLYMPIA, WA 98504-7600	DATE: JUNE 29, 2012
		SHEET 2 of 2

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APPENDIX A
CHEMISTRY SAMPLING AND ANALYSIS PLAN

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APPENDIX A
CHEMISTRY SAMPLING AND ANALYSIS PLAN
THIN LAYER CAPPING PILOT STUDY
CUSTOM PLYWOOD SITE, ANACORTES, WASHINGTON

1.0 INTRODUCTION

This chemistry sampling and analysis plan (SAP) describes the scope of work for the thin layer capping pilot study at the Custom Plywood site. During the study, we will collect data to determine the effectiveness of carbon-amended sand capping material in reducing bioavailability of chlorinated dibenzo-*p*-dioxins and dibenzofurans (D/F) to clams. Site sediment is contaminated with D/F in concentrations ranging from 5 to 330 pg/g TEC (Hart Crowser 2011, 2012). Large eelgrass beds extend into areas with contaminated sediment. Thin layer capping has been identified as an interim remedial action for areas where eelgrass is present. The objective of the pilot study is to determine whether capping the contaminated sediment in eelgrass beds provides a sufficient level of protectiveness without significant adverse impacts to existing marine habitat. This SAP describes the methods, procedures, and schedule to acquire the chemical data needed to make this determination.

2.0 OBJECTIVES AND SAMPLING DESIGN

2.1 Objectives

The scope of work described in this SAP is designed to acquire the necessary data to accurately characterize the effects of capping material on sediment, porewater, and tissue D/F concentrations in six test plots (Figure A-1) and one off-site reference plot. The bioaccumulation of D/F in clam tissue will be measured in two ways: standard 28-day bioaccumulation assays, and long-term bioaccumulation tests.

The data we collect will include the following:

- Polychlorinated dibenzodioxin/furan (PCDD/PCDF) congeners in sediment, passive sampling devices (PSDs), and clam tissue;
- Sediment total organic carbon and other conventional parameters; and
- Clam tissue percent lipids

2.2 Sediment, Tissue, and PSD Sampling Locations

Figure A-1 shows the general location of the test plots. Sampling locations will be in the center of each test plot, as shown on Figure A-2. Figure A-3 shows the profile of the six test plots and illustrates the thickness of the carbon and sand layers in each plot. For tissue sampling, divers will embed clam cages approximately 6 inches into the surface sediment in each test plot and the reference plot. The clams in the cage will be exposed to the conditions in the plots for 28 days and then will be retrieved and composited for chemical analysis. Each clam cage will be equipped with a PSD that extends into the sediment approximately 6 inches and is also exposed to the water column above the sediment surface. The PSD can be divided at the time of collection into portions that are above and below the sediment surface. Details of cage design are further described in Cho (2007, attached to this appendix, see Figure 3).

A summary of target sampling locations and coordinates are presented in Table A-1.

2.3 Sampling Schedule

We will begin initial sampling as soon as approved by Ecology, and currently expect to begin in July 2012. To evaluate trends and effects over a 2-year period, sampling events will be scheduled periodically after the first event. Each sampling event will collect surface sediment, clams from clam cages, and PSDs attached to clam cages. Two sets of clam cages will be used: Clam cages for standard bioaccumulation testing will be deployed 28 days before they are retrieved during each sampling event, and clam cages for long-term bioaccumulation testing will be placed in the reference plot, control plot, and carbon-only plot, and then collected according to the sampling schedule detailed in 2.3.1.

2.3.1 Sequence of Sampling

We will collect samples as shown in Table 2 of the Custom Plywood Interim Action Thin Layer Capping Pilot Study Work Plan (Work Plan). During the first sampling episode, clam cages for 28-day and long-term bioaccumulation tests will be deployed. During the following sampling episodes, the sequence of events will generally be as follows:

- Collect surface sediment from the center of each test plot;
- Embed clam cage for standard bioaccumulation test at center of each test plot, with clams and PSD; and

- According to the schedule in Table 2 in the Work Plan, retrieve standard bioaccumulation test clam cages and long-term bioaccumulation test clam cages, with clams and PSDs.

3.0 FIELD PROCEDURES

3.1 Positioning Methods

Once the vessel is at the sampling location, either a two- or three-point anchor system will be deployed or engine power will be used to maintain position throughout sample acquisition. Test and reference plot areas will be marked in the field by divers using low-relief monuments, and coordinates will be recorded using a survey-grade Global Positioning System (GPS) unit. Monuments will be temporary, for the duration of the study; after the final assessment, the monuments will be removed.

Navigation systems will be used to provide a target horizontal accuracy of less than one meter. The GPS receiver will be placed above the block on the sampling device deployment boom to accurately record the sampling location position. Once the sampler has been deployed, the actual position will be recorded when the sampler is on the bottom and the deployment cable is in a vertical position. Horizontal coordinates will be referenced to NAD 83 State Plane North coordinates.

3.2 Water Depth Measurement

Water depths will be measured directly by lead-line or sonar and converted to mudline elevations using the predictive tide charts. Water depth will be compared with existing bathymetry data for the site. The lead-line measurements also serve as a check on location positioning, as the actual water depth at the location coordinates should closely match the predicted depth at those locations.

3.3 Equipment Decontamination Procedures

The stainless steel power grab sampling equipment, sampling utensils, and clam cages will be thoroughly cleaned before each use according to the following procedure:

- The grab sampler, sampling spoons/tools, and clam cages will be rinsed with sea water to dislodge any sediment. If sediment remains, the equipment will be brushed and rinsed again with sea water.

- Non-disposable sampling utensils and mixing bowls will be decontaminated using a Liquinox detergent wash followed by potable water and deionized water rinses.

All decontamination, sampling, and sample processing will be conducted using disposable powder-free nitrile gloves. Gloves will be disposed of between samples to prevent cross contamination.

3.4 Sample Collection and Processing

Hart Crowser will coordinate with Ecology and other agencies as necessary to obtain the necessary permits for collection of all marine organisms.

3.4.1 Surface Sediment

Sample Collection

Sediment samples for chemical analysis will be collected from the upper 10 cm. The top 10 cm is selected to be consistent with Washington State SMS procedures. Surface sediment samples will be collected from the center of each plot (see Figure A-2) using either a 0.1 square meter (m^2) vanVeen sampler or a 0.2 m^2 pneumatic power surface grab sampler. These surface sediment samples will be collected during each round of sampling prior to the placement of the clam cage at the same location.

Sediment samples collected with the vanVeen or power grab sampler will be carefully inspected to ensure that the following acceptability criteria are satisfied:

- The sampler is not over-filled so that the sediment surface is pressed against the top of the sampler;
- Overlying water is present (indicating minimal leakage);
- The overlying water is not excessively turbid (indicating minimal sample disturbance);
- The sediment surface is relatively flat (indicating minimal disturbance or winnowing); and
- The desired penetration depth is achieved (e.g., several centimeters more than the targeted sample depth).

If sediment acceptance criteria are not achieved, the sample may be rejected and the location resampled.

Sample Processing

Sediment samples that meet the acceptance criteria described above will be processed in the following manner:

- Water overlying sediment in the sampler will be decanted or siphoned off taking care to avoid sample disturbance.
- The depth of the sediment from the top of the sampler will be measured and the condition of the sediment surface such as biological activity or vegetation will be documented before sampling.
- The sediment will be visually classified using ASTM D 2488 and the description recorded on the Sediment Sampling Form.
- Sediment from the top 10 cm will be collected from the sampler using a decontaminated stainless steel spoon or other disposable sampling tool, taking care to exclude material in contact with the sampler.
- The collected sediment will be placed in a stainless steel bowl and thoroughly homogenized with the spoon or sampling tool until the sample is uniform in color and texture.
- Labeled sample jars will be temporarily stored in an insulated cooler with ice before shipment to the laboratory.

3.4.2 Clams

Clam Placement

Clam D/F bioaccumulation will be measured by both standard 28-day and long-term analysis of clam tissue. Clam baskets for the 28-day tests will be deployed in each of the test plots, and additional clam baskets for longer-term monitoring will be deployed only in the Reference, Control, and Carbon test plots. Each clam basket consists of a 15-cm diameter, mesh covered, PVC tube. One basket will be driven into the center of each plot (see Figure A-2). A minimum of five *Macoma nasuta* clams with shell lengths of approximately 4 cm will be deployed into each of the baskets. Initial placement will occur before capping material has been placed. Subsequent clam basket placements will occur after capping

materials have been placed. Additional baskets may be placed to ensure adequate tissue volume is available for analysis.

Macoma nasuta clams, which are abundant in Fidalgo Bay, will be supplied from stock used in standard laboratory bioaccumulation protocols to minimize variability in initial conditions. Clams will be placed onto the sediment surface within each tube and allowed to burrow. Clams that do not burrow within a day will be replaced.

Sample Collection

For the standard bioaccumulation test, the clams will be removed by carefully scooping out the sediment inside the tubes after 28 days. Clams used for long-term bioaccumulation tests will be removed at 60, 90, 120, and 210 days after initial placement (see Table 2 in the Work Plan). Clams will be separated from the sediment, rinsed with site water, temporarily stored in a stainless steel bucket, and then depurated by storing in aerated site seawater for 24 hours. Clams will then be placed in a clean, labeled zipper-seal plastic bag and placed on ice before shipment to the laboratory.

A minimum of five clams will be collected per composite clam tissue sample. All organisms collected for a composite sample will be included in the same polyethylene bag. The shell length and weight for each clam retained for analysis will be recorded in the biological sampling log. Clams will be shipped to the analytical laboratory where they will be shucked to collect the soft tissues.

Sample Processing

Processing of tissue at the laboratory will be conducted according to the following procedure:

- A high-quality ceramic or stainless-steel scalpel or knife will be used to schuck the clams. Any knife with visible rust will not be used.

- Whole body tissue will include visceral cavity material, meat, gut ball, as well as the siphon/mantle.

- An equipment rinsate blank will be prepared before each set of dissections. After decontamination is conducted, rinse blanks will be prepared by rinsing decontaminated equipment (e.g., cutting surface, dissection knife) with laboratory-purified water before the dissection begins. The rinsate will be collected and analyzed for D/F.

- Samples will be homogenized in a blender or tissue grinder and placed in individually labeled sample containers. Samples will then be immediately placed in a freezer.

3.4.3 Passive Sampling Devices (PSDs)

Sample Collection

Before placement of each clam cage, a PSD constructed from a strip of polyoxymethylene will be attached to the cage vertically and placed so that approximately six inches of the PSD will be beneath the sediment surface (at the same depth as the clams) and a few inches will remain above the surface (in the water column immediately above the clams). Additional detail on construction of the PSDs is found in Fagervold, *et al.* (2010) and Chai, *et al.* (2012).

When clams are collected, the PSD will be removed from the clam cage, cut into two sections: above and below the sediment surface, and rinsed in site water. The PSD sections will be labeled and sealed in a glass container for laboratory analysis.

Sample Processing

PSD processing at the laboratory will be conducted following the procedures described in Fagervold, *et al.* (2010) and Chai, *et al.* (2012). In brief, PSDs will be extracted and the extracts analyzed for D/F.

3.5 Sample Identification

Each sample will be given a unique sample identifier.

3.5.1 Sediment

Sediment samples will be identified in the following manner:

SS-Test Plot ID–Date where

- SS indicates Sediment Sample
- Test Plot ID is the number of the Test Plot (See Figure A-2)
- Date is yyyy-mm-dd = year-month-day

3.5.2 Clam Tissue Samples

Clam samples will be identified as:

CT-Test Plot ID–Date where

- CT indicates Clam Tissue
- Test Plot ID is the number of the Test Plot (See Figure A-2)
- Date is yyyy-mm-dd = year-month-day

3.5.3 Passive Sampling Devices (PSDs)

PSDs will be identified as:

PSDx-Test Plot ID–Date where

- PSD indicates Passive Sampling Device
- x will be "a" indicating the portion of the PSD above the sediment surface or "b" indicating the portion of the PSD below the sediment surface
- Test Plot ID is the number of the Test Plot (See Figure A-3)
- Date is yyyy-mm-dd = year-month-day

3.6 Sample Containers and Labels

Sample container requirements vary according to analyte and sample matrix. Pre-cleaned sample containers will be obtained from the analytical laboratory. Sample containers shall be cleaned following the requirements described in Specifications and Guidance for Contaminant-Free Sample Containers (EPA 1992, OSWER Directive 92.0-05a). Required storage temperatures and holding times are summarized in Table A-2.

