# Feasibility evaluation of a blended cover with activated carbon for in-situ stabilization of DDT in sediment

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## ABSTRACT

Activated carbon (AC) sediment amendment is an in-situ remediation technology in which the applied AC immobilizes organic contaminant flux from sediments, thereby reducing contaminant bioavailability and associated risks. While various studies have demonstrated the feasibility of in-situ AC treatment, hesitation to apply this technology exists due to limited experience under field-specific scour conditions and hydrodynamic forces. To address this concern, we conducted a feasibility study for an AC-blended cover at the Lauritzen Channel of the United Heckathorn Superfund Site in Richmond, California, United States, which was contaminated with dichlorodiphenyltrichloroethane and its metabolites (DDx) as well as dieldrin. Vessel activities causing sediment disturbance were identified as key factors for remedy selection. A blended cover with AC and coarse materials was designed to withstand varied hydrodynamic conditions and AC stability was tested in a current flume. The cover comprised medium-size gravel ($D_{50}$ = 15 mm, $D_{90}$ = 19 mm) with 4 % granular AC by weight. Flume erosion studies showed minimal AC loss (1–2 % of total AC) under shear forces of 9–31 Pa, which was equivalent to or exceeded the estimated worst-case erosional conditions in the channel induced by a hypothetical, stationary tugboat propelling at high power thrust. The treatability performance of the engineered blended cover design was evaluated through mesocosm studies using site sediment and various cover options. Post-treatment assessments on days 5 and 145 showed rapid reductions in freely dissolved ($C_{free}$) DDx and dieldrin in the blended cover layers and surface water. For example, by day 145, $C_{free}$ DDx was reduced by over 98 %, meeting US EPA remedial goals for the site. It is concluded that the combination of both stability and performance testing demonstrates that an engineered blended cover-AC design would be a feasible remedial option at the site, and that this testing approach can be applied to evaluate in-situ treatment in other sediment cleanup activities.

## 1. Introduction

It has been two decades since activated carbon (AC) amendment was first demonstrated in the field as an in-situ sediment remediation technology for persistent organic contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organic pesticides (Zimmerman et al., 2004). This in-situ treatment technology relies on the strong sorption affinity and large sorption capacity of AC to immobilize organic contaminants in sediments or soils and thereby greatly reduces contaminant bioavailability and associated risks (Cho et al., 2009; Millward et al., 2005). Numerous laboratory studies and pilot and field-scale demonstrations have validated the AC technology, with either virgin or reactivated AC, and increased its technological maturity and confidence level (Ghosh et al., 2011; Patmont et al., 2015).

However, as for any sediment remedial strategy, it is necessary to assess the feasibility of the remedial technology at each location under site-specific conditions and to optimize the technology to ensure its success in addressing potential site-specific concerns.

A site-specific concern for in-situ AC sediment amendment is the stability of the amendment and sediment against erosive forces. Since AC possesses a lower density (wetted density 1.2–1.4 g/cm³) compared to sand and gravel (2.0–2.6 g/cm³), there are questions about whether it may preferentially erode when exposed to sufficiently high hydrodynamic forces. These forces can arise from natural phenomena, such as waves, currents, and tidal actions, or from anthropogenic sources, such as ship wakes and propeller wash. To address the issue of AC stability, an engineering solution is an appropriately designed blended cover consisting of a mixture of AC and coarse media, e.g., gravel. A schematic of a

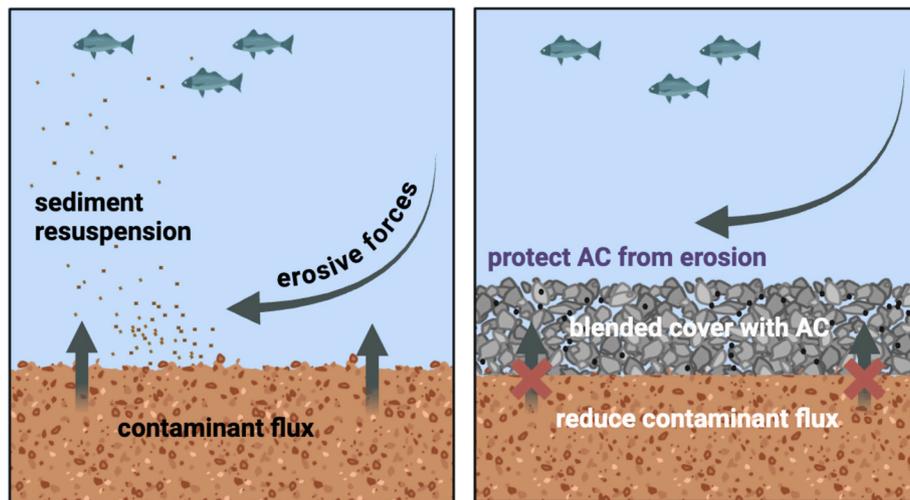**Fig. 1.** Schematic of the blended cover amendment. The blended cover will prevent AC erosion by erosive forces and reduce contaminant flux from underlying contaminated sediment. Images created with Biorender.com.



**Fig. 2.** Lauritzen Channel and the United Heckathorn Superfund Site, California, USA. The marker indicates the grab sampling locations for the treatability study. The maps were generated by ArcGIS Online.

blended cover is shown in Fig. 1 in which a thin layer, e.g., 15 cm, of gravelly material is mixed with AC and applied over contaminated sediment. This blended cover design enhances stability against hydrodynamic forces, which would otherwise erode amendments comprising AC and fine-grain sediment alone (Patmont et al., 2015). A blended cover dissipates the hydrodynamic energy like conventional rock armoring or riprap protects channel banks and underlying sediment against erosion. The blended cover solution is promising and has been implemented in a handful of field applications (Patmont et al., 2015; US EPA, 2021). Nonetheless, there has not yet been a comprehensive mechanistic examination of the protection effect by the blended cover design against AC erosion and the blended cover's performance in reducing chemical flux to overlying water.

The objective of this study is to examine the performance of an engineered blended cover and demonstrate its feasibility for in-situ AC amendment under site-specific erosive forces. The United Heckathorn Superfund Site (US EPA, 2024) in Richmond, California, United States

(the Site) is chosen as a study location. The Site comprises the Lauritzen Channel (Fig. 2), which contains sediment impacted by dichlorodiphenyltrichloroethane (DDT) and its metabolites (collectively called DDx), dieldrin, and other contaminants of concern. The Lauritzen Channel is approximately 550 m long, with a width that varies from 40 m near its northern end to 120 m near its southern connection to the Santa Fe Channel (CH2M HILL, 2011). Historically, channel depths along the waterline ranged from $-3$ m to $-12$ m MLLW (Mean Lower Low Water) (CH2M HILL, 2011). The Site contains residual DDx following large-scale remedial dredging in the late 1990s (Tomaszewski et al., 2007). The physical disturbance of the sediment bed by vessel activities and propeller wash are important site-specific factors to be considered, along with the heterogeneity of DDx contamination and the presence of co-contaminants, for follow-on remedial decision-making at the Site (CH2M HILL, 2015).

This study presents a pair of feasibility tests for the AC-blended cover remediation approach, specifically focusing on blended cover stability

and blended cover treatment of DDx. First, laboratory experiments were designed to assess the stability of a blended cover under site-specific fluid shear induced by bench-scale propeller thrusts or flume-generated currents based on prior estimates of maximum vessel scour and bed shear stress (CH2M HILL, 2015). These tests simulated the estimated maximum site-specific hydrodynamic disturbance as a worst-case scenario. AC loss from the blended cover was quantified for each disturbance event. Secondly, the effectiveness of the blended cover design was assessed in reducing chemical availability. In that effort, mesocosm laboratory studies using Site sediment were conducted to test various amendment and blended cover material options. Passive sampling using polyethylene (PE) sheets was employed in the mesocosms to assess the changes in the availability of DDx, as well as the Site co-contaminant dieldrin, after the blended cover was applied to sediment obtained from Lauritzen Channel.

## 2. Methods

### 2.1. Blended cover stability study

#### 2.1.1. Hydrodynamic conditions at the United Heckathorn site

The objective of our study was to simulate field-relevant disturbances in laboratory-scale setups to test the erosion of AC from blended covers. For the site hydrodynamic conditions in the Lauritzen Channel, we referred to the US EPA's draft Focused Feasibility Study (FFS) by CH2M Hill (2015), which undertook sediment transport studies (FFS Appendix D). The study determined that ship wakes and tugboat propeller washes are the primary forces potentially disturbing or scouring the bottom sediment in the Lauritzen Channel. While direct field measurements for these scouring events were not available, a propeller scour analysis was conducted for EPA using model simulations for various scenarios as part of the FFS (CH2M HILL, 2015). These included permutations of two different types of tugboats, five different percentages of the maximum power of a tugboat, five different transects within the Lauritzen Channel, and two operating modes: a transiting mode and a stationary mode. In that work, the net bottom velocity was calculated as the sum of the bottom velocity due to the vessel wake and the bottom velocity due to the propeller wash.

