Remediation and Restoration

Sediment Remediation Using Activated Carbon: Effects of Sorbent Particle Size and Resuspension on Sequestration of Metals and Organic Contaminants

Robert Rämö,a,* Stefano Bonaglia,a Inna Nybom,b Anne Kreutzer,c Gesine Witt,c Anna Sobek,b and Jonas S. Gunnarsson,a

aDepartment of Ecology, Environment and Plant Sciences, Stockholm University, Stockholm, Sweden
bDepartment of Environmental Science, Stockholm University, Stockholm, Sweden
cDepartment of Environmental Technology, Hamburg University of Applied Sciences, Hamburg, Germany

Abstract: Thin-layer capping using activated carbon has been described as a cost-effective in situ sediment remediation method for organic contaminants. We compared the capping efficiency of powdered activated carbon (PAC) against granular activated carbon (GAC) using contaminated sediment from Oskarshamn harbor, Sweden. The effects of resuspension on contaminant retention and cap integrity were also studied. Intact sediment cores were collected from the outer harbor and brought to the laboratory. Three thin-layer caps, consisting of PAC or GAC mixed with clay or clay only, were added to the sediment surface. Resuspension was created using a motor-driven paddle to simulate propeller wash from ship traffic. Passive samplers were placed in the sediment and in the water column to measure the sediment-to-water release of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and metals. Our results show that a thin-layer cap with PAC reduced sediment-to-water fluxes of PCBs by 57% under static conditions and 91% under resuspension. Thin-layer capping with GAC was less effective than PAC but reduced fluxes of high–molecular weight PAHs. Thin-layer capping with activated carbon was less effective at retaining metals, except for Cd, the release of which was significantly reduced by PAC. Resuspension generally decreased water concentrations of dissolved cationic metals, perhaps because of sorption to suspended sediment particles. Sediment resuspension in treatments without capping increased fluxes of PCBs with log octanol–water partitioning coefficient (K_{OW}) > 7 and PAHs with log K_{OW} of 5–6, but resuspension reduced PCB and PAH fluxes through the PAC thin-layer cap. Overall, PAC performed better than GAC, but adverse effects on the benthic community and transport of PAC to nontarget areas are drawbacks that favor the use of GAC. Environ Toxicol Chem 2022;41:1096–1110.© 2022 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls; Metals; Marine pollution; Sediment remediation; Resuspension

INTRODUCTION

Activated carbon amendment is a promising approach for in situ remediation of contaminated sediments, which offers a less intrusive and more cost-effective treatment than conventional methods such as dredging or isolation capping (Ghosh et al., 2011; Kupryianchyk et al., 2015; Patmont et al., 2014). Activated carbon has a high sorption affinity for hydrophobic organic contaminants (HOCs) that readily accumulate in sediment, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs; Chai et al., 2012; Millward et al., 2005; Zimmerman et al., 2004). Activated carbon amendment increases sorption and sequestration of HOCs in the sediment and reduces aqueous concentrations, resulting in lower bioavailability and bioaccumulation of HOCs in benthic organisms (Kupryianchyk et al., 2012; McLeod et al., 2007; Millward et al., 2005; Zimmerman et al., 2004). Activated carbon amendment has been primarily studied for sequestration of HOCs, but activated carbon may also increase the sequestration of metals in sediment. Netzer and Hughes
(1984) reported pH-dependent sorption of Pb, Cu, and Co to activated carbon. Van Sprang and Janssen (2001) reported sequestration of Cd and Ni and described activated carbon as a weak cation exchanger. Also, activated carbon is known to be an effective sorbent for Cd and Zn in wastewater treatment (Ku & Peters, 1987).

Capping efficiency, that is, reduction of freely dissolved contaminants and their bioavailability, has been found to depend on both the dose of activated carbon and its particle size (Zimmerman et al., 2005), where powdered activated carbon (PAC; <300 µm) is more efficient than granular activated carbon (GAC; 300–2000 µm). The higher sorption capacity of finer particles is due to a larger proportion of the total surface area of the particle being readily accessible from the outside of the particle, which allows for rapid sequestration (Sun & Ghosh, 2007; Tomaszewski et al., 2007; Zimmerman et al., 2005). However, prolonged contact times allow for mass transport further into the particles, and GAC may over time achieve a similar capping efficiency to PAC (Choi, Cho, Werner, & Luthy, 2014; Kupryianchyk et al., 2013b; Werner et al., 2006).

Several techniques have been used to place activated carbon in aquatic environments. Mixing activated carbon into sediment results in a homogenous distribution of activated carbon in the sediment with a high initial remediation effectiveness (Choi, Cho, & Luthy, 2014; Choi, Cho, Werner, & Luthy, 2014) but disturbs the contaminated sediment and its benthic community. In situ thin-layer capping, where activated carbon is deposited on the sediment surface, often requires no specialized equipment and therefore is more cost-effective than mechanical mixing (Kupryianchyk et al., 2015; Patmon et al., 2014). Bioturbation is expected to distribute the activated carbon from a thin-layer cap into the biologically active layer over time (Cornelissen et al., 2011, 2012; Lin et al., 2014).

The suitability of thin-layer capping depends on the capping materials, ongoing emission of contaminants and deposition of contaminated sediment, site conditions such as water currents and bathymetry, and erosional forces such as sediment resuspension (Abel & Akkanen, 2018; Cornelissen et al., 2012; Graham et al., 2013; Lampert et al., 2011). Resuspension may lead to dispersal of contaminated particles and facilitates contaminant desorption into the overlying water (Birdwell & Thibodeaux, 2007; Kalnejaïs et al., 2010; Latimer et al., 1999). Because activated carbon particles have near-neutral buoyancy, they may be transported from a site of application by storms, currents, and propeller wash, leading to erosion of the thin-layer cap over time. Various pelletized forms of activated carbon and clay mixtures have been formulated to improve deployment and retention of activated carbon thin-layer caps, including SediMite® and AquaGate® (Abel & Akkanen, 2019; Chadwick et al., 2017; Menzie et al., 2016); but these are not evaluated in the present study.

Abel and Akkanen (2018) studied activated carbon thin-layer capping in a shallow lake in Finland and reported high losses of PAC following storm events, as well as rapid burial of the thin-layer cap under freshly deposited contaminated sediment. Cornelissen et al. (2011) studied thin-layer capping in a Norwegian harbor and reported 70% loss of PAC from a pure thin-layer cap after 1 year; however, a blend of PAC and clay improved retention rates and reduced losses to 40%. In a large field experiment in the Grenland fjords (Norway), a thin-layer cap of activated carbon mixed with clay was found to persist 9 years posttreatment, and the thin-layer cap remained effective despite recontamination by sediment transported from surrounding areas (Schaanning et al., 2021).

Generally, field experiments have favored PAC thin-layer capping rather than GAC because of the higher initial remediation efficiency, but it is clear that cap retention is sometimes an issue. Larger particles generally require more energy to resuspend than smaller ones (Graham et al., 2013), which means that using GAC may improve retention of a thin-layer cap compared to PAC. However, the smaller activated carbon particles have higher initial remediation efficiency, which means there is a trade-off to make between initial remediation efficiency and long-term retention of a thin-layer cap in sites with sediment resuspension.

The aims of the present study were to assess the effects of activated carbon thin-layer