3.7 Field Documentation Procedures

Field notes will be maintained during sampling and processing operations. The following will be included in the field notes:

- Names of the field sampling crew, including vessel operator and person(s) collecting and logging the samples;

- Weather conditions;

- GPS coordinates of each sampling location;

- Mudline elevation of each sampling location as measured from mean lower low water (MLLW);
- Date and time of collection of each sample; and
- Any deviation from the approved sampling plan.

3.8 Procedures for Disposal of Excess Sediments

Any remaining excess sediment left over in the power grab after sample containers are filled will be returned to the site at least 10 meters away from all test plots. If sheen or evidence of contamination is observed, the excess sediment will be drummed for disposal.

4.0 SAMPLE HANDLING PROCEDURES

4.1 Sample Storage Requirements

4.1.1 Chemical and Physical Analyses

Samples will be preserved according to the requirements of the specific analytical methods to be employed, and all samples will be extracted and analyzed within method-specified holding times. Sample storage temperatures and holding times are summarized in Table A-2.

4.1.2 Biota Samples

Unused biota samples will be frozen at –18°C and stored in the dark.

4.1.3 PSD Samples

Each PSD section will be stored in glass containers for delivery to the laboratory for analysis.

4.2 Chain of Custody Procedures

Chain of custody forms will be used to document the collection, custody, and transfer of samples from their initial collection location to the laboratory, and their ultimate use and disposal. Entries for each sample will be made on the custody form immediately after each sample is collected.

Sample custody procedures will be followed to provide a documented record that can be used to follow possession and handling of a sample from collection through analysis. A sample is considered to be in custody if it meets at least one of the following conditions:

- The sample is in someone's physical possession or view;
- The sample is secured to prevent tampering (i.e., custody seals); and/or
- The sample is locked or secured in an area restricted to authorized personnel.

A chain of custody form will be completed in the field as samples are packaged. At a minimum, the information on the custody form shall include the sample number, date and time of sample collection, sampler, analyses, and number of containers. Two copies of the custody form will be placed in the cooler prior to sealing for delivery to the laboratory with the respective samples. The other copy will be retained and placed in the project files after review by the Project Chemist. Custody seals will be placed on each cooler or package containing samples so the package cannot be opened without breaking the seals.

4.3 Delivery of Samples to Analytical Laboratories

After sample containers have been filled, they will be packed on ice in coolers. The coolers will be transferred to the laboratory for chemical analysis. Specific procedures are as follows:

- Samples will be packaged and shipped in accordance with U.S. Department of Transportation regulations as specified in 49 CFR 173.6 and 49 CFR 173.24.
- Individual sample containers will be packed to prevent breakage.
- The coolers will be clearly labeled with sufficient information (name of project, time and date container was sealed, person sealing the cooler, and the Hart Crowser office name and address) to enable positive identification.
- A sealed envelope containing custody forms will be enclosed in a plastic bag and taped to the inside lid of the cooler.
- Signed and dated custody seals will be placed on all coolers prior to shipping.

- Samples will either be shipped by overnight courier or will be hand delivered to the laboratory by Hart Crowser personnel.

- Upon transfer of sample possession to the testing laboratories, the custody form will be signed by the persons transferring custody of the coolers. Upon receipt of samples at the laboratory, the shipping container custody seal will be broken and the laboratory sample-receiving custodian will compare samples to information on the chain of custody form and record the condition of the samples received.

5.0 LABORATORY ANALYTICAL METHODS

Samples will be analyzed according to EPA methods as described in Update III to Test Methods for Evaluating Solid Waste; Physical/Chemical Methods, SW-846 (EPA 1986), Methods for Chemical Analysis of Water and Wastes (EPA 1983), and the Puget Sound Estuary Program Protocols (PSEP 1991 and updates), as referenced in Ecology's Sediment Sampling and Analysis Plan Appendix (SAPA; Ecology 2008). Sample methods, preparation, analyses, and practical quantitation limits are presented in Table A-3.

5.1 Chemical Analyses and Target Detection Limits

The testing laboratory will be specifically required by Hart Crowser to make every effort to attain the low reporting limit necessary for D/F analysis in tissue, sediment, and PSDs. All reasonable means including additional cleanup steps and method modifications will be used to bring reporting limits to these low levels. In addition, an aliquot of each sediment sample for analysis will be archived for additional analysis, if necessary.

For biota samples, lipid content will be determined so that D/F concentrations can be reported on a lipid-normalized basis.

Sediment and tissue chemical analysis will be performed using the specified methods for the following analytes:

- Sediment Total Organic Carbon (Ecology/EPA Method 9060);

- D/F (EPA Method 1613B); and

- Tissue percent lipids (Bligh-Dyer Method).

6.0 QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

This section describes QA procedures for physical, chemical, and bioassay testing.

6.2 QA/QC for Chemical Analyses

The quality of analytical data generated is controlled by the frequency and type of internal QC checks developed for analysis type. The quality of laboratory measurements will be assessed by reviewing results for analysis of method blanks, matrix spikes, duplicate samples, laboratory control samples, surrogate compound recoveries, instrument calibrations, performance evaluation samples, interference checks, etc., as specified in the analytical methods to be used. The following general procedures will be followed for all laboratory analyses:

- Laboratory blank measurements at a minimum frequency of 5 percent or one per batch of 20 samples or fewer for each matrix;
- Matrix spike (MS) and matrix spike duplicate (MSD) analysis, for organic analyses, to assess accuracy and precision at a minimum frequency of 5 percent or one per batch of 20 samples or fewer for each matrix;
- Analysis of surrogate compounds, for all organic analyses, to assess accuracy; and
- Laboratory control sample analysis to assess accuracy in the absence of any matrix effect at a minimum frequency of 5 percent or one per batch of 20 samples or fewer for each matrix.

Analytical method-specific requirements and criteria are summarized in Tables A-3 through A-6.

6.4 Data Quality Assurance Review Procedures

A project chemist at Hart Crowser will perform an independent data quality review of the chemical analytical results provided by the laboratories. This report will assess the adequacy of the reported detection limits in achieving the project screening levels for sediment; the precision, accuracy, representativeness, and completeness of the data; and the usability of the analytical data for project objectives. Exceedances of analytical control limits will be summarized and evaluated.

A data evaluation review will be performed on all results using QC summary sheet results provided by the laboratory for each data package. The data evaluation review is based on the Quality Control Requirements previously described and follows the format of the EPA National Functional Guidelines for Organic (EPA 2008) and Inorganic (EPA 2010) Data Review modified to include specific criteria of individual analytical methods. Raw data (instrument tuning, calibrations, chromatograms, spectra, instrument printouts, bench sheets and laboratory worksheets) will be available for review if any problems or discrepancies are discovered during the routine evaluation or if Ecology desires a more comprehensive data validation be performed. The following is an outline of the data evaluation review format:

- Verify sample numbers and analyses match the chain of custody request;
- Verify sample preservation and holding times;
- Verify instrument tuning, calibration, and performance criteria were achieved;
- Verify that laboratory blanks were performed at the proper frequency and that no analytes were present in the blanks;
- Verify field and laboratory duplicates, matrix spikes, and laboratory control samples were run at the proper frequency and that control limits were met;
- Verify surrogate compound analyses have been performed and that results met the QC criteria; and
- Verify required detection limits have been achieved.

Data qualifier flags, beyond any applied by the laboratory, will be added to sample results that fall outside the QC acceptance criteria. An explanation of data qualifiers to be applied during the review is provided below:

- **U** The compound was analyzed for but was not detected. The associated numerical value is the sample reporting limit.
- **J** The associated numerical value is an estimated quantity because QC criteria were slightly exceeded or because reported concentrations were less than the practical quantitation limit (lowest calibration standard).

- **UJ** The compound was analyzed for, but not detected. The associated numerical value is an estimated reporting limit because QC criteria were not met.

- **R** Data are not usable because of significant exceedance of QC criteria. The analyte may or may not be present; resampling and/or re-analysis are necessary for verification.

7.0 DATA ANALYSIS, RECORDKEEPING, AND REPORTING REQUIREMENTS

7.1 Analysis of Chemistry Data

Sediment, clam tissue, and PSD chemistry results will be evaluated across the test plots and for the series of sampling events. These data will be compared to clam tissue and PSD results. D/F and TOC data in surface sediments will be evaluated to determine differences among carbon-amended sand capping material, sand capping material, and control and reference plots.

7.2 Recordkeeping Procedures

Project records will be kept and maintained in accordance with SMS requirements for a minimum of 10 years following completion of issuance, modification, or renewal of applicable project permits, administrative order, certification, or project cleanup site delisting, whichever is greater. Records will include:

- This SAP and related quality assurance documentation;

- Field records identifying sampling dates, types, composites, locations, and depths;

- Sampling personnel, equipment, methods, and procedures;

- Sediment analysis records (laboratory analytical documentation);

- Any departures from SAP and quality assurance plans.

7.3 Reporting Procedures

7.3.1 Chemical Analysis Laboratory Reports

The laboratory data reports will consist of complete data packages that will contain complete documentation and all raw data to allow independent data reduction and verification of analytical results from laboratory bench sheets, instrument raw data outputs, and chromatograms. Each laboratory data report will include the following:

- Case narrative identifying the laboratory analytical batch number, matrix and number of samples included, analyses performed and analytical methods used, and description of any problems or exceedance of QC criteria and corrective action taken. The laboratory manager or their designee must sign the narrative.

- Copy of chain of custody forms for all samples included in the analytical batch.

- Tabulated sample analytical results with units, data qualifiers, percent solids, sample weight or volume, dilution factor, laboratory batch and sample number, Hart Crowser sample number, and dates sampled, received, extracted, and analyzed all clearly specified. Surrogate percent recoveries will be included for organic analyses.

- Surrogate spike recoveries will be reported in all organic reports where appropriate. The reports shall also specify the control limits for surrogate spike results, as well as the spiking concentration. Any out of control recoveries will be reported immediately to the Project QA Manager. Any out of control recoveries (as defined in the method) will result in the sample being rerun (both sets of data are to be reported).

- All calibration, quality control, and sample raw data including chromatograms, quantitation reports, and other instrument output data.

- Blank summary results indicating samples associated with each blank.

- Matrix spike/matrix spike duplicates result summaries with calculated percent recovery and relative percent differences.

- Laboratory control sample results, when applicable, with calculated percent recovery.

- Electronically formatted data deliverable (diskette) results.

7.3.2 Reports to Ecology

Hart Crowser will prepare a report summarizing sediment sampling procedures and laboratory testing results. The report will include a map with confirmed sediment sampling locations, tabulated analytical testing data with comparisons to SMS criteria, and complete laboratory analytical documentation.

At a minimum, the report will include the following sections

- Introduction/Purpose;

- Vicinity map;

- Summary of field sampling and laboratory procedures and any deviations from the SAP;

- Figure and table documenting sample locations and coordinates;

- Tabulated results of sediment, clam tissue, and PSD chemistry data;

- Data validation review and laboratory report sample summary and quality control results;

- Discussion and interpretation of results with respect to the Pilot Test objectives; and

- Conclusions.

Sampling analytical data will also be submitted to Ecology electronically in EIM data entry templates.

8.0 PROJECT PERSONNEL AND RESPONSIBILITIES

Key staff members for the work specified in Appendix A are listed below with their project functions:

- Mike Ehlebracht, LHG, Program Management;

- Brad Helland, PE, Project Manager;

- Roger McGinnis, PhD, Environmental Chemistry and Quality Assurance and Data Validation;

Based on availability, subcontractors will include RSS (Vessel Operator) for collecting site and reference location sediment samples and for placement and retrieval of clam cages. Chemical analysis will be performed by Analytical Resources, Inc.