The transiting mode was simulated for two minutes. The effect on bottom velocities along the transect were minimal after this time interval due to movement of the transiting vessel. Simulations for the stationary analysis lasted for 10 min, mimicking a tugboat pushing against the side of a barge ship. From the EPA's FFS, the Site experiences maximum bottom velocities of 1.69 m/s for the transiting mode, and 1.62 m/s for the stationary mode (CH2M HILL, 2015). Both values were generated from the worst-case scenario, with 100 % throttle due to a large tugboat at a stationary transect location. The corresponding maximum bed shear stresses were 2.89 Pascal (Pa) and 2.52 Pa respectively, for the site sediment surface at the depth of 4.5 m (CH2M HILL, 2015).

Bed shear produced by the horizontal flow, at maximum velocity, is also influenced by bottom roughness. The maximum shear stress estimated by CH2M HILL ((2015)) was based on smooth, native sediment surface. However, the addition of a blended cover containing AC would increase surface roughness. This increased bottom roughness from a blended cover configuration was considered when our study re-evaluated the maximum bed shear. We made conservative corrections using the approach described in the FFS:

$$\tau_b = \rho C_f V_b^2 \qquad (1)$$

where $\tau_b$ is bed shear stress (Pa), $\rho$ is the sediment bulk density (g/cm$^3$), $V_b$ is the bottom velocity (m/s), $C_f$ is the bottom friction coefficient (−, dimensionless). For the case of a blended cover, we revised the bottom friction coefficient following the method reported in the FFS:

$$C_f = k^2 \left( ln \left( 11 \frac{h}{k_s} \right) \right)^{-2} \qquad (2)$$

where $k$ is von Karman's constant (−), $k_s$ is the effective bed height roughness (m), and $h$ is the water depth (m). The effective bed height was calculated as twice the average $D_{90}$, and the water depth ($h$ = 4.5 m) was determined using the given values of $\tau_b$ and $V_b$ in the draft FFS. Maintaining the other site parameters, and for angular material with $D_{90}$ = 19.4 mm, the bottom friction coefficient for the blended cover was recalculated as 0.0031 (−). The corresponding maximum bottom stress under this maximum propeller scenario with AC blended cover was recalculated as 8.95 Pa, approximately three times higher than the maximum shear stress expected for native sediment. The 8.95-Pa value was used as a benchmark in conducting the flume experiments of this study. The testing comprised a propeller study to mimic 1.69 m/s maximum velocity and a confined flume study to simulate bed shear produced by horizontal flow for maximum fluid shear stress of at least 9 Pa.

#### 2.1.2. Bench-scale propeller scour study

Prior to the flume study, we conducted a bench-scale propeller scour study to evaluate various materials, test the quantification method for eroded AC, optimize the testing design, and confirm in advance the stability of the designed blended covers under predicted maximum site disturbance. The experimental method and results are detailed in the Appendix (A1.1 and A2.1). Briefly, a 10-cm diameter three-blade mechanical mixer head was used as a scaled-down propeller, positioned above a test chamber, which was placed in a 340-L aquarium filled with a deionized water with a 15-cm blended cover layer. The blended covers are designed to be 15-cm thick, which is adequate to control contaminant flux from the sediments to the overlying water and to cover the biologically active zone, where most benthic organisms live.

Various blended cover configurations were tested (Table A1) including a control option consisting of an AC and sand mixture without coarse material. After installing the blended cover in the test chamber, the propeller was employed for 10-min scouring test segments. Acoustic doppler velocimeter (ADV) (Vectrino P20439–2, Nortek AS, Norway) measurement confirmed that the mixer's rotation at 2000 rpm was able to reach a maximum bottom velocity close to the target bottom velocity of 1.69 m/s. After 10 min of propeller scouring, the eroded AC was vacuum-collected, and quantified for its mass. This test phase was repeated until AC erosion was negligible for each layering condition (three to six times) except for the control study with sand. The control test was conducted only once because without the blended cover the sand and AC were eroded readily in bulk from the test chamber as soon as the first test was initiated.

For material selection, we considered blended cover materials similar in size to 1.5-in. (3.8-cm) minus aggregate base (AB), which is widely used in road construction and would be considered as a viable option for field application in blended cover installations. To highlight the mobilization of AC, we chose white-colored materials to create a visual contrast with the black AC. In terms of shape, both rounded and angular materials were evaluated, considering any interlocking effects resulting from angular shapes. We utilized polished pebbles for the rounded materials, and crushed marble chips for the angular materials. The AC used in this study was reactivated AC manufactured from previously used granular coal-based or coconut-based AC with a particle size range of 0.43–2.38 mm (DSR A, 8 × 40, Calgon, PA). Again, this choice was made considering real-world applications with readily available bulk materials. Each cover option contained 4 wt% AC, relative to the main cover material's weight. In each cover, a small amount of pea gravel, 5-mm in size and equivalent in volume to the AC, was added to assist in blending the AC with the larger cover material. The product information for the test materials is summarized in the Appendix (Table A2). The size distribution of cover material and pea gravel
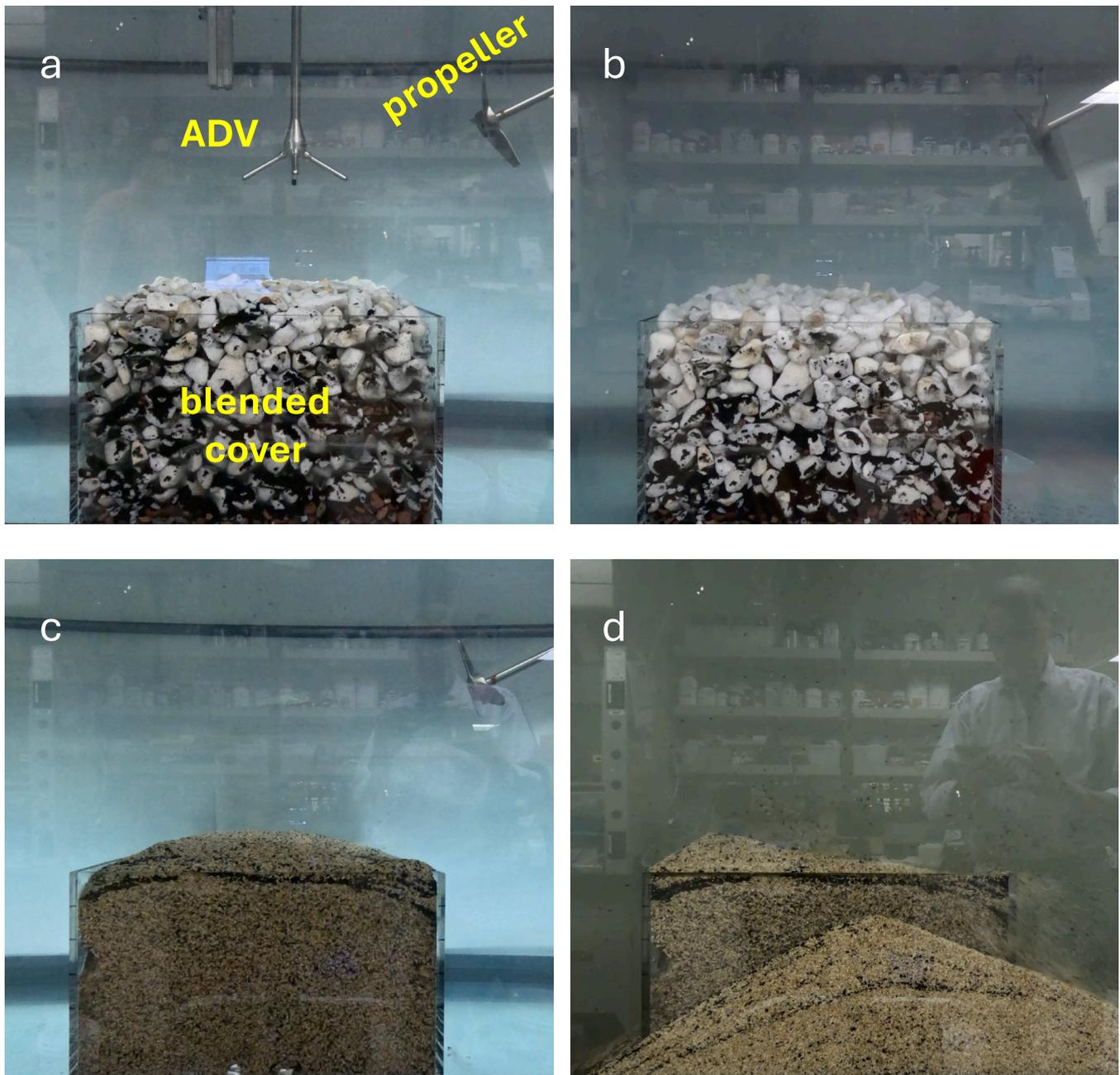
**Fig. 3.** Bench-scale propeller study. Top two figures show the scour test on a blended cover with angular gravel, pea gravel, and granular activated carbon (4 wt%): a- before scour test; b-after 30-min of scouring. Bottom two figures are from the scour test for the sand and AC mixture: c-before scour test; d- after 10-min of scouring showing a mound of bulk sand and AC eroded from the test chamber.

were determined by sieve analysis, and representative size values for the materials were obtained such as $D_{50}$ and $D_{90}$ (Table A3 and Fig. A2).