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TABLES

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Table A-1 – Test Plot Sample Location Coordinates

	WGS84 Decimal Degrees		Washington State Plane North, NAD83, US Feet	
Test Plot	**Latitude**	**Longitude**	**Northings**	**Eastings**
1	48.49309	-122.59899	1212314.1	549557.7
2	48.49303	-122.59900	1212310.8	549536.4
3	48.49298	-122.59901	1212306.9	549515.3
4	48.49292	-122.59903	1212301.4	549495.1
5	48.49286	-122.59906	1212295.6	549474.8
6	48.49281	-122.59909	1212287.8	549455.7

Note: Coordinates reflect the center of each test plot, where clam cages, PSDs, and sediment samples will be collected.

Table A-2 – Sample Containers, Preservation, and Holding Times

Sample Type	Sample Preservation Technique	Maximum Holding Time
Grain Size[1]	Cool, <6°C	6 months
Total solids[2]	Cool, <6°C	14 days
Total organic carbon[2]	Cool, <6°C	14 days
D/F[2] after extraction	Freeze, -18°C Cool, <6°C	1 year 40 days

Notes:

[1] Grain size will be collected in a 16-oz wide mouth plastic jar or large plastic bag.
[2] Soil sample for chemical analysis will be collected in two 16 oz (or larger) wide mouth glass jars, to provide sufficient volume for sieving at the laboratory.

D/F - polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

Table A-3 – Sample Preparation and Analysis Methods and Quantitation Limits

Parameter	Preparation Method	Analysis Method	Sediment/PSD		Clam Tissue	
			Level of Detection or Estimated Detectiion Limit	Level of Quantitation or Reporting Limit	Level of Detection or Estimated Detectiion Limit	Level of Quantitation or Reporting Limit
CONVENTIONALS:						
Total Solids in %	---	PSEP	0.10%	0.10%	n/a	n/a
Total Organic Carbon in %	---	EPA 9060/Ecology (a)	0.1%	0.1%	n/a	n/a
Percent Lipids		Bligh-Dyer	n/a	n/a	0.01%	0.01%
Grain Size	---	PSEP (Mod ASTM D422 with Hydrometer)	1%	1%	n/a	n/a
CHLORINATED DIOXIN/FURAN CONGENERS (Vista limits)			**ng/kg (as received)**	**ng/kg (as received)**	**ng/kg (wet weight)**	**ng/kg (wet weight)**
1,2,3,4,6,7,8-HpCDD	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,4,6,7,8-HpCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,4,7,8,9-HpCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,4,7,8-HxCDD	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,4,7,8-HxCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,6,7,8-HxCDD	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,6,7,8-HxCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,7,8,9-HxCDD	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,7,8,9-HxCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,7,8-PeCDD	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
1,2,3,7,8-PeCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
2,3,4,6,7,8-HxCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
2,3,4,7,8-PeCDF	EPA 3540C	EPA 1613B	0.1	2.5	0.1	2.5
2,3,7,8-TCDD	EPA 3540C	EPA 1613B	0.1	0.5	0.1	0.5
2,3,7,8-TCDF	EPA 3540C	EPA 1613B	0.1	0.5	0.1	0.5
OCDD	EPA 3540C	EPA 1613B	0.1	5	0.1	5
OCDF	EPA 3540C	EPA 1613B	0.1	5	0.1	5

Notes:
All values are estimates and may change based on sample-specific circumstances.
a. Recommended Methods for Measuring TOC in Sediments, Kathryn Bragdon-Cook, Clarification Paper, Puget Sounc
Dredged Disposal Analysis Annual Review, May 1993.

Table A-4 – Quality Control Procedures for Conventional Parameter Analyses

	Suggested Control Limits						
Analyte	**Initial Calibration**	**Continuing Calibration**	**Calibration Blanks**	**Laboratory Control Samples**	**Matrix Spikes**	**Laboratory Triplicates**	**Method Blank**
Grain size	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	20 % RSD	Not applicable
Total organic carbon	Correlation coefficient ≥0.995	90 to 110 percent recovery	Analyte concentration ≤ PQL	80 to 120 percent recovery	75 to 125 percent recovery	20 % RSD	Analyte concentration ≤ PQL
Percent lipids	Correlation coefficient ≥0.990	85–115 percent recovery	Not applicable	65–135 percent recovery	65–135 percent recovery	20 % RSD	Analyte concentration ≤ PQL
Total solids	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	20 % RSD	Analyte concentration ≤ PQL

Table A-5 – Quality Control Procedures for Dioxins/Furans

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action*
Ongoing Precision And	1 per analytical	Recovery within	1. Check calculations
Recovery	batch	acceptance criteria	2. Reanalyze batch
	(≤ 20 samples)	in Table 7.	
Stable-isotope-labeled	Spiked into each	Recovery within	1. Check calculations
compounds	sample for every	limits in Table 7.	2. Qualify all associated results as estimated
	target analyte		
		Ion abundance	1. Re-analyze specific samples.
		ratios must be	2. Reject all affected results outside the criteria.
		within criteria in	3. Alternatively, use of secondary ions that meet appropriate theoretical criteria is allowed if inteferences are suspected. This alternative must be approved by the DMMP agencies.
		method	
		1613B	
Laboratory duplicate	5% or 1 per batch	Relative percent	1. Evaluation of the homogenization procedure and
	(≤ 20 samples)	Difference ≤ 30%	evaluation method
			2. Reanalyze batch
Method blank	1 per analytical	Detection ≤	1. If the method blank results are greater than the
	batch	minimum level in	reporting limit, halt analysis and find source of
	(≤ 20 samples)	Table 2 of Method	contamination; reanalyze batch.
		1613B	2. Report project samples as non-detected for
			results ≤ to the reported method blank values.
GC/MS Tune	At the beginning of each	>10,000 resolving power @	
	12 hour shift.	m/z304.9825	
	Must start and end each	Exact mass of 380.9760	
	analytical sequence.	within 5 ppm of theoritical	
		value.	
Initial Calibration	Initially and when	Five point curve for all	
	continuing calibration	analytes. RSD must meet	
	fails	Table 9 requirements for all	
		target compounds and	
		labeled compounds.	1. Re-analyze affected samples.
		Signal to noise ratio (S/N) > 10.	2. Reject all data not meeting method 1613B requirements.
		Ion abundance (IA) ratios within	
		method specified limits.	
Window Defining/Column	Before every initial and	Valley < 25% for all peaks near	
Performance Mix	continuing calibration	2378-TCDD/F peaks.	
Continuing Calibration	Must start and end each	%D must meet limits	
	analytical sequence.	for target compounds & labeled	
		compounds. S/N > 10. IA	
		ratios within method specified	
		limits.	
Confirmation of 2,3,7,8- TCDF	For all primary-	Confirmation	Failure to achieve resolution on the primary column or to verify presence of 2,3,7,8-TCDF by second column confirmation requires qualification of associated 2,3,7,8 TCDF results as non-detected at the associated value.
	column detections of	presence of 2,3,7,8-	
	2,3,7,8-TCDF	TCDF in accordance	
		with method 1613B	
		requirements	
Sample data not achieving	Not applicable	Not applicable	Rather than simply dilute an extract to reduce interferences, the lab should perform additional cleanup techniques indentified in the method to insure minimal matrix effects and background interference. Thereafter, dilution may occur. If re-analysis is required, the laboratory shall report both initial and re-analysis results.
target reporting limits or method			
performance in presence of			
possibly interferring compounds			
Standard Reference Material	One per analytical batch	Result must be within 20% of the 95% confidence interval	1. Extraction and analysis should be evaluated by the lab and re-analysis performed of the entire sample batch once performance criteria can be met.
			2. If analysis accompanies several batches with acceptable RM results, then the laboratory can narrate possible reason for RM outliers.

*If re-analysis is required, the laboratory shall report initial and re-analyis results.

Table A-6 – QC Acceptance Criteria for Dioxins/Furans

	Test Conc., ng/mL[1]	IPR[2]		OPR[3] (%)	I-CAL[4]	CAL/VER[5] (%) (Coeff. of Variation)	Labeled Compound %Rec. in Sample		NIST 1944 Acceptance criteria (ug/kg)
		RSD (%)	Recovery		%		Warning Limit	Control Limit	
Native Compound									
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-129	-	-	0.133 ± 0.009
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-	0.039 ± 0.015
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-130	-	-	0.019 ± 0.002
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-	0.045 ± 0.007
2,3,4,7,8-PeCDF	50	17	72-150	70-130	20	82-122	-	-	0.045 ± 0.004
1,2,3,4,7,8-HxCDD	50	19	78-152	70-130	20	78-128	-	-	0.026 ± 0.003
1,2,3,6,7,8-HxCDD	50	15	84-124	76-130	20	78-128	-	-	0.056 ± 0.006
1,2,3,7,8,9-HXCDD	50	22	74-142	70-130	35	82-122	-	-	0.053 ± 0.007
1,2,3,4,7,8-HxCDF	50	17	82-108	72-130	20	90-112	-	-	0.22 ± 0.03
1,2,3,6,7,8-HxCDF	50	13	92-120	84-130	20	88-114	-	-	0.09 ± 0.01
1,2,3,7,8,9-HxCDF	50	13	84-122	78-130	20	90-112	-	-	none[6]
2,3,4,6,7,8-HxCDF	50	15	74-158	70-130	20	88-114	-	-	0.019 ± 0.018
1,2,3,4,6,7,8-HpCDD	50	15	76-130	70-130	20	86-116	-	-	0.80 ± 0.07
1,2,3,4,6,7,8-HpCDF	50	13	90-112	82-122	20	90-110	-	-	1.0 ± 0.1
1,2,3,4,7,8,9-HpCDF	50	16	86-126	78-130	20	86-116	-	-	0.040 ± 0.006
OCDD	100	19	86-126	78-130	20	79-126	-	-	5.8 ± 0.7
OCDF	100	27	74-146	70-130	35	70-130	-	-	1.0 ± 0.1
Labelled Compounds									
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130	
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130	
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130	
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-130	35	72-130	40-120	23-130	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130	
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130	
$^{13}C_{12}$-OCDD	200	48	20-138	25-130	35	70-130	25-120	17-130	
Cleanup Standard									
$^{37}Cl_4$-2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130	

[1] QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume

[2] IPR: Initial Precision and Recovery demonstration

[3] OPR: Ongoing Precision and Recovery test run with every batch of samples.

[4] Initial Calibration

[5] CAL/VER: Calibration Verification test run at least every 12 hours

[6] NIST has decertified acceptance criteria for 1,2,3,7,8,9-HxCDF

FIGURES

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ST-27
ST-19
HC-SS-14
ST-11
ST-3
HC-SS-9
HC-SS-10
HC-SS-13
ST-26
HC-SS-8
HC-SS-11
SS-20
SS-16
ST-22
ST-18
SS-17
ST-2
ST-14
SS-19
HC-SS-12
ST-10
SC-50A
CT-03
SS-22
A3-32
SS-21
HC-SS-7
ST-6
SC-50
SC-51
SC-49
SS-18
SC-42
SC-46
HC-SS-2
HC-SC-15
SC-45
CT-02
SC-59
SC-58
SS-23
SC-39
HC-SS-5
ST-21
SS-15
HC-SS-1
SC-43
SC-47
SC-44
SC-41
SC-40
HC-SS-3
HC-SS-4
SC-48
CT-01A
ST-1
CT-01B

Test Plot
Sample Point
Approximate extent of Eelgrass Beds
Interim Remedial Action Boundary

Dioxin/Furan Concentration in ppt

- 5 to10 ppt
- 10 to 25 ppt
- 25 to 50 ppt
- > 50 ppt

Note: Area-weighted mean Dioxin/furan concentration: 24.5 ppt. Calculation completed using the inverse distance weighted (IDW) techinique.

N

0 75 150 300 Feet

Custom Plywood Site
Anacortes, Washington

Dioxin/Furan Concentration Interpolation

17800-05 7/12

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Figure
A-1

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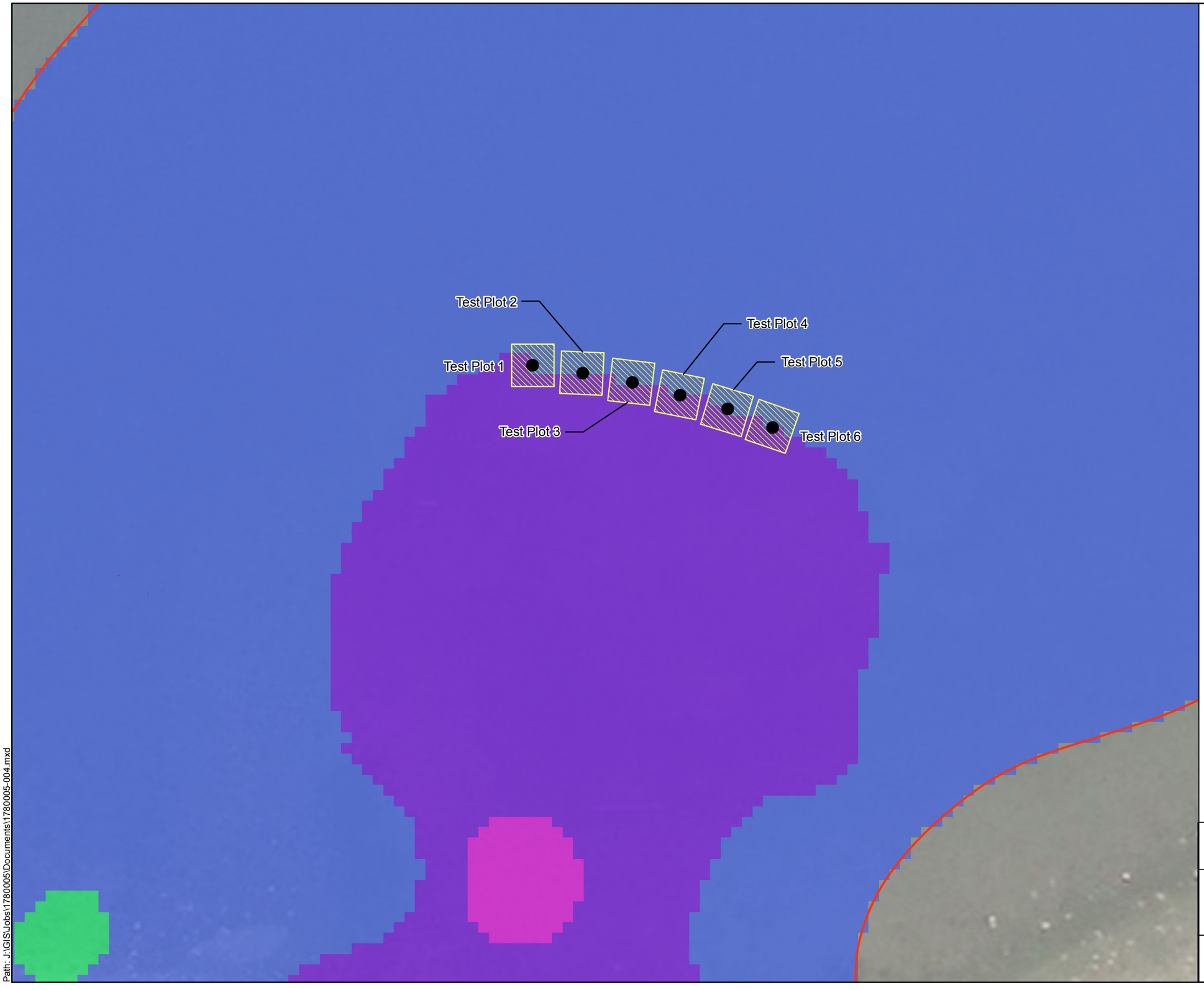

Test Plot

Sample Location

Interim Remedial Action Boundary

Dioxin/Furan Concentration in ppt

5 to10 ppt

10 to 25 ppt

25 to 50 ppt

> 50 ppt

Note: Area-weighted mean Dioxin/furan concentration: 24.5 ppt. Calculation completed using the inverse distance weighted (IDW) techinique.

N

0 20 40 80 Feet

Custom Plywood Site
Anacortes, Washington

Test Plot Area Map

17800-05 7/12

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Figure
A-2

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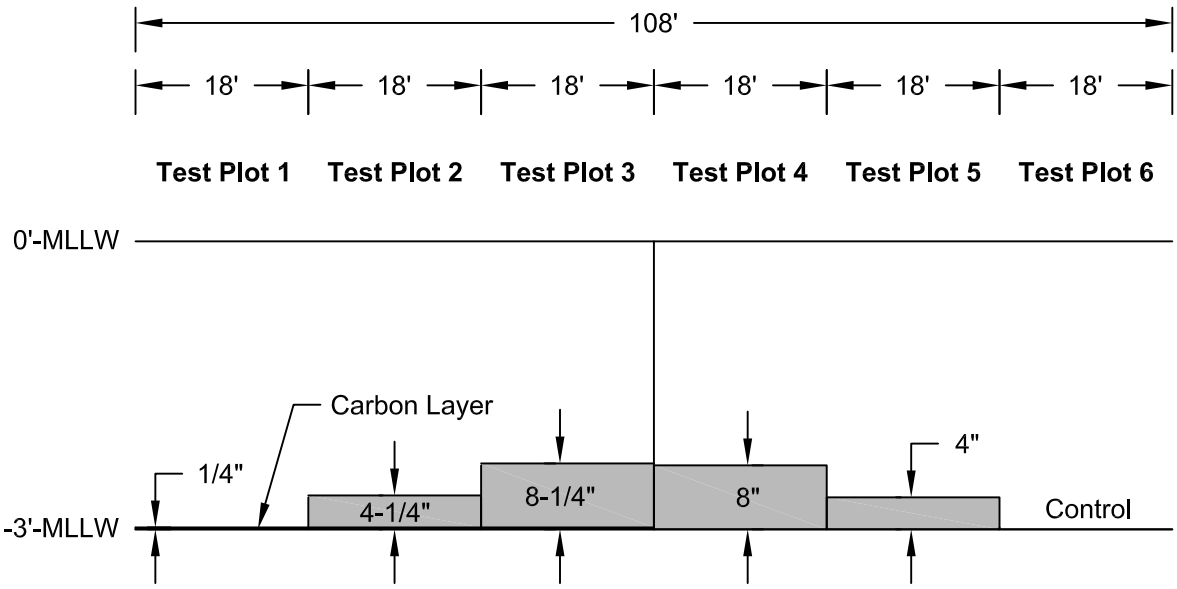

Horizontal Scale in Feet
0 20 40
0 2 4
Vertical Scale in Feet
Vertical Exaggeration x 10

Custom Plywood Site
Anacortes, Washington

Test Plot Area Cross Section

17800-05 7/12

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Figure
A-3

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Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness

Yeo-Myoung Cho [a], Dennis W. Smithenry [b], Upal Ghosh [c], Alan J. Kennedy [d], Rod N. Millward [e], Todd S. Bridges [d], Richard G. Luthy [a,*]

[a] *Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA*
[b] *Department of Education, Santa Clara University, Santa Clara, CA 95053, USA*
[c] *Department of Civil and Environmental Engineering, University of Maryland Baltimore County, Baltimore, MD 21250, USA*
[d] *Environmental Laboratory, US Army Engineer Research and Development Center, Vicksburg, MS 39180, USA*
[e] *Formerly, Weston Solutions, 98 Main Street, Suite 428, Tiburon, CA 94920, USA*

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Abstract

Previous laboratory studies have shown reductions in PCB bioavailability for sediments amended with activated carbon (AC). Here we report results on a preliminary pilot-scale study to assess challenges in scaling-up for field deployment and monitoring. The goals of the preliminary pilot-scale study at Hunters Point Shipyard (San Francisco, USA) were to (1) test the capabilities of a large-scale mixing device for incorporating AC into sediment, (2) develop and evaluate our field assessment techniques, and (3) compare reductions in PCB bioavailability found in the laboratory with well-mixed systems to those observed in the field with one-time-mixed systems. In this study we successfully used a large-scale device to mix 500 kg of AC into a 34.4 m^2 plot to a depth of 1 ft, a depth that includes the majority of the biologically active zone. Our results indicate that after 7 months of AC-sediment contact in the field, the 28-day PCB bioaccumulation for the bent-nosed clam, *Macoma nasuta*, field-deployed to this AC-amended sediment was approximately half of the bioaccumulation resulting from exposure to untreated sediment. Similar PCB bioaccumulation reductions were found in laboratory bioassays conducted on both the bivalve, *M. nasuta* and the estuarine amphipod, *Leptocheirus plumulosus*, using sediment collected from the treated and untreated field plots one year after the AC amendment occurred. To further understand the long-term effectiveness of AC as an *in situ* treatment strategy for PCB-contaminated sediments under field conditions, a 3-year comprehensive study is currently underway at Hunters Point that will compare the effectiveness of two large-scale mixing devices and include both unmixed and mixed-only control plots.

Keywords: Polychlorinated biphenyls; *In situ* treatment; Bioavailability; Activated carbon; Sediments; San Francisco Bay, USA; Field validation

* Corresponding author. Tel.: +1 650 7233921; fax: +1 650 7258662.
E-mail address: luthy@stanford.edu (R.G. Luthy).

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1. Introduction

Hydrophobic contaminants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dichloro-diphenyl-trichloroethane (DDT), associate with fine-grained, organic-rich, sediment material. This association results in a contaminant reservoir in shallow estuarine and coastal regions from which benthic organisms may accumulate toxic compounds that are then passed up the food chain to fish. Contaminated sediments pose challenging cleanup and management problems, as conventional environmental dredging techniques are expensive, invasive, and sometimes ineffective. *In situ* treatment strategies may be more effective at reducing risk while decreasing expenditures on sediment management.

In prior research, we observed that PCBs and PAHs in sediment may associated with coal-derived and char particles, in which the compounds are strongly bound and therefore less bioavailable (Bucheli and Gustafsson, 2001; Ghosh et al., 2003; Talley et al., 2002). Building on this observation, we have tested in the laboratory a new concept for *in situ* sediment management in which activated carbon (AC) is mixed into contaminated sediments to repartition hydrophobic organic compounds and reduce their availability to water and biota. The physicochemical (Zimmerman et al., 2004; Zimmerman et al., 2005) and biological (McLeod et al., 2004; McLeod et al., 2007; Millward et al., 2005) results of these laboratory tests have been encouraging. For example, when PCB-contaminated sediment collected from South Basin at Hunters Point Naval Shipyard, San Francisco Bay, CA, USA, was contacted with 3.4% (dry weight) AC on a roller for one month, we observed 87% reductions (Zimmerman et al., 2004) in aqueous equilibrium PCB concentrations and up to 84% reductions (McLeod et al., 2007) in the bioaccumulation of PCBs by the clam, *Macoma balthica*. Six months contact with AC reduced aqueous equilibrium concentrations by over 90% (Zimmerman et al., 2004). These promising laboratory results provide us with a strong basis for expanding the scope of our studies to test the AC treatment technology under field conditions.

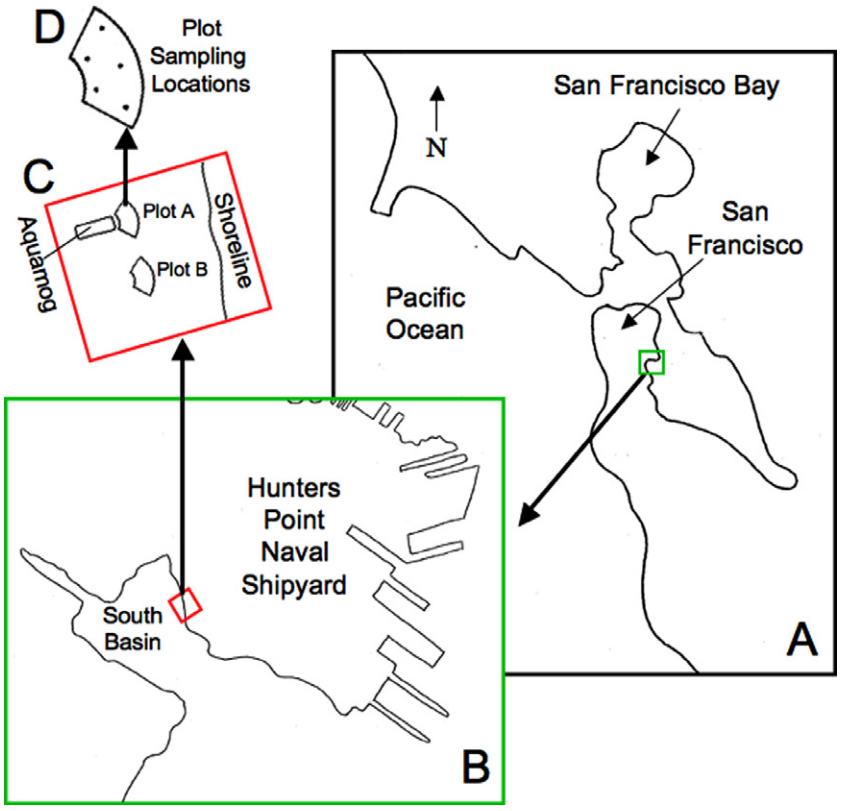

Fig. 1. Schematic of (A) San Francisco Bay; (B) Hunters Point Naval Shipyard and South Basin; (C) Plot A, Plot B, and Aquamog; and (D) five sampling locations in each plot.