The bench-scale propeller study demonstrated the successful protection of the selected blended cover materials and AC under scouring conditions created by high-speed propeller rotation of up to 2000 rpm. For the rounded materials ($D_{50} = 18.3$ mm), less than 1 % of the AC mass eroded during three consecutive 10-min scouring events. The angular materials ($D_{50} = 14.8$ mm), which were significantly smaller than the rounded materials, still managed to limit AC erosion to not more than 1 % (Fig. 3). Furthermore, erosion was sharply reduced after a few minutes during the scouring event, and the blended cover system stabilized, minimizing further erosion. In contrast, the AC-sand mix layer without protective cover material showed substantial erosion with just one 10-min run, losing 18 % of the installed layer (Fig. 3). This illustrates

the stabilizing effect of coarser cover materials. For subsequent flume tests, the angular materials were chosen for testing, as they bear closer resemblance to the aggregate base in shape.

*2.1.3. Flume study*

A current flume at Stanford's Fluid Mechanics Laboratory (Fig. A3) was utilized to assess the stability of the blended cover and the erodibility of AC particles under a range of hydrodynamic conditions (Fig. 4). The flume generates a uni-directional flow and is optimal for assessing bed shear produced by horizontal flow, as well as characterizing and quantifying various properties of a blended cover configuration. To increase the flow rate and prevent supercritical flow conditions, we constructed an enclosed channel system in the flume (Fig. 4 and Fig. A4) using transparent acrylic panels. The dimensions of the cross-sectional
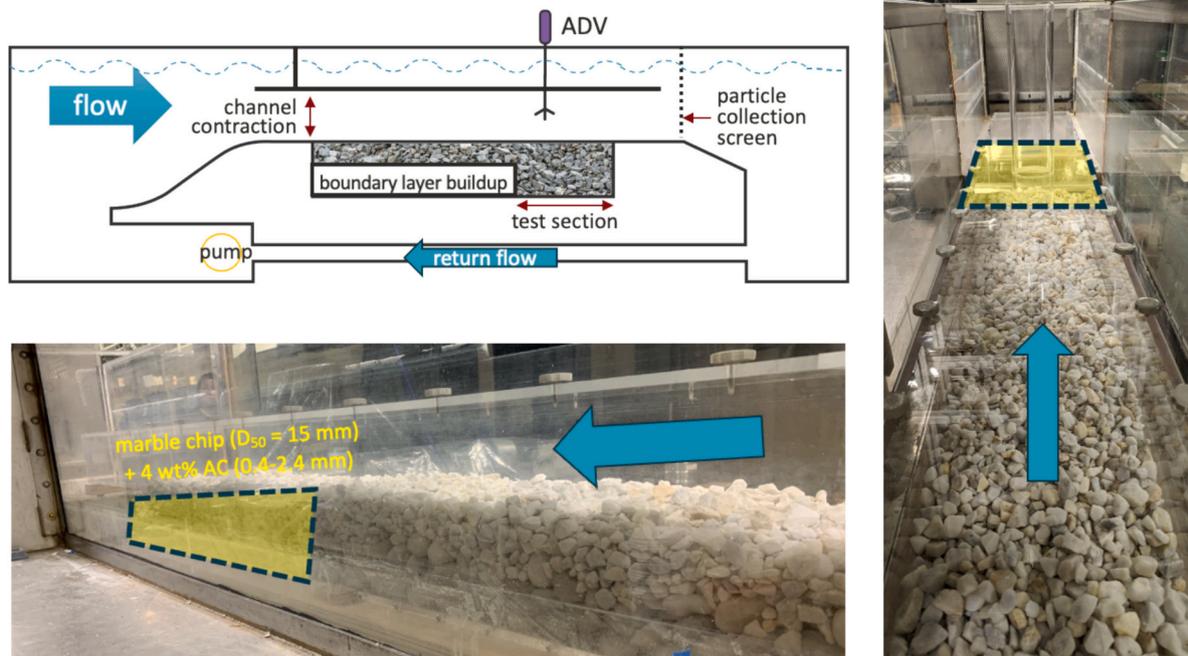
**Fig. 4.** (Left top) 2-D schematic of the flume, illustrating a flow contraction section, acoustic doppler velocimeter (ADV), and an AC collection screen. Note: schematic is not to scale. (Left bottom) Side view of the flume. The blue arrow indicates the direction of flow across the flow development section and test section. (Right) Top view of the flume with flow build-up section preceding the test section. The yellow area indicates the location of the test section, and the blue arrow indicates the direction of flow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**
Test configurations for the flume study.

| | Test configuration | Flow rate | Test duration and repeat | Objectives |
|---|---|---|---|---|
| Base condition | Cover material only, no AC | Varied (0.7–1.0 m/s) | Several times of 10 min tests | Determine flow velocity based on pump power; measure shear stress of the blended cover; and monitor the movement of cover material visually |
| AC test | Cover material with 4 wt% AC | 1.0 m/s | Three times of 10 min tests | Quantify and visually monitor AC erosion |
| AC test with simulated disruption | ~ 5 L of cover material removed | 1.0 m/s | Three times of 10 min tests | Quantify and visually monitor AC erosion |
| Infiltration | Cover material only put back into the test area. 100 mL (~ 55 g) of AC spiked to the system | 1.0 m/s | Three times of 2 min tests | Quantify and visually monitor AC infiltration into the blended cover |
| Post-testing | Cover material only | Varied | Several 10 min tests | Determine the vertical velocity profile |

area of the system were 30 cm wide and 15 cm high. The system had a 90 cm inlet section with a smooth bottom. The inlet was followed by 120 cm of cover material (without AC) to allow the flow to develop and a 60 cm test section with AC-blended cover material. The final section was a 15 cm outlet with a smooth bottom (Fig. A4). An ADV was placed over

the middle of the test section, through an acrylic tube, positioned 13 cm above the blended cover surface, which allowed for flow rate measurement at 3 cm above the surface. Four manometer ports were positioned throughout the system to monitor pressure drop across the system and measuring bottom stress. Downstream, at the end of the flume, a steel mesh of size #40 was employed to collect eroded material before water was recycled back through the system.

As previously described, crushed marble chips ($D_{50} = 14.8$ mm) were chosen for the flume study. These chips offer an interlocking effect and a contrasting white color to the black AC, providing better visualization (Fig. A5). As with the bench-scale propeller experiment, the cover material was amended with 4 wt% AC, and 5-mm pea gravel was added to facilitate homogeneous mixing of AC and marble chips. The blended cover had a final thickness of 15 cm and was placed in a test section of the chamber (Fig. 4). A 5 cm layer of blended cover material, without AC, was employed atop 5–7.5 cm rock pieces (lower space filler) ahead of the test section to avoid spin up effects and fully establish the flow turbulence and achieve the same bottom roughness as the test section containing the cover layer.

Table 1 details various tests conducted within the flume system. Initially, the test section was loaded with cover material, excluding AC, which is referred to as a 'base condition' run. The flume was operated at several pump power settings (58 %, 75 %, and 90 %), maintaining each power setting for a ten-minute test duration. During this period, velocity and pressure head measurements were taken to determine the bottom shear stresses of the blended cover in the enclosed channel system, and to validate that the system achieved the benchmark site worst-case maximum bottom stress of 9 Pa or greater. Any erosion or movement of blended cover material was monitored. Upon completing the initial runs, the test section was replaced with the blended cover material containing 4 wt% AC, which we refer to as an 'AC test' run. For these AC-amended tests, the ADV was removed and the PVC pipe was sealed off to protect the ADV from possible damage by mobilized particles and to prevent eroded AC particles from accumulating inside the ADV's acrylic tube. The flume was operated at 75 % power for three consecutive 10-min tests. After each run, eroded AC was wet-vacuumed and collected

using a #200 sieve outside of the flume. The AC was then dried for 24 h in a 60 °C oven and subsequently weighed for quantification. Test runs were documented using a GoPro camera positioned at the side of the flume.