With assistance from the US Navy, we recently conducted a preliminary treatability study (Smithenry et al., 2004) at the Hunters Point tidal mudflat in South Basin (Fig. 1) to assess how the AC treatment technology may be applied in the field. This test site was selected for several reasons. First, PCBs are identified as the major risk driver for South Basin and most of the sediment in this area has PCB concentrations between 1 and 10 mg/kg (Battelle, 2003). Second, Hunters Point sediment sampling and modeling studies (Battelle et al., 2004) indicate that the South Basin area is a net depositional zone and is comprised of cohesive sediments. Third, Sedflume experiments and hydrodynamic modeling indicated that when AC is mixed into the sediment the critical shear stress for erosion is not diminished and that AC will remain in place due to the cohesive nature of the sediment and the slightly depositional nature of the site (Zimmerman, 2004). Fourth, our initial laboratory feasibility studies were conducted with sediments from the site and provide suitable data for comparison of field results. Last, the site managers at Hunters Point have indicated that they are willing to consider the use of this technology in their final remedial decisions.

In our preliminary field study, the goals were to (1) identify, deploy, and test the capabilities of a large-scale mixing device for incorporating AC into the upper sediment layer, (2) develop and evaluate our field assessment techniques, and (3) compare the reductions in PCB bioaccumulation found in the field to those observed in the laboratory. The Aquamog (Fig. 2), a shallow-draft barge with a rotovator attachment owned by Aquatic Environments, Inc. (Alamo, CA, USA), was identified as a device capable of working on the tidal mudflat and suitable for mixing AC into the sediment. A field test deployment of this device was completed at the end of August 2004. In this paper, we present the results of our field test design and place them into the context of the results gained in our laboratory. In addition, we emphasize the experience gained in scaling-up our AC treatment technology from the laboratory to the field and discuss how this knowledge is useful in carrying out a more comprehensive field evaluation.

2. Materials and methods

2.1. Field methods

2.1.1. Site description and plot locations

As represented in Fig. 1, the two sediment plots (Plots A and B) were separated by 4 m and were located approximately 30.5 m from the shoreline within the tidal mudflat region of Hunters Point South Basin. This location was selected because it was accessible from the shore for sediment sampling and away from any possible impacts of potential ongoing PCB releases from the landfill on the north side of the cove (Battelle, 2003). The locations of Plots A and B, identified by taking GPS (NAD83) coordinates at the center of each plot, are N 37° 43.328/W 122° 22.580 and N 37° 43.321/W 122° 22.579, respectively. Sampling locations in each plot are identified, along with the positioning of the Aquamog, in Fig. 1. The plots were made to be wedge-shaped to fit the radial operation of the rotovator attachment on the Aquamog. Plot A was selected for AC amendment, while Plot B served as an unmixed control.

2.1.2. Experimental design

The overall experimental design for the field test involved two wedge-shaped sediment plots at Hunters Point, each having a surface area of 34.4 m^2 and an approximate total PCB concentration of 2 mg/kg, which is an average concentration down to 1 ft depth. After the Aquamog was mobilized to the plots in late August 2004, it was used to amend Plot A with a 3.4 dry wt.% AC dose down to 1 ft, corresponding to the biologically active zone. Plot B remained untreated, serving as a spatial control. The activated carbon, TOG®-NDS 50×200, was purchased from Calgon Carbon (Catlettsburg, KY, USA), having a particle size range of 75 μm to 300 μm. One month before AC treatment occurred with the Aquamog, both plots were assessed at five sampling locations for (1) amount of total organic carbon (TOC), (2) total PCB concentrations in the 0–1 ft sediment horizon, (3) 28-day PCB bioaccumulation in *Macoma nasuta*, and (4) 28-day PCB uptake into semipermeable membrane devices (SPMDs). These assessments are described in further detail below. Five sampling locations were evenly distributed over the plot, each location representing one fifth of the plot in order to provide average values for the plot. One month after AC treatment occurred, the assessments were completed at the same sampling locations. Seven months after AC treatment, sediment cores were taken for

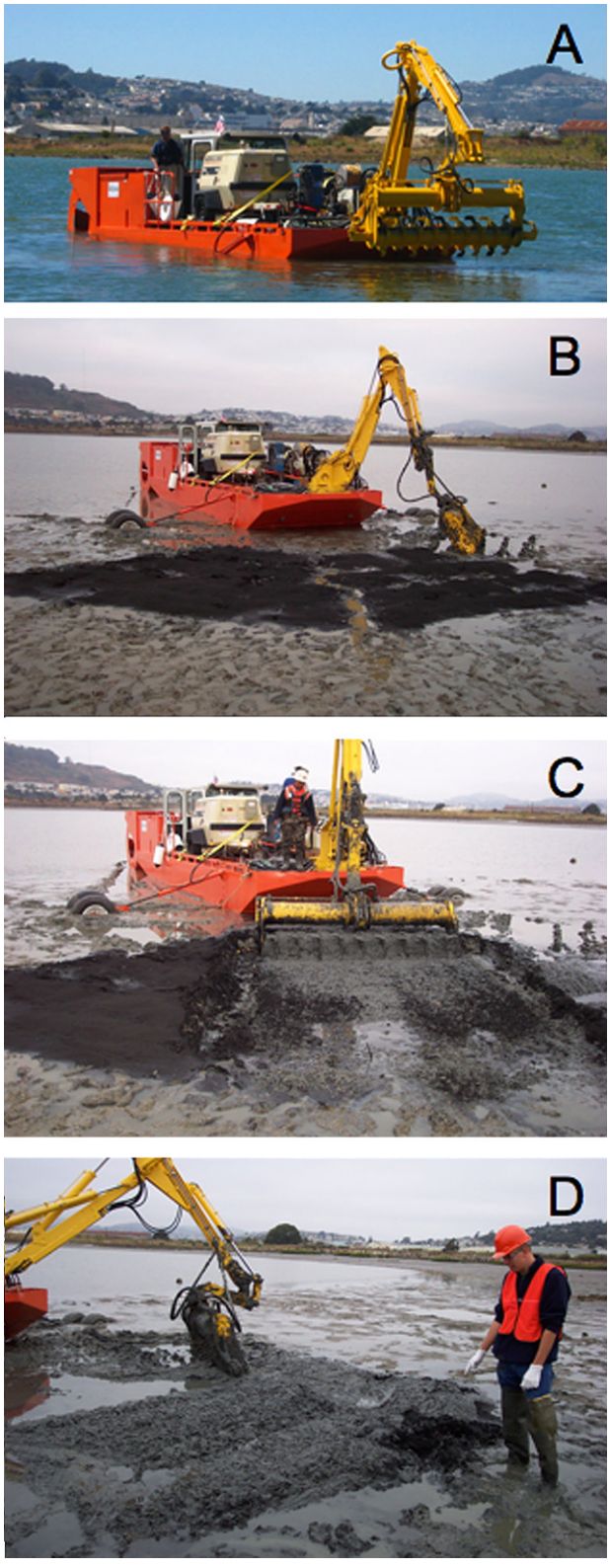

Fig. 2. (A) Mobilizing Aquamog to Plot A at high tide; (B) before, (C) during, and (D) after mixing activated carbon into sediment.

TOC measurement at the same five locations for Plot A while 28-day SPMD PCB uptake and 28-day clam PCB bioaccumulation were assessed at three new locations for both plots. The 7-month post treatment assessment was not originally planned for this study, so fewer sampling locations were reselected for the clam bioassay and the SPMD assessments to save time and costs. In addition to these four assessments, the water column above Plot A was sampled one day before, immediately after, and one month after AC treatment occurred in order to assess any PCB resuspension that may arise due to the disruption of sediment consolidation.

2.1.3. Development of field sampling devices

Besides identifying a mixing device that could incorporate activated carbon into sediment at the field scale, sampling devices used in the laboratory had to be redesigned for use in the field. A depiction of the scale-up that occurred for four field sampling devices is shown in Fig. 3. First, instead of mixing AC into sediment in the laboratory by rolling glass bottles (Fig. 3A) for a month or more, AC was distributed in the field onto the sediment surface and then tilled into the sediment for only one half hour using the rotovator on the Aquamog (Fig. 3B). As we needed to measure how well the AC was distributed into the sediment, we took sediment cores (Fig. 3C) and later assessed the vertical distribution of total organic carbon in the cores. Second, in addition to placing clams into sediment submerged in seawater contained in aerated laboratory aquaria (Fig. 3D), in the field we designed 46-cm-long PVC clam tubes with a 15-cm diameter (Fig. 3E) that could be pushed into the sediment (Fig. 3F and G). The openings on the sides of the clam tubes allowed for pore water and overlying seawater exchange, while the plastic-coated wire mesh attached to the tube retained the clams inside the tube (clams burrowed to a maximum of 6 in.) and extending the wire mesh beyond the top of the tube protected the clams from predators. Third, instead of placing SPMDs into vials containing sediment (Fig. 3H) and then rolling them in the lab, SPMDs were suspended vertically inside the clam tube (Fig. 3I) to afford sediment contact. Lastly, the effect of AC amendment on sediment stability was assessed in the laboratory

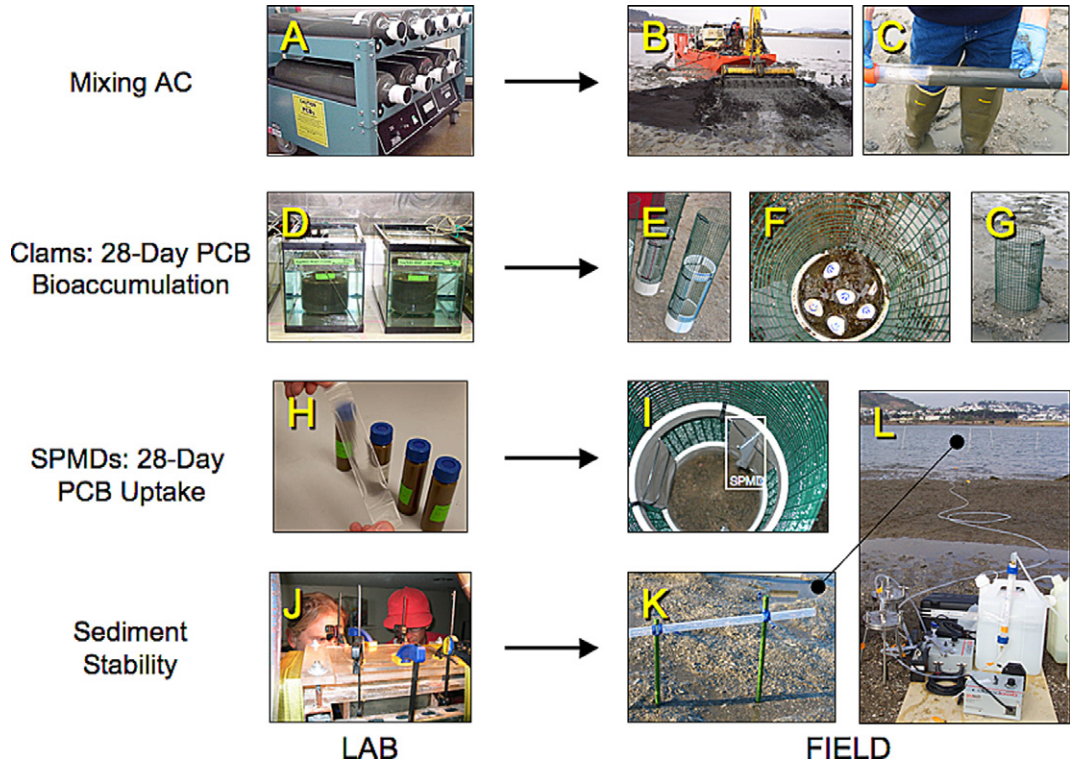

Fig. 3. Comparisons of laboratory and field techniques for assessing (A)–(C) AC mixing, (D)–(G) PCB bioaccumulation in clams, (H)–(I) PCB uptake in SPMDs, and (J)–(L) stability of AC-treated sediment.

through Sedflume studies (Fig. 3J); in the field the water column above the sediment plot was sampled through a tube (Fig. 3K) and pumped through a filter and resin column (Fig. 3L) in order to gauge the amount of suspended solids and PCBs released after AC treatment.

2.1.4. Aquamog description

The Aquamog is a barge-like machine with a rotovator attachment typically used to disrupt weed growth in marshy areas. This equipment was identified as being capable of mixing AC into the sediment. A significant feature of the Aquamog lies in its ability to float at high tide (Fig. 2A) with minimal draft and settle onto the sediment surface at low tide (Fig. 2B). This obviates the possibility of getting stuck in the cohesive sediment. The Aquamog can travel on open water at a few kilometers per hour using its paddling system located in the rear of the barge. Its rotovator attachment is connected to the barge with an arm that has a radial reach of 0.6–5 m from the bow and a side-to-side span of nearly 180°. The attachment is 2 m wide and is connected to the arm at its midpoint. The barge is 3 m wide and 9 m long.

2.1.5. Deployment of Aquamog

The Aquamog was mobilized at high tide and anchored into position in the front of Plot A at Hunters Point Parcel F. At the beginning of low tide on August 31, 2004, the Aquamog settled onto the sediment surface. At this point, 500 kg of AC were manually poured from 23-kg drums to form an even layer (Fig. 2B). This quantity of AC and corresponding surface area were calculated to provide a 3.4 wt.% dry weight AC dose if the Aquamog mixed the AC down to 1 ft. The Aquamog's rotovator was turned at approximately 60 rpm and pulled back and forth across Plot A for approximately 30 min until the AC appeared well-mixed by visual observation. A picture taken midway through this mixing process is shown in Fig. 2C. A picture of the final mixed Plot A is shown in Fig. 2D.

2.1.6. Sediment core sampling

Five, 5-cm diameter sediment core samples were collected from both Plots A and B in order to evaluate average total PCB concentrations in 0–1 ft subsurface sediment and total organic carbon levels before and after AC treatment of Plot A. A sediment PCB concentration for each plot was obtained by averaging of sediment concentrations of five cores ($n = 5$). In previous tests, we found total organic carbon (TOC), as measured by elemental analysis, to be an effective indicator for the amount of AC mixed in the sediment (Smithenry et al., 2004). The core samples were taken to a minimum depth of 1 ft in 50-cm-long cellulose acetate butyrate core liners purchased from Wildlife Supply Company (Buffalo, NY, USA). Sediment cores were collected, capped, and stored in a 4 °C cold room until they were processed.

2.1.7. Clam deployment

In an attempt to measure clam PCB bioaccumulation in the field, five *M. nasuta* with shell lengths between 3.0 and 4.3 cm were deployed into each of the mesh-covered 15-cm diameter PVC tubes driven into each plot before and after the AC treatment. These clams, which are native to the San Francisco Bay, were field-collected at Dillon Beach, CA, USA by Aquatic Research Organisms (Hampton, NH, USA). Background PCB levels in these clam tissues were below detection limits (0.01 ppb). Clams were placed onto the sediment surface within each tube's diameter and allowed to burrow. Clams that did not burrow within one day were replaced. After a 28-day exposure, the clams were removed by carefully scooping out the sediment inside the tubes. Clams were separated from the sediment, rinsed with site water, placed in polyethylene containers and transported to the laboratory in a cooler for further processing.

2.1.8. SPMD sampling

Before and after AC treatment, an SPMD was deployed inside each of the clam tubes in each plot. The SPMDs are biomimetic devices that passively measure PCB uptake. The SPMDs were custom-made by Environmental Sampling Technologies (St. Joseph, MO, USA) to be 10 cm long and contain 0.1 g triolein, a surrogate for fish lipid. The SPMDs were vertically suspended inside each clam tube onto two hooks mounted on the inner wall with the top hook three centimeters below the sediment surface. This design allowed the SPMD to be suspended and stretched vertically, keeping it away from the clam tube wall. After a 28-day exposure, the

SPMDs were removed, rinsed with deionized water, placed into 100-mL wide-mouth glass bottles with Teflon-lined caps, and stored in a 4 °C cold room until they were processed.

2.1.9. Water column sampling

It was expected that the potential for increased resuspension of sediments and PCBs, if any, would be the greatest as the first high tide covered the exposed Plot A. Thus, overlying water was sampled in duplicate during the first incoming high tide following AC treatment. For comparison, overlying water above Plot A was also sampled during the incoming high tide one day before and one month after AC treatment. The sample collection apparatus is shown in Fig. 3L. Sampling involved pumping 40 L of water through Teflon tubing to a glass fiber filter contained in a stainless-steel filter holder to trap suspended particles and then passing the filtered water through a XAD-2 resin trap in a glass column to measure dissolved PCBs. The method is similar to the surface water sampling method used in the US EPA Lake Michigan Mass Balance Study (http://www.epa.gov/glnpo/lmmb/methods/). Some modifications were made to the method to suit the unique field conditions of the sampling. Due to the shallow water over the treatment plot, a peristaltic pump was used to deliver the water to the in-line filter holders and XAD traps. Teflon tubing was used to collect water samples and was pre-equilibrated with field water by passing about 5 L of water before the start of PCB sampling. The inlet of the Teflon sampling tube was tied to stakes, positioned at 15 cm above the sediment surface, located at the center of Plot A, and remained submerged under water during high tide. The water sample was passed through pre-combusted glass fiber filters with a nominal pore size of 0.7 μm, and then through a pre-cleaned XAD-2 resin adsorbent column. The filter and resin media were prepared for sampling following the method used in the US EPA Lake Michigan Mass Balance Study. The clean filters were wrapped in clean aluminum foil and stored in polyethylene bags until used. After sampling, the filter papers were folded into quarters and stored in clean 250-mL wide-mouth glass bottles with Teflon-lined caps. The ends of the XAD columns were closed using Teflon-lined nylon end-caps during transport before and after sampling. The filter papers containing suspended particulates and the XAD-2 resin columns containing trapped dissolved PCBs were stored at 4°C until they were later processed.

2.2. Laboratory methods

2.2.1. Core sampling and total organic carbon (TOC) analysis

To assess the depth and homogeneity of the AC mixed in the sediment, each 1 ft sediment core samples was divided into six core cross sections of 2-inch lengths. Each cross section was homogenized by stirring manually with a stainless-steel spatula, and then approximately 1 g of sediment was subsampled for elemental analysis. These subsamples were dried and ground using an agate mortar and pestle. Approximately 4 mg of each subsample was weighed into a silver boat. Weighed samples were then acidified *in situ* with 6% sulfurous acid to remove carbonate phases (Verardo et al., 1990). Each sediment sample was analyzed for total organic carbon (TOC) using a Carlo Erba NA-1500 elemental analyzer. Carbon analysis errors were $<0.5\%$ based on an acetanilide standard (71.1 wt.% C).

2.2.2. Sediment extraction

After TOC subsamples were removed, the remainder of the six cross sections from each core was homogenized and a 10-g portion of sediment was removed to measure total sediment PCB concentrations. After drying and grinding, 3 g of the dried sediment was transferred to a 50-mL beaker. Sediment samples were extracted with sonication in a 50% acetone and 50% hexane mixture, following a procedure based on US EPA Method 3550B. The extract was concentrated using a nitrogen blow-down apparatus before cleanup.

2.2.3. SPMD extraction

After retrieval, the SPMDs were cleaned by rinsing with deionized water, swirling for 30 s in 1 M hydrochloric acid, rinsing with the series of deionized water, acetone, and isopropyl alcohol, and air-drying for approximately 30 s. The SPMDs were then submerged in approximately 125 mL of hexane and dialyzed at room temperature for 24 h. The dialysate was removed, and dialysis with fresh hexane was repeated for 8 h. Dialysates were combined with hexane rinse, the total volume was recorded, and aliquots were taken for cleanup.

2.2.4. Tissue extraction (field-deployed clams)

After clams were transferred to the laboratory, clams were depurated for 48 h in clean sediment that was collected from Palo Alto Baylands Nature Preserve, Palo Alto, CA, USA. After depuration, the clams were sacrificed by first opening the shell with a scalpel. Excess water on the inside of the clam was drained by tilting each shell and contacting it with a dry paper towel. The wet tissue was then removed with the scalpel, immediately frozen and stored at −15 °C. The tissue samples were shipped overnight (on dry ice in a cooler) to Battelle Duxbury Operations for tissue analyses. The analysis of PCBs was performed according to low-level methods developed for the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program (Lauenstein and Cantillo, 1993), as described in BDO SOP 5-190 (Battelle Duxbury Operations). Upon arrival, the tissues were homogenized by macerating the tissues using a Tekmar tissuemizer (Tekmar, Cincinnati, OH, USA) and 75 mL of dichloromethane (DCM) until uniform slurries were attained. This procedure was repeated once and the extracts decanted between tissumizing steps. A third extract was accomplished by adding 50 mL of DCM to the tissue in the extraction vessel and shaking for 0.5 h. A 10-mL portion of the extracts was air-dried to determine the DCM-extractable lipid concentration. The remaining portion of extracts was solvent exchanged into hexane prior to PCB congener analyses.

2.2.5. Laboratory PCB bioaccumulation assays

In addition to the *M. nasuta* deployed in the field, further PCB bioaccumulation studies were conducted in the laboratory with *M. nasuta* and *Leptocheirus plumulosus* using the sediment collected from Plots A and B in Hunters Point South Basin 1 year after AC treatment occurred. Sediment samples from the field were not homogenized for use in the laboratory trials in order to preserve field conditions as closely as possible. Cakes of sediment with an approximate depth of 6 in. were taken, directly placed into 20-L buckets, and moved to the laboratory. Subsamples of the sediment were sent to the US Army Engineer Research and Development Center (US Army ERDC) for the *L. plumulosus* bioassays and the remaining sediment was transferred into 2-L beakers with a diameter of 14 cm, a similar width to that of PVC clam cages for *M. nasuta*.

In the 28-day laboratory exposures, *M. nasuta* with shell lengths between 2.5 and 3.3 cm (Aquatic Research Organisms, USA) were placed in the beakers in which the contained sediment had been previously submerged in aquaria containing 31‰ filtered seawater (Long Marine Lab, Institute of Marine Sciences, University of California Santa Cruz, USA) at 15 °C. Four replicates containing six clams each were performed for each sediment sample. The seawater was aerated gently and exchanged once a week. After 28-day exposures, clams were depurated for 24 h in clean sediment (collected from Palo Alto Baylands Nature Preserve, Palo Alto, CA, USA) and then 48 h in seawater prior to being sacrificed. The procedure of clam sacrificing was the same as described in the previous Section 2.2.5. The tissues were stored at −15 °C.

Three replicates of *L. plumulosus* were exposed to sediment from each plot using procedures described by (Millward et al., 2005). Briefly, wet sediment was added to each replicate 1-L beaker on a 100 g dry-weight basis. Each beaker contained 25 juvenile amphipods exposed to sediments for 28 days at 25.0 ± 1.0 °C using 20‰ reconstituted seawater (Crystal Sea Marine Mix, Marine Enterprises International, Baltimore, MD, USA) as overlying water. After 28 days of contact, the amphipods were removed from the sediment and allowed to clear gut contents for 2–4 h before being placed in storage at −80 °C.