After the AC-test runs, roughly 5 L of the cover material from the test area were manually removed. This represented approximately a 2.5 cm top layer thickness removal or about 1/6 of the volume of blended cover material originally in the test section. This was done to simulate a scenario in which the upper layer is partially removed, exposing new AC on the surface. While this action reduces the overall surface elevation and causes the surrounding container wall to be exposed above surface, it resembles real-world conditions to some extent as the partial removal results in a lowered surface compared to the adjacent area. Since the buried AC depth varied across the test area, the removal of top material was uneven, as gravel was cleared until the underlying AC became visible. This procedure simulated potential disruptions or disturbances to the blended cover itself, referred to as 'test with simulated disruption.' After this removal, the flume was operated for three additional 10-min runs at the same 75 % power level as the AC test runs. The eroded AC was quantified, and the blended cover's performance was visually assessed.

Subsequently, the extracted cover material was repositioned in the test area. The entire 1.8-m blended cover section, which includes both the test section and boundary layer build-up section, was evaluated for infiltration of AC particles in additional tests. Approximately 55 g (equivalent to 100 mL in volume) of soaked AC particles were introduced at the flow inlet. The flume was operated for about 2 min, a duration adequate for the AC to traverse the full system length at a flow rate of 1.0 m/s. The AC particles that flowed through the flume without interference were collected and quantified to determine the remaining amount that infiltrated and embedded within the blended cover. This infiltration test was performed three times in total with the same volume of AC added each run.

Lastly, the flume was operated at 75 % pump power, and flow velocities were measured at five different heights above the bed surface for 10 min per run, to determine a vertical velocity profile.

## 2.2. Blended cover treatability study

### 2.2.1. Sediment collection and processing

On March 20, 2023, Site sediment was collected using a Van Veen grab sampler from a vessel at two sampling locations near the head of Lauritzen Channel (Fig. 2). Fifteen grab samples were taken to obtain 150 L of sediment. The sediment sampling depth was 10–15 cm. Sediment was placed in 20-L containers with double-lined plastic bags, stored in a cooler with ice bags for transportation (total eight coolers for 150 L). The coolers were transported to the Stanford lab and stored in the constant temperature room at 4 °C until further processing. The sediment was sieved using a 4 mm mesh screen to eliminate large debris and gravel and then combined in a 110-L cooler, homogenized manually with a shovel, and stored at 4 °C until mesocosm construction. The sampling area (the northern head of the channel) showed surface total DDx concentration ranging from 4 to 8 mg/kg, and dieldrin concentration ranging from 70 to 140 μg/kg (Anchor QEA, 2024).

### 2.2.2. Mesocosms of remedy performance

Quiescent sediment flux experiments employed a simulated blended cover and Site sediment. Briefly, a 10-cm-thick blended cover containing 4 wt% AC was placed over 10-cm of Site sediment in 75-L glass aquaria (Lifegard Aquatics Rimless Clear Glass Aquarium 6 mm, 60.8 cm × 29.8 cm × 39.4 cm, Amazon) and then filled with synthetic seawater. To ensure homogeneity of sediment properties across the experimental options, a portion of sediment was transferred into a pre-measured 20-L bucket (Home Depot, CA) from the storage cooler. The sediment was then homogenized and evenly distributed into the tanks. After transferring all the sediment, the bucket was weighed again to determine the

**Table 2**
Testing options for the blended cover treatability study.

| Test Identifier | CTRL | DSR3 | DSR1.5 | TOG1.5 |
|---|---|---|---|---|
| Activated carbon | none | 4 wt% AC[1] | 4 wt% AC[1] | 4 wt% PAC[2] |
| Blended cover | none | 7.6-cm gabion[3] + 3.8-cm AB[4] mixture (1:1) | 3.8-cm AB | 3.8-cm AB |

[1] Regenerated granular activated carbon, Calgon DSR A (0.4–2.4 mm).
[2] Powdered activated carbon, Calgon TOG (0.075–0.3 mm).
[3] CEMEX 3-in. × 4-in. Gabion.
[4] CEMEX 1.5-in. Class II aggregate base (AB).

mass of sediment placed. This process was repeated until the sediment reached the 10 cm mark in the tank. A total of 18.0 kg of sediment was placed in each tank.

The target blended cover thickness was set at 10 cm. As shown in Table 2, three blended cover options (DSR3, DSR1.5 and TOG1.5) with two different AC particle sizes and blended cover material sizes were tested for remedy performance. Aggregate base was the blended cover material, considering potential use in actual field applications. Non-amended Site sediment was used as a control (CTRL). The blended cover material and AC were mixed in a 20-L bucket as a batch for every 2.5 cm emplacement. A total of four emplacements were conducted to achieve a 10 cm blended cover layer. The AC amendment dose was 4 wt % of the blended cover. A 4 % dose was chosen to address the wide range of DDT contamination at the site, which reaches up to 2000 ppm, while also providing a faster kinetic response. After the blended cover installment, synthetic seawater (35 parts per thousand salinity, Instant Ocean®) was slowly added to the tanks. The test systems were acclimated for five days before deploying the passive sampler device (PSD) to allow the settling of suspended material. The sediment layer compacted during this period, resulting in a final thickness of approximately 7.5 cm. The water above the layer surface was maintained at a depth of 20 cm.

Porewater and overlying water concentration profiles of DDx and dieldrin in the blended cover were monitored using PSDs. Four subsections were analyzed per each PSD: one in the bottom sediment layer, two in the blended cover layer, and one in overlying/near surface layer. All options were tested in triplicate. The experiment was conducted in a controlled temperature room at 13 °C, which is the annual average temperature of SF bay water (https://seatemperature.info/san-francis co-bay-water-temperature.html). Schematics and photos of the mesocosms are shown in Fig. 5 and Fig. A6. Temporal trends of the blended cover performance were monitored by conducting PSD sampling at 5 days and 145 days after the blended cover installation. During each assessment, PSDs were deployed for 28 days.

### 2.2.3. Passive sampling

In-situ passive sampling techniques were applied to assess the bioavailable fraction of DDx and dieldrin in the test systems. Low-density PE with no additives and a thickness of 51 μm (Brentwood Plastics, St. Louis, MO) was chosen as a passive sampling sorbent, for which the sampling method has been well-developed and validated (Lin et al., 2017; Oen et al., 2011). Detailed passive sampling methods, DDx/dieldrin analysis methods, and freely dissolved DDx/dieldrin concentration calculation methods are provided in the supporting information (Appendix A1.3). Briefly, DDx/dieldrin concentrations in PE samplers were determined using GC-μECD analysis (Lin et al., 2017; Thompson et al., 2016) following EPA sample cleanup methods (EPA Methods 3660B and 3620C). The performance reference compound (PRC) technique (Tomaszewski and Luthy, 2008) was used to calculate freely dissolved DDx/dieldrin concentrations. 2,4,5-Trichlorobiphenyl (PCB 29) was used as the PRC due to its similarity in PE partition coefficient and molar volume as DDx (Table A 4). The variability of impregnated PCB29 was less than 10 %. Its depletion after 28 days of exposure was 66 %.
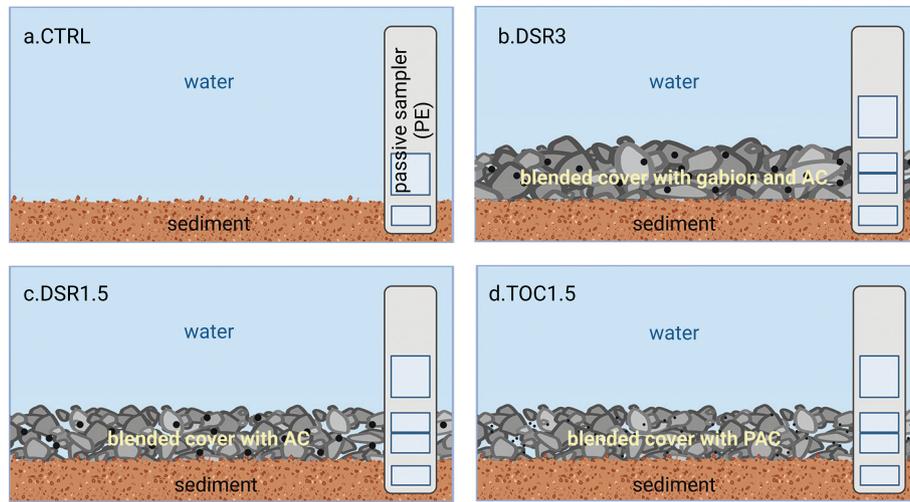
**Fig. 5.** Schematics of the blended cover mesocosm treatability study: a- non-amended control, Site sediment only, b- a mixture of 3.8-cm aggregate base (AB) and 7.6-cm gabion (1:1) as a blended cover amended with AC, c- 3.8-cm AB with AC, and d- 3.8-cm AB with PAC. Images created with Biorender.com, not to scale.