2.2.6. Tissue extraction (laboratory bioaccumulation studies)

Of the six whole clam tissues obtained from each replicate exposure, three were selected at random, frozen at −80 °C for 24 h, and freeze-dried (VirTis® Benchtop 4 K Freeze Dryer model 4KBTXL-75, Gardiner, NY, USA) for 3 days. The three dried tissues of each replicate were then combined, crushed, and homogenized to fine powder. From the resulting homogenate for each replicate, a subsample was taken to a 50-mL beaker and the weight was recorded. After spiking the subsample with 10 μL of analyte surrogate (PCB 14 and PCB 65), it was extracted three times with sonication in 20 mL of DCM, following a procedure based on US EPA Method 3550B. The solvent of the extract was exchanged to hexane using a nitrogen blow-down apparatus and the extract was concentrated before cleanup. Amphipod tissues were extracted as described by Millward et al. (2005) using a modified US EPA method 3550B adapted for small wet weights of tissue (~100 mg).

2.2.7. XAD-2 and filter extraction

The XAD-2 resin and the glass fiber filters were extracted in a soxhlet extraction system with a 50% acetone and 50% hexane mixture. The soxhlet extraction procedure followed US EPA method 3540 C. The extract was concentrated in a rotary evaporator (Buchi SafetyVAP model R200A, Buchi, Switzerland) and a nitrogen blow-down apparatus (N-evap model 250 G, Organomation Inc, Berlin, MA, USA) before cleanup.

2.2.8. Extract cleanup

Extracts obtained from SPMDs, sediment, XAD-2 resin, and glass fiber filters were cleaned from organic interferences using a deactivated silica gel column following US EPA method 3630C. Extracts from the field deployed clam tissues were cleaned through an alumina column, concentrated, and further purified by gel permeation column/high performance liquid chromatography (GPC/HPLC) as described by BDO SOP 5-128 following the NS&T methods (Lauenstein and Cantillo, 1993). Clam tissue extracts obtained from the laboratory bioaccumulation study were cleaned via sulfuric acid/potassium permanganate and then eluted through a deactivated silica/alumina column (Lauenstein and Cantillo, 1993; USEPA, 2000). Sulfur interferences were removed by contacting with activated copper following EPA method 3660B. Amphipod tissue extracts were cleaned and concentrated down to 40 μL as described by Millward et al. (2005) using US EPA method 3630C.

2.2.9. PCB analysis

PCB congeners in extracts from field-deployed clam tissues were measured following BDO SOP 5-182 using an Agilent 6880 gas chromatography/electron capture detector (GC/ECD) (Battelle Duxbury Operations). This protocol determined the concentrations of 18 PCB congeners. In the case of laboratory-deployed clam tissues, SPMDs, sediment, XAD-2, and glass fiber filters, US EPA Method 8082 was applied to analyze PCB congeners in extracts obtained from those samples. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m × 0.25 mm ID) and a micro electron capture detector was used for analysis. A 5-level PCB calibration table was prepared using a known PCB mixture containing 250 μg/L of Aroclor 1232, 180 μg/L of Aroclor 1248 and 180 μg/L of Aroclor 1262 yielding a total PCB concentration of 610 μg/L. The known PCB calibration mixture was obtained from the US EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, MI, USA. Concentrations of individual PCB congeners in the mixture were obtained from Mullin (Mullin, 1994). Two internal standards were used: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, 92 PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks are calibrated as the sum of congeners. PCB analysis of amphipod tissues was done as reported by Millward et al. (2005) using US EPA method 8270 and selective-ion monitoring on a Hewlett-Packard 5890 series II gas chromatograph-mass spectrophotometer. Seventeen congeners or coeluting peaks were analyzed and summed to give a total PCB level in a sample.

3. Results and discussion

3.1. Homogeneity of AC mixing

A spatial representation of the TOC results for Plot A before and after AC mixing treatment is given in Fig. 4. This representation indicates that (1) the amount of carbon in Plot A increased after AC treatment, and (2) some areas of Plot A had more homogenous AC mixing than others. The low standard deviations among the core cross sections for Cores 4 and 5 indicate that the Aquamog did the best mixing near its bow. In fact, the average TOC values for two well-mixed cores (Core 4: 3.7% ± 0.4 and Core 5: 4.2% ± 0.5) match well with the expected value of 3.8 wt.% C for a 3.4 wt.% AC dose to this sediment. The expected value was calculated as follows: if 3.4-g AC (TOC = 86.1%) is added to 100-g Plot A sediment (TOC = 1.0%), then the resulting 103.4-g mixture would contain a total 3.93-g TOC (3.8%). As the rotovator moved farther away from the bow, the mixing was less homogeneous, with fair mixing occurring at Cores 2 and 3 and poor mixing near Core 1. As expected, when sediment cores taken from Plot A 7 months after AC treatment were analyzed for TOC, no significant differences in the AC amount at the individual sampling loca-

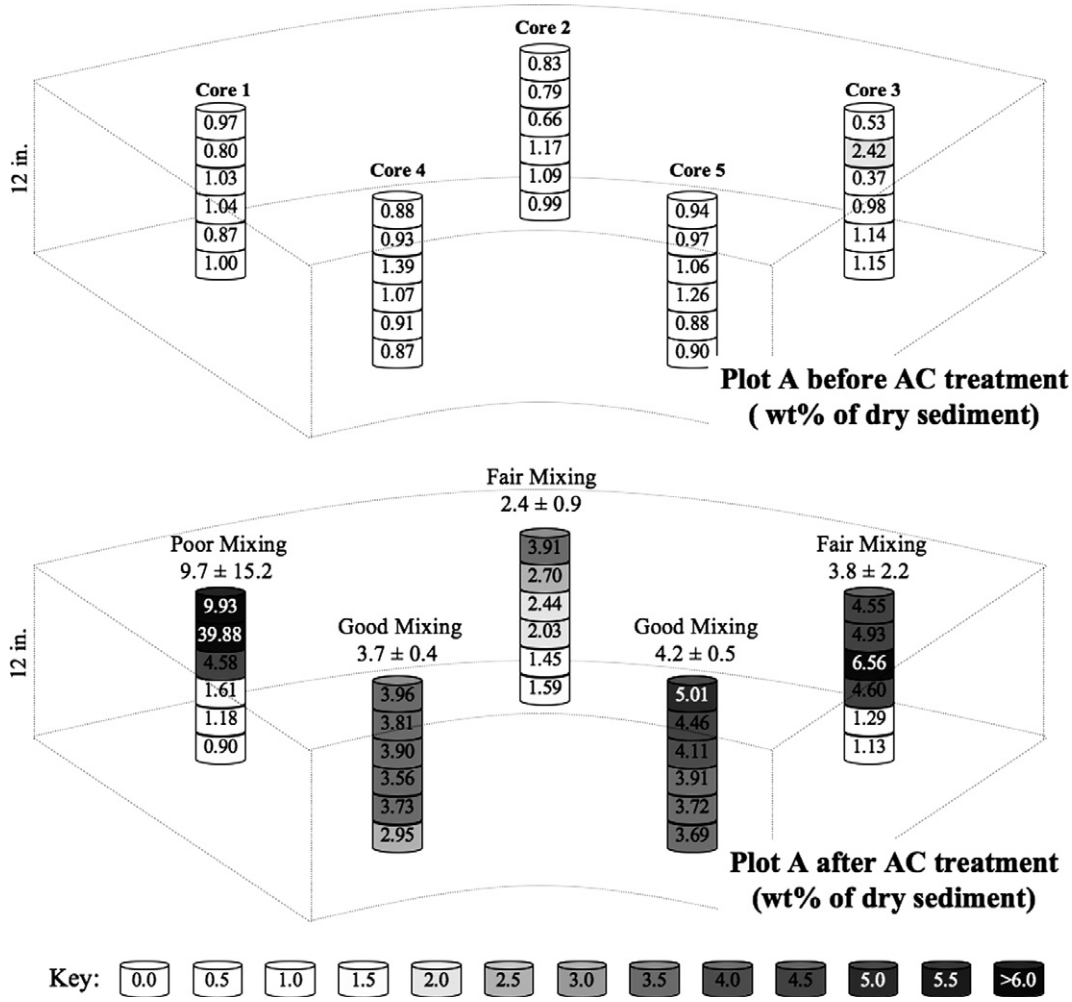

Fig. 4. Comparison of TOC values from sediment cores taken before and after AC treatment in Plot A.

tions were found when the TOC values between the 1- and 7-month samplings were subjected to a paired student's *t*-test at the 95 percent confidence level. It should be noted that the average TOC values for Plots A ($1.0\% \pm 0.3$) and B ($0.7\% \pm 0.4$) were found to be similar before AC treatment.

3.2. PCB uptake into SPMDs

The total PCB uptakes into the SPMDs for Plots A and B throughout three sampling intervals (before AC addition, one month after AC addition, and 7 months after AC addition) are shown in Fig. 5. These uptakes were normalized by the different sediment PCB concentrations in Plot A (2100 ± 300 ng/g) and Plot B (1600 ± 300 ng/g) sediment concentration of each plot. Whereas the normalized SPMD uptakes in the two plots were not significantly different from each other before AC addition, the AC-treated Plot A showed 34% less SPMD uptake than that of Plot B one month after AC treatment (*t*-test, $p = 0.01$). The difference between the two plots increased up to 62% after 7 months of AC-sediment contact (*t*-test, $p < 0.01$). This suggests that transfer of the PCBs to the AC continued during months 1–7 following mixing of Plot A. In comparison, in the laboratory we have observed up to 77% reductions in PCB uptake for SPMDs that had been contacted with well-mixed (6 months on a roller) AC-amended Hunters Point sediment (Zimmerman et al., 2005). This difference between field and laboratory SPMD uptake is likely due to the considerable differences in mixing conditions and contact of the AC with the sediment. In the field, the AC was mixed into the sedi-

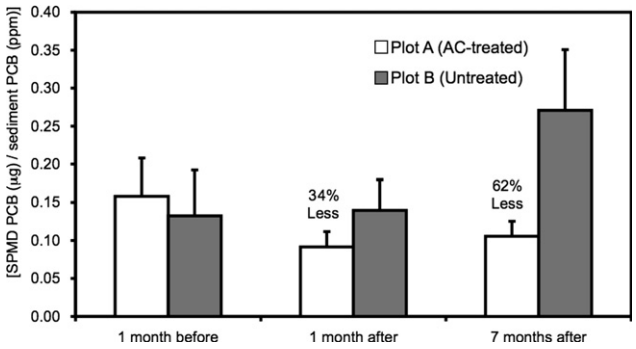

Fig. 5. Comparison of PCB uptakes into SPMD normalized by sediment PCB concentration exposed to the AC-treated Plot A and the untreated Plot B sediment for 28 days. Each column and error bar represents the mean and one standard deviation ($n = 3$–5).

ment for a total of 30 min compared to the mixing times in the laboratory of up to 6 months. Nonetheless, up to 62% of reduction in SPMD uptake in the field is encouraging and leads us to expect further reductions over time as the PCBs continue to repartition into the AC in Plot A. The reduction in SPMD uptake is also significant considering that the mixing of Plot A homogenized the sediment and may have enhanced contact with the SPMD in comparison to the unmixed sediment in Plot B. This last point emphasizes the importance of having a mixing-control plot where the sediment is mixed yet no AC is added. In this way, the impact of mixing can be separated from the variable of AC addition. Mixing control plots have been incorporated into the experimental design for a larger field study that is currently underway at Hunters Point (Smithenry et al., 2005). Additionally, we observed some variation of SPMD uptakes from the untreated Plot B among the three sampling points without any noticeable changes of sediment properties. The variability of SPMD uptakes from Plot B through the sampling period might be due to field condition factors such as tidal pumping, seasonal effect, pore water PCB concentration, and other field factors like sediment structure.