## 3. Results

### 3.1. Blended cover stability

#### 3.1.1. Bottom shear stress of blended cover

'Base condition' flume runs confirmed the flow velocity with a specific level of pump power. The flume and the contraction channel system achieved a mean flow velocity up to 1.01 m/s. The flow rate plateaued beyond 75 % pump power and subsequent tests were conducted at 75 % power to avoid overstraining the pump. The bottom shear generated by the system's flow rate was evaluated to determine whether the flow contraction system was able to create the bottom shear stress equivalent or exceeding the target 9 Pa estimated for a blended cover under worst-case propeller scour at the Site.

To compute the bottom shear, we utilized the manometer readings (Fig. A4 and Table A7). For the case of a straight duct with a constant cross-sectional area undergoing steady, fully developed turbulent flow, the perimeter- and time-averaged momentum balance simplifies to:

$$\frac{P_u - P_d}{L} = \frac{1}{R_H}\overline{\tau_w} \tag{3}$$

where $P_u, P_d$ are the upstream and downstream pressure (Pa) respectively, $L$ is the length of the duct (m), $R_H$ is the hydraulic radius of the duct (m), and $\overline{\tau_w}$ is the average wall shear stress (Pa) (Kundu et al., 2016). The hydraulic radius is calculated as $R_H = A/P \cong (WH)/2(W+H)$, where $W$ and $H$ are the width and height of the flow channel (m) respectively. This is simplified as $R_H = H/3$, where $W = 2H$ in this study. The pressure terms in Eq. 3 were converted into head measurements and then rearranged to compute shear stress for both the smooth inlet section and the blended cover section:

$$\overline{\tau_w} \cong \frac{\rho g H(h_u - h_d)}{3L} \tag{4}$$

where $h_u$ and $h_d$ are the upstream and downstream head measurements (m), $\rho$ is the water density (kg/m³), $g$ is the acceleration due to gravity (m/s²). The average wall shear stress is determined by perimeter-weighting the wall stress from all four sides. Consequently, the wall stress for a specific side can be extracted using the perimeter-weighted equation. The shear stresses for both the smooth acrylic surface and the blended cover can be obtained from the average wall shear stresses using the following relationships.

$$\overline{\tau_{w,bc}} \cong \frac{\overline{\tau_s}(W + 2H) + \overline{\tau_{BC}}W}{2W + 2H} = \frac{2\overline{\tau_s} + \overline{\tau_{BC}}}{3} \tag{5}$$

$$\overline{\tau_{w,inlet}} = \overline{\tau_s} \tag{6}$$

$\overline{\tau_{w,bc}}$ is the average wall shear stress of the blended cover section (test section + boundary layer build up section) (Pa) and $\overline{\tau_{w,inlet}}$ is the average wall shear stress of the inlet section (Pa). $\overline{\tau_{BC}}$ is the wall shear stress of the blended cover surface (Pa) and $\overline{\tau_s}$ is the wall shear stress of the acrylic surface (Pa). The bottom stress of the blended cover layer, calculated at a flow velocity of 1.0 m/s, was 22.4 Pa. This greatly exceeds the expected shear stress expected for a cover layer at the Site (~ 9 Pa).

We also utilized two other methods for shear calculation: assuming a logarithmic velocity profile with depth (logarithmic law of the wall) and vertical momentum flux, as detailed in the Supporting Information (Appendix A2.2). Each method for evaluating shear stress has its own assumptions with pressure drop measurements being perhaps the most direct and providing a shear stress value of 22.4 Pa. Still, considering the three methods, we estimated bottom shear stress values between 8.6 and 30.9 Pa at a flow velocity of 1.0 m/s (75 % pump power). These values are comparable to, or greater than, the target worst-case simulated site conditions of 8.95 Pa. This suggests that the flume system effectively replicated the most challenging field disturbances from vessel activities, allowing us to assess the stability of the blended cover under these conditions.

Under the applied bottom shear stress, we observed minimal displacement of the aggregate base cover materials during the flume tests. However, incipient movement of a few cover aggregates did occur on the surface. On rare occasions, cover aggregate material dislocation occurred, though, only one or two pieces were dislodged during each 10-min run. This loss accounts for less than 0.01 % of the total cover material mass. Therefore, it is evident that the blended cover effectively resisted the prevailing estimated maximum shear stress on the cover bed. This suggests that the critical shear stress for the cover material aggregate base is likely equal to, or exceeds, the test conditions (9–31 Pa). Further, the applied bottom stress in this study is much larger than the calculated critical shear stress of the Site sediment (0.1 Pa to 1. 28 Pa (CH2M HILL, 2015)). Hence, the blended cover material will not erode under the expected worst-case scouring conditions at the Site.

Finally, the stability of the blended cover itself agrees with critical shear stress approximation by particle-size classification (Berenbrock and Tranmer, 2008). The approximate critical bed shear stress for coarse gravel is in the range of 12–26 Pa, while that for coarse sand is in the range of 0.3–0.5 Pa.
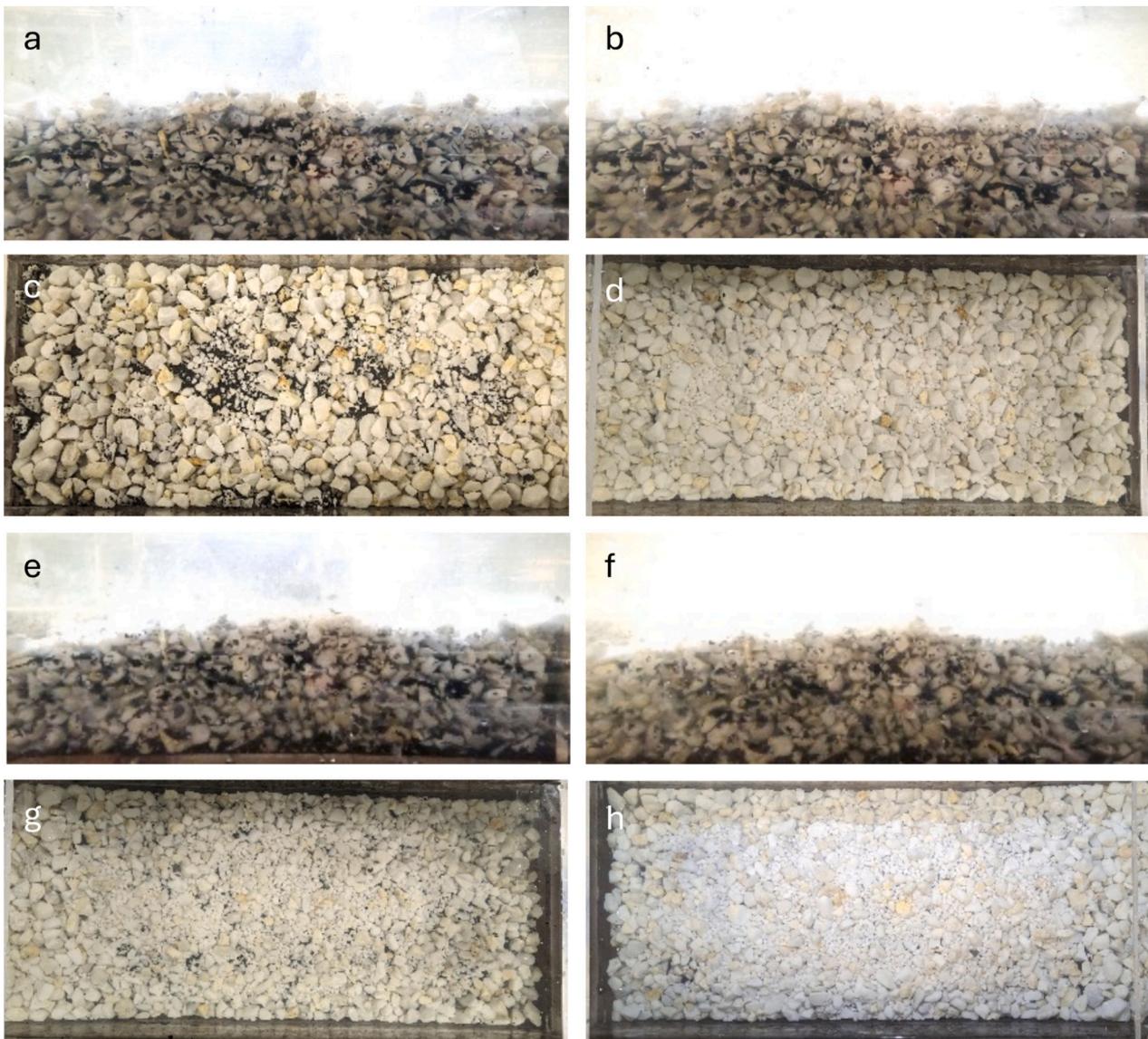
**Fig. 6.** (a-d) Flume test: side view of the test section before and after 30 min scouring (a and b), top view of the test section before (c) and after (d) showing loss of AC from the top of the aggregate base. (e-h) Flume with simulated disruption test: side view before and after (e and f), top view before and after (g and h).

### 3.1.2. Erosion protection of AC by the engineered blended cover

Fig. 7 highlights the percentage of remaining AC during three, consecutive, 10-min erosion tests for the blended cover at maximum shear (1.0 m/s, corresponding to 9 to 31 Pa). The amount of eroded AC quantities in the flume experiment remained below 2 %. Assuming a homogeneous distribution of AC throughout the layer, the loss of AC was limited to the top few mm of the cover layer. Once that AC mass is eroded (primarily in the first scouring event, Fig. 6a-d), additional loss of AC from the lower layers of the cover is expected to be minimal. Thus, repeated propwash scour events are not expected to result in additional erosion and removal of the AC from the blended layer.

Although the difference was less than 1 %, the AC loss rates in the test runs study (1.8 %) are greater than those observed in the bench-scale propeller study (1 %). This is attributed to the presence of some suspended particles from the flume apparatus, like sand particles, corroded metal flakes, and sealant chips. These particles, along with the dislodged AC, were caught by the exit particle screen (Fig. A18). While larger non-AC particles were removed using a tweezer, many remained due to separation challenges. This could potentially lead to an overestimation of the retrieved AC. Possible overestimation of the amount of eroded AC suggests the experiments in this study represent a conservative

demonstration of the blended cover's performance under the examined conditions.

The greater disturbance in the flume, compared to the propeller test, along with unidirectional disturbance, could also enhance AC displacement from the test area. The top-view of the blended cover, Fig. 6c and d, vividly illustrates AC loss from the top-most exposed AC, with erosion being most pronounced in the initial minutes of a run and decreasing greatly thereafter. Along with AC erosion from the surface of the blended cover, there was a clear indication of AC particles infiltrating downward in the bed, facilitated by the horizontal flow turbulence and mixing into the hyporheic zone. This infiltration phenomenon resembles widely-known sand or fine sediment infiltration into a gravel bed that occurs frequently in river or stream systems (Gibson et al., 2011).

We assessed the resilience of the blended cover by removing its top-layer to simulate disturbance of the blended cover material. Notably, no AC was detected in the removed layer. Even after removing approximately 1/6 of the cover material's volume, the exposed AC was less than in the undisturbed blended cover prior to the scouring tests (see Fig. 6g). This strongly indicates the AC particle's likely penetration deeper into the blended cover. In the flume test, the repositioning of AC led to a

**Table 3**

Amount of eroded AC during the bench-scale scouring tests and flume tests after three, consecutive, 10-min erosion tests.

| Test | Configuration | AC loss (wt% of total AC amended) | Cover material loss (wt% of total material installed) |
|---|---|---|---|
| Bench-scale propeller study | Rounded gravel, @ 2000 rpm | 0.2 % | 0.0 % |
| | Angular gravel, @ 2000 rpm | 1.0 % | 0.2 % |
| | Sand, @ 2000 rpm (one 10-min test only) | 17.8 % | 17.8 % |
| Flume study | Angular gravel, @ 1.0 cm/s | 1.8 % | NA |
| | Top 2.5 cm gravel removed, @ 1.0 cm/s | 1.1 % | NA |

minimal erosion of approximately 1.1 % after removal of the top 2.5 cm of the blended cover. Collectively, these findings confirm the blended cover configuration's effectiveness in safeguarding AC against agitation. Moreover, the tests demonstrate that losses remained under 2 % throughout a 30-min maximum scouring event. We observed little-to-no AC erosion after the first minute or two during the third consecutive test in-a-row. Table 3 summarizes results of both bench scale propeller tests and flume erosion tests.

To further explore the likelihood of AC downward infiltration into the bed driven by flow, we introduced AC into the water ahead of the test section. Each 100 mL AC spike simulates a 2.5 % AC erosion from

the test section. Impressively, over half of the AC was captured within the 1.8 m of the blended cover sections as it flowed through the flume (Fig. 8). Repeated tests consistently showed an average capture efficiency of 71.3 % ($n = 3$) of AC within the bed (Fig. 8). This indicates not only the additional protective role of the blended cover against previously mobilized AC, but also underscores the contrasting nature of horizontal flows in both mobilizing unarmored AC and assisting its settlement into armored positions.

### 3.2. Blended cover treatability

#### 3.2.1. Passive sampler DDx/dieldrin uptakes ($C_{PE}$)

Fig. 9a presents concentrations measured directly from the PE passive sampler devices and shows a large statistically significant difference in the PE DDx uptake between the unamended control and the three blended cover-amended systems (t-test, $p < 0.05$). Notably, the blended cover-amended systems demonstrated significant effectiveness at just 5 days post-treatment, resulting in a substantial reduction in surface water contaminant concentrations of 97 % and higher (compared to the surface water in the unamended sediment). Furthermore, noteworthy reductions were observed in DDx PE uptakes within the blended cover with reductions of 97 % and higher. Whereas surface water PE uptake was unaffected by the sizes of blended cover material or AC, the finer blended cover material or finer AC appeared more effective in reducing contaminant concentrations in sediment, though not to a statistically significant degree.

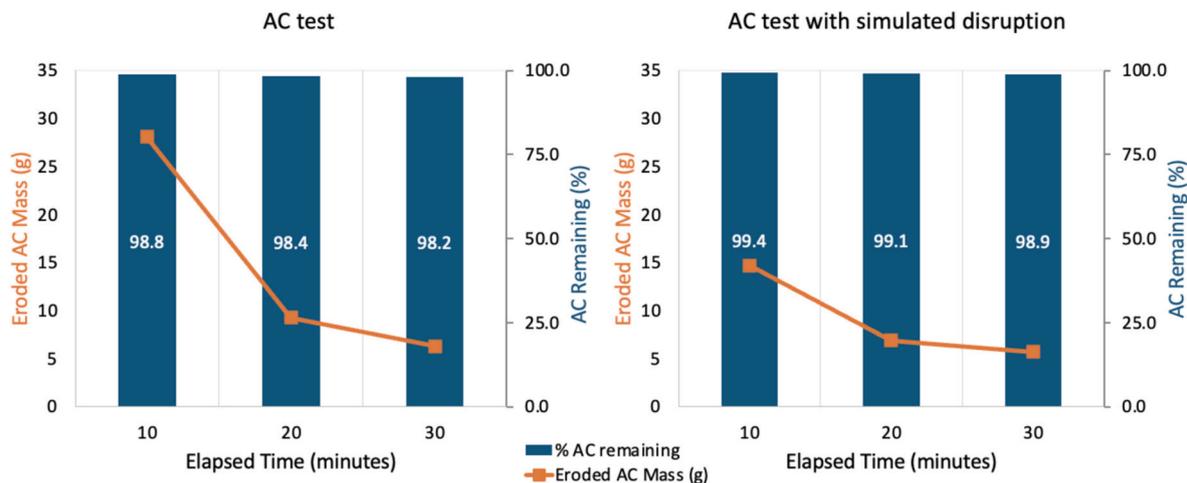The treatment effect was affirmed with sampling after 5 months (day



**Fig. 7.** (Left) Dry mass of eroded AC and percentage of remaining AC relative to the total AC added during the successive 10-minutue scouring events for the flume tests. (Right) eroded AC (g) and remaining AC (%) for the flume with simulated disruption test by removing the top-most gravel layer.