3.3. PCB Bioaccumulation

As an indication that our clam deployment procedures were effective, and that the AC had no effect on *M. nasuta* mortality, an overall survival rate of 98% was found for the clams retrieved after the 28 days of field exposure. Fig. 6a shows the PCB bioaccumulations factors (BAF = tissue concentration/sediment concentration) for field-deployed *M. nasuta* in the AC-treated Plot A and the untreated Plot B for 28-day exposures. The BAFs of Plot A were significantly less compared to Plot B at 7 months post-treatment assessment by 53% (t-test, $p = 0.02$). Although the p value for the difference at one month after AC treatment was not less than the 0.05 alpha level ($p = 0.19$), the 24% difference appeared to be reasonable when compared to the difference of PCB uptakes into SPMDs observed at the same time. To consider the possible effect of AC on lipid contents in clams, lipid-normalized BAFs (BAF/lipid content) are also presented (Fig. 6b). Similar to the non-normalized BAFs, the lipid-normalized BAFs for clams exposed to AC-amended sediment were significantly less in comparison with untreated sediment at 7-month post assessment (49%, $p < 0.01$). Also, the one-month post assessment gave a 32% difference, although the p value did not indicate significance (t-test, $p = 0.06$). Our small sample sizes and kinetic factors affecting PCB uptake by the AC in the field likely prevented us from seeing significant differences in the one-month data set.

As expected from the PCB uptakes into the SPMDs in the control Plot B, the BAFs as well as the lipid-normalized BAFs from Plot B were varied even with constant sediment properties during three assessments (one month before, one month after and 7 months after AC treatment occurred). Therefore, it is difficult to directly compare the time series BAFs obtained from each plot. Rather, in this study, the spatial control (Plot B) played a prominent role in proving the effectiveness of AC treatment in reducing PCB bioaccumulation in *M. nasuta* as well as PCB uptake into SPMDs.

To ascertain the AC treatment effect on PCB bioaccumulation, another round of PCB bioaccumulation studies with *M. nasuta* and *L. plumulosus* were later conducted in the laboratory with non-homogenized and non-altered sediment collected from both plots one year after AC treatment occurred. As shown in

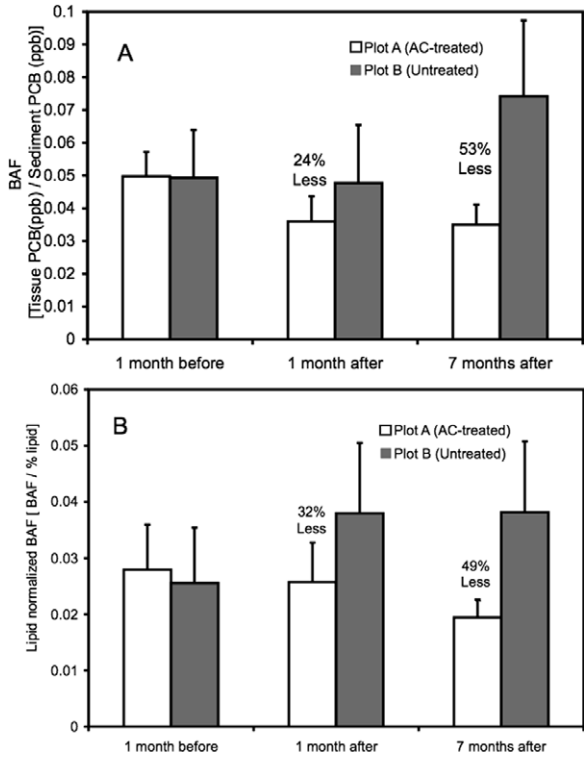

Fig. 6. Comparison of bioaccumulation for field-deployed *M. nasuta* for 28 days. (a) Bioaccumulation factors (BAF = tissue PCB concentration/sediment PCB concentration) and (b) lipid-normalized BAFs for *M. nasuta* exposed to the AC-treated Plot A and the untreated Plot B sediment. PCB tissue concentrations are based on wet weight. Each column and error bar represents the mean and one standard deviation ($n = 3$–5).

Fig. 7, the BAFs obtained from exposures to Plots A and B indicated the lower transfer of PCB from sediment to clam and amphipod tissues in the AC-treated Plot A sediment. The BAFs were significantly less for both *M. nasuta* (t-test, $p = 0.02$) and *L. plumulosus* (t-test, $p = 0.04$) exposed to the AC-treated Plot A sediment relative to the untreated Plot B sediment, with 51% and 50% differences, respectively. The clam BAF values observed in the laboratory are one order of magnitude larger than those from the field, which are likely due to the different units of the PCB tissue concentrations (wet weight versus dry weight) and the different numbers of PCB congeners for analyses (18 versus 92). Although there was the possibility during coring and sampling of some inevitable alteration of the sediment state and layered structure, and the surrounding environment, these laboratory results were well matched with the field results for the seven-month post-treatment bioaccumulation. This is believed to provide another line of evidence of AC amendment effectiveness in the field.

As expected from the differences in mixing conditions, the differences in 28-day PCB bioaccumulation (~50%) observed for the one-time-mixed AC-amended sediment obtained from the field were less than the laboratory-scale reductions (~80%) reported (McLeod et al., 2007; Millward et al., 2005) for biota exposed to AC-amended sediment that had been continuously mixed for one month in the laboratory. Nevertheless, the 50% difference in PCB bioaccumulation is striking for a one-time-mixed system under field conditions as it suggests that significant reductions can occur at time scales that are relevant to field remediation efforts. The PCB bioaccumulation differences found between this system mixed for 30 min versus those mixed for one month are in-line with the modeling efforts that describe of the aqueous PCB concentrations in one-time-mixed AC-amended sediment systems (Werner et al., 2006). According to this model, after five or more years of AC-sediment contact, the reductions in aqueous PCB concentrations observed for one-time-thoroughly-mixed systems (field) may approach those found for systems mixed for extended periods in the laboratory.

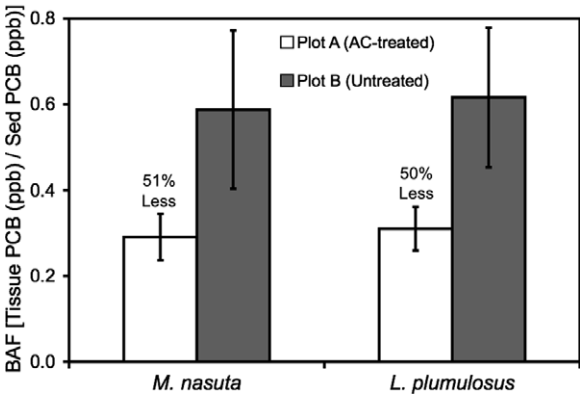

Fig. 7. Comparison of bioaccumulation factors for *M. nasuta* clams and *L. plumulosus* amphipods exposed to the AC-treated Plot A and the untreated Plot B sediment for 28 days in laboratory tests with field cores collected one year after treatment. PCB concentrations in *M. nasuta* tissue are based on dry weight; *L. plumulosus*, wet weight. Each column and error bar represents the mean and one standard deviation ($n = 4$).

Indeed, this convergence is not surprising when one considers that the majority of PCBs discharged into Hunters Point South Basin sediment between 1954 and 1974 had migrated to the char and coal-derived particles (Ghosh et al., 2003) that were introduced into the sediment through historic anthropogenic activities. With these ideas in mind, we anticipate that PCBs will continue to be repartitioned in the field and that this mass transfer process will be augmented by bioturbation, wave action, and tidal pumping. Therefore, we project that further reductions in bioaccumulation will be observed in the field over time, as we already observed within relatively short periods (one month to 7 months).

3.4. PCB resuspension in water column

As shown in Fig. 8a, the average total PCB concentrations in the aqueous phase above Plot A were similar one day before, immediately after, and one month after mixing AC into sediment. This shows that the AC amendment and mixing resulted in no measurable release of PCBs into the water column. Likewise, as shown in Fig. 8b, there was essentially no increase in PCBs associated with suspended particles in the water column observed during the first high tide immediately after AC treatment. There was a large increase in suspended particle-associated PCBs during the third sampling event one month later. This increase is attributed to wind-induced turbulence.

Average wind speed and wind direction during the sampling times were calculated based on available surface weather observation data from the nearest National Oceanic and Atmospheric Administration (NOAA) monitoring station at San Francisco Airport. Average wind speeds during the sampling periods for the three days (D1: one day before, D2: immediately after, and D3: one month after AC treatment) were 9.0, 9.6, and 12.1 km/h, respectively. Wind gusts of 24 km/h were also registered on D3. Thus, there was an increase in wind speed during the sampling times on D2 and D3. Wind direction was also different on the three sampling days. Average wind direction was 310, 270, and 250 degrees on D1, D2, and D3, respectively. Thus, D1 wind would have blown along the shoreline, while D3 wind would have blown from the center of the basin towards land. The large increase in D3 wind speed and the change in wind direction likely increased the sediment resuspension on that day. This increase in sediment resuspension was confirmed through estimates of suspended solids concentrations obtained from the dried filter papers: 12 mg/L on D1, 22 mg/L on D2, and 36 mg/L on D3. Overall, these results suggest that wind speed and direction have a greater impact on resuspension of particle-associated PCBs than the immediate effect of mechanical mixing of AC with sediment. The observed wind induced effects are likely representative of more basin-wide phenomena than that localized over the relatively small test plots.

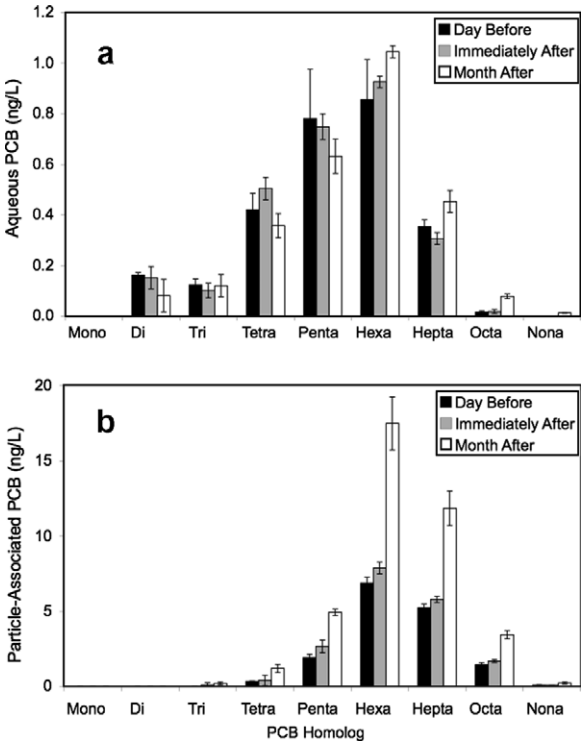

Fig. 8. Comparison of (a) aqueous PCB concentration and (b) particle-associated PCB concentration sampled above Plot A during high tide one day before, immediately after, and one month after AC treatment. Each column and error bar represents the mean and one standard deviation ($n = 2$).

4. Conclusion

We recently completed a preliminary study at Hunters Point to assess an *in situ* mixing AC treatment technology for PCB-contaminated sediment under field conditions. We successfully deployed a large-scale mixing device and used it to amend a sediment plot with a 3.4 wt.% AC dose. Our results show that this device mixed AC homogeneously into most of the sediment plot. The effectiveness of the AC treatment was demonstrated by a series of assessments. In just one month after AC treatment, 34% less PCB uptake into SPMDs and 24% less PCB bioaccumulation in *M. nasuta* deployed in the field was found upon exposure to AC-amended sediment in comparison to untreated sediment. Seven months after the AC treatment occurred, the differences further increased up to 62% less in SPMD uptake and 53% less in clam bioaccumulation, which implies the possibility of the long-term effectiveness of AC. Those field results were in alignment with the results of supplementary laboratory bioaccumulation assays, which showed approximately 50% less PCB bioaccumulation in *M. nasuta* and *L. plumulosus* exposed to AC-amended sediment obtained from the field one year after treatment in comparison to untreated sediment. Further reductions in PCB bioaccumulation are expected in the field as the contact time between AC and sediment increases. The knowledge and experience gained in this preliminary study is currently being applied to a larger field study that began in 2006 (Smithenry et al., 2005). The main goal of this more comprehensive field study, which will compare two mixing devices and comprise unmixed and mixed-only control plots, will be to further understand the long-term effectiveness of AC as an *in situ* treatment strategy under field conditions for PCB-contaminated sediments.

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