**Fig. 8.** AC Infiltration test: The left image shows the AC that infiltrated the flow build-up section after the first addition of AC (100 mL, approximately 55 g). The right image displays the AC trapped after two more consecutive AC introductions.
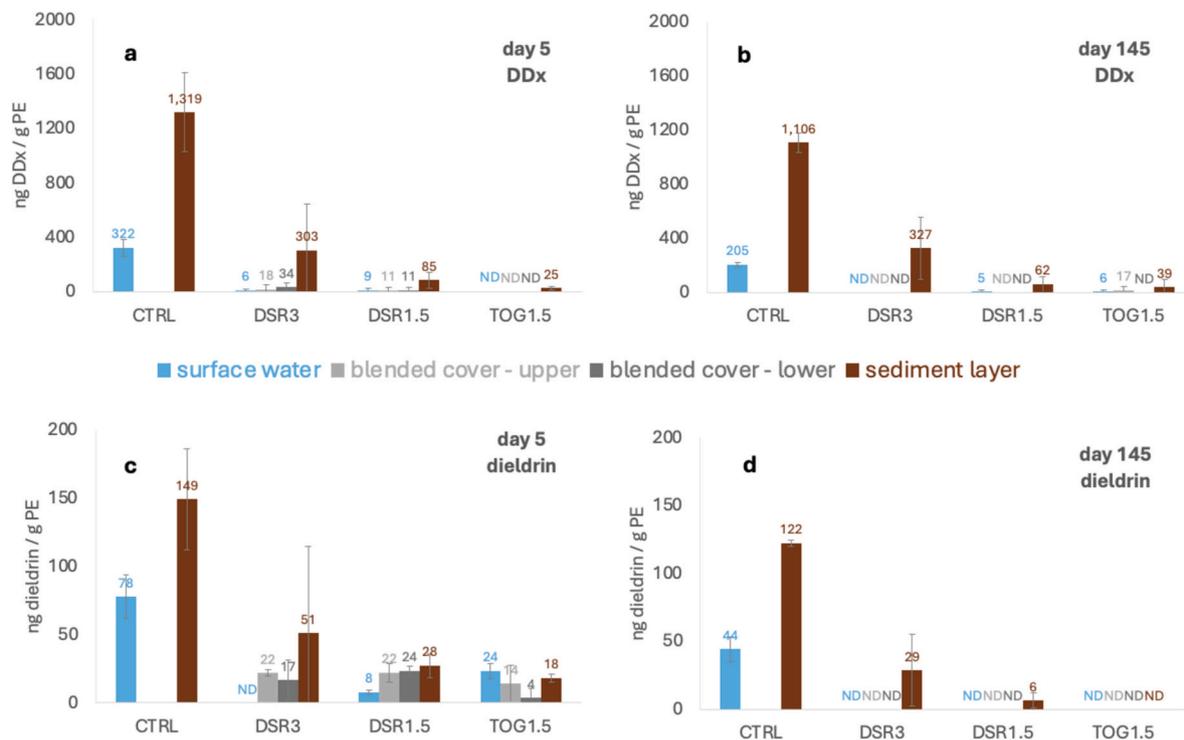
**Fig. 9.** DDx/dieldrin PE uptakes ($C_{PE}$) from passive sampler deployment 5 days and 145 days after blended cover treatment. Bars represent the mean values, and error bars indicate one standard deviation ($n = 3$) for overlying surface water, within the blended cover, and in the sediment layer. ND refers to < MDL.

**Table 4**

The percentage reduction in PE and aqueous concentrations of DDx and dieldrin in the blended cover compared to those of the control sediment. With consideration of MDL, detectable percentage reductions for DDx and dieldrin are 99 % and 95 %, respectively. Values represent averages and one standard deviation ($n = 3$).

| | | DSR3 | | DSR1.5 | | TOG1.5 | |
|---|---|---|---|---|---|---|---|
| | | 5 d | 145 d | 5 d | 145 d | 5 d | 145 d |
| $C_{PE}$ | DDx | 98 ± 1 % | >99 % | 99 ± 1 % | >99 % | >99 % | >99 % |
| | Dieldrin | 87 ± 7 % | >95 % | 86 ± 5 % | >95 % | 94 ± 6 % | >95 % |
| $C_{free}$ | DDx | >99 % | >99 % | >99 % | >99 % | >99 % | >99 % |
| | Dieldrin | 87 ± 6 % | >95 % | 85 ± 5 % | >95 % | 94 ± 6 % | >95 % |

145; Fig. 9b), and a similar 98 % and greater reduction of DDx in surface water and blended cover layers was observed as compared to the 5-day post-treatment measurements. The surface water PE uptake in the control group decreased somewhat from about 322 ng/g to 205 ng/g. This is attributed to the increased desorption of DDx from sediment during initial placement and release from suspended sediment during placement, followed by later sorption onto other surfaces.

For dieldrin, a parallel pattern emerged, with a noticeable temporal enhancement in blended cover performance (Fig. 9c and d). The initial reduction in dieldrin PE uptake from surface water during post-assessment (day 5, Fig. 9c) was 69 % to >92 %. On day 145 (Fig. 9d), the concentration of dieldrin accumulated in the PE during treatments was non-detect, indicating at least an 86 % reduction in dieldrin availability relative to surface water in the unamended controls. This trend was also observed in PE uptakes from the blended cover layers, achieving greater than 95 % compared to the unamended sediment, signifying effective reduction of dieldrin within the blended cover layers (Table 4).

Overall, PE uptake data effectively showcased the performance of the blended cover in reducing contaminant concentrations in porewater and surface water, irrespective of the size of blended cover material or AC. The study underscored the advantageous role of AC in reducing the availability of DDx/dieldrin in contaminated sediment layers, extending beyond merely blocking the flux out of the sediment layer.
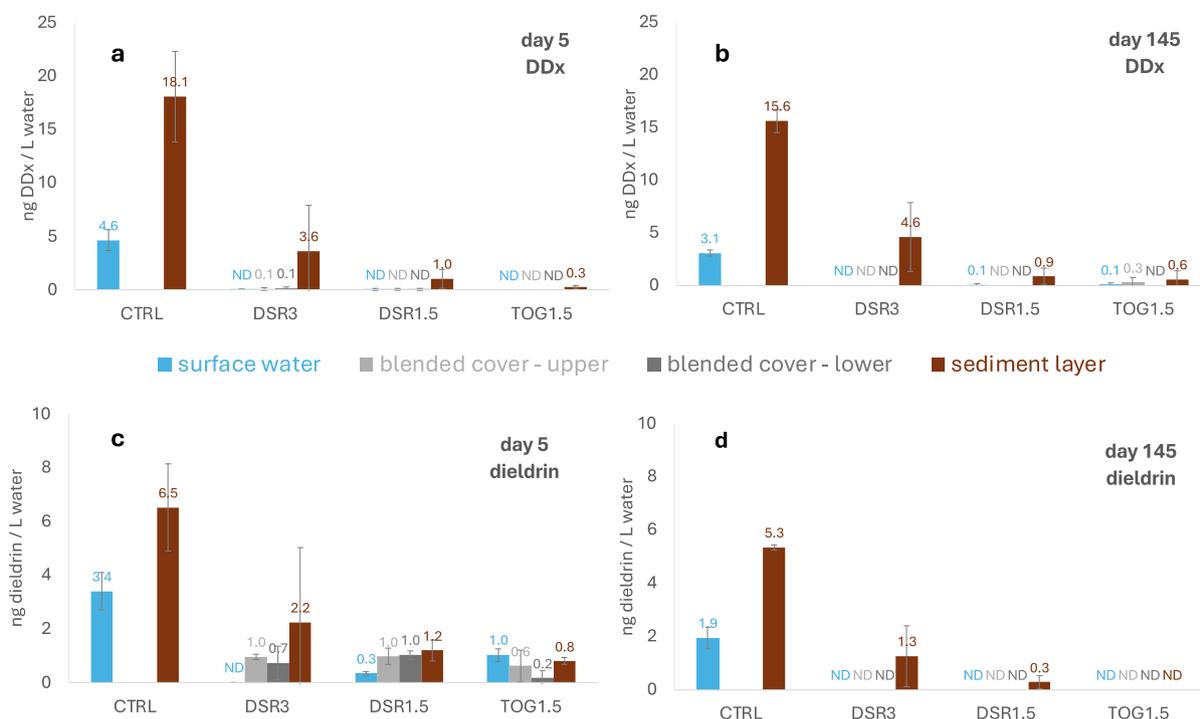
*3.2.2. Freely dissolved DDx/dieldrin concentration ($C_{free}$)*

To delve deeper into treatability, the freely dissolved fraction of DDx and dieldrin ($C_{free}$) was computed, as illustrated in Fig. 10. Like PE uptake, this analysis reaffirmed a notable performance, achieving a reduction in DDx $C_{free}$ of 97 % in surface water and 99 % in the blended cover layers relative to the unamended controls (Fig. 10a and b). Surface water concentrations for DDx $C_{free}$ were nondectable to 0.1 ng/L. For dieldrin, $C_{free}$ in the overlying water concentrations for the treatments were 71 % to 91 % lower than controls at day 5 and more than 95 % lower than controls at day 145 (Fig. 10c and d). $C_{free}$ dieldrin in the blended cover layers was 85 % to more than 95 % lower than controls at day 5 and more than 94 % than controls at day 145 (Table 4).

The observed $C_{free}$ values can be compared with the EPA Record of Decision (ROD) preliminary remedy goals for the Site of 0.59 ng/L for DDx and 0.14 ng/L for dieldrin. For DDx, the blended cover remedy effectively lowered both surface water and blended cover $C_{free}$ below the ROD remedy goal. In the case of dieldrin, after 145 days, $C_{free}$ in the overlying water and blended cover layers of the treatments was non-detect (< 0.3 ng/L), which was likely similar to or below the ROD remedy goal of 0.14 ng/L.

## 4. Conclusions

This study demonstrated that an engineered blended cover of aggregate and AC offers an in-situ remedy treatment method to withstand site-specific disturbances that might otherwise pose concerns for the success of the remedy. Using the Lauritzen Channel at the United Heckathorn Superfund Site as a study site, we evaluated the feasibility of an engineered AC-blended cover option under site-specific disturbances,

**Fig. 10.** Freely dissolved DDx/dieldrin ($C_{free}$) from passive sampler deployment 5 days and 145 days after blended cover treatment. Bars represent the mean values, and error bars indicate one standard deviation (n = 3) for overlying surface water, within the blended cover, and in the sediment layer. ND refers to < MDL.

considering both stability and treatability. First, the simulated the worst-case scour scenario anticipated at the channel employed a confined horizontal flume and evaluated AC erosion. The flume created a fluid shear stress of 22 Pa with a possible range of 9–31 Pa, which is comparable to, if not greater than, the worst-case bottom stress as estimated by vessel scour events. A mesocosm study validated the treatment effectiveness of the AC-amended blended cover design with various sizes of blended cover materials and AC in reducing the availability of site contaminants: DDx and dieldrin. The highlights and implications of the findings are:

- An engineered blended cover, with medium-size angular gravel (sized lower than 20 mm, with $D_{50}$ = 15 mm), proved effective in safeguarding AC erosion under scour conditions that mimicked estimated worst-case maximum shear stress at the United Hecka-thorn Site. The test results build confidence in an engineered AC-blended cover suitability for high-energy areas at the site that would result from maximum tugboat thrust. When considering the minimal loss of AC observed ($\approx$1–2 %, limited to the uppermost several mm of the blended cover layer), it is evident that as long as the cover material remains stable, the erosion of AC due to shear stress remains negligible.
- Given the standard engineering safety factors on AC dosing, which can sometimes increase to 100–200 %, a minor loss in the range of a few percentage points is insignificant and can be reasonably integrated into the remedy design. Consequently, a blended cover constructed at 4 % AC by weight would, after repeated worst-case scour events, stabilize at an AC content of 3.96 % AC by weight. This dosage far exceeds lower AC dosages (e.g., 0.5 % to 1 % AC by weight) that have been demonstrated to reduce the availability and mobility of organic compounds in sediment (Tomaszewski et al., 2007; Zimmerman et al., 2005).
- By adjusting the size of the cover material or controlling the positioning of AC within the blended cover, this engineering approach can be refined to allow the AC blended cover to withstand even more intense hydrodynamic forces. The blended cover also offers the added benefit of AC entrapment. Compared to fine grain smooth surfaces, a more interlocking, crushed gravel surface like the one used in our blended cover testing, could capture any displaced AC. Flume tests revealed 71 % entrapment within 2 m in the enclosed flume channel. While turbulence mobilizes unarmored AC, turbulence also assists in embedding the AC into the blended cover through hyporheic flow phenomena.

- For DDx and dieldrin, the blended cover amendment effectiveness was readily apparent in reducing the freely dissolved fraction in the blended cover and surface water, $C_{free}$, by greater than 94 % (dieldrin) and greater than 98 % (DDx) by the end of the 145-day study. The blended cover was effective with different AC sizes (GAC and PAC) and different blended cover material sizes. The blended cover amendment successfully met the preliminary EPA ROD remedy goals for the Site for DDx, and likely met the remedy goals for dieldrin, based on evaluation of concentrations in both surface water and within the blended cover layer.

- The results from this study can guide the design of a proposed engineered AC-blended cover remedy. When combined with model simulations, the study bolsters confidence in the predictive capabilities of such simulations. Variations in materials can be effectively tested in calibrated model simulations.

**CRediT authorship contribution statement**

**Yeo-Myoung Cho:** Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Brooke J. Pauken:** Writing – review & editing, Visualization, Methodology, Investigation. **Anna E. Tovkach:** Writing – review & editing, Visualization, Methodology, Investigation. **Oliver B. Fringer:** Supervision, Methodology, Conceptualization. **Stephen G. Monismith:** Supervision, Methodology, Conceptualization. **Richard G. Luthy:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data will be made available on request.

**Acknowledgement**

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2024.104445.

**References**

Anchor QEA, 2024. Data Summary Report – Sediment Sampling. Stanford University, Geosyntec Consultants, and Exponent. United Heckthorn Superfund Site.

Berenbrock, C., Tranmer, A.W., 2008. Simulation of flow, Sediment Transport, and Sediment Mobility of the Lower Coeur d'Alene River, Idaho, pp. 2008–5093.

CH2M HILL, 2011. Third Five-Year Review Report for United Heckathorn Superfund Site Richmond, California. USEPA Region, p. 9.

CH2M HILL, 2015. Draft Focused Feasibility Study United Heckathorn Superfund Site, USEPA Region, p. 9.

Cho, Y.-M., et al., 2009. Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. Environ. Sci. Technol. 43 (10), 3815–3823.

Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: a new direction in contaminated sediment management. Environ. Sci. Technol. 45 (4), 1163–1168.

Gibson, S., Heath, R., Abraham, D., Schoellhamer, D., 2011. Visualization and analysis of temporal trends of sand infiltration into a gravel bed. Water Resour. Res. 47 (12).

Kundu, P.K., Cohen, I.M., Dowling, D.R., 2016. Chapter 12 - turbulence. In: Kundu, P.K., Cohen, I.M., Dowling, D.R. (Eds.), Fluid Mechanics, Sixth edition. Academic Press, Boston, pp. 603–697.

Lin, D., et al., 2017. Toolset for assessment of natural recovery from legacy contaminated sediment: case study of Pallanza Bay, Lake Maggiore, Italy. Water Res. 121, 109–119.

Millward, R.N., Bridges, T.S., Ghosh, U., Zimmerman, J.R., Luthy, R.G., 2005. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). Environ. Sci. Technol. 39 (8), 2880–2887.

Oen, A.M.P., et al., 2011. In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. Environ. Sci. Technol. 45 (9), 4053–4059.

Patmont, C.R., et al., 2015. In situ sediment treatment using activated carbon: a demonstrated sediment cleanup technology. Integr. Environ. Assess. Manag. 11 (2), 195–207.

Thompson, J.M., Hsieh, C.H., Hoelen, T.P., Weston, D.P., Luthy, R.G., 2016. Measuring and modeling organochlorine pesticide response to activated carbon amendment in tidal sediment mesocosms. Environ. Sci. Technol. 50 (9), 4769–4777.

Tomaszewski, J.E., Luthy, R.G., 2008. Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. Environ. Sci. Technol. 42 (16), 6086–6091.

Tomaszewski, J.E., Werner, D., Luthy, R.G., 2007. Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. Environ. Toxicol. Chem. 26 (10), 2143–2150.

US EPA, 2021. Summary of Study for Lower Duwamish Waterway: Enhanced Natural Recovery and Activated Carbon: Fact Sheet, EPA Region 10, Seattle, WA.

US EPA, 2024. EPA's Superfund Site Information for UNITED HECKATHORN CO. https://cumulis.epa.gov/supercpad/CurSites/csitinfo.cfm?id=0902440&msspp=med.

Zimmerman, J.R., Ghosh, U., Millward, R.N., Bridges, T.S., Luthy, R.G., 2004. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physicochemical tests. Environ. Sci. Technol. 38 (20), 5458–5464.

Zimmerman, J.R., et al., 2005. Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. Environ. Toxicol. Chem. 24 (7), 1594–1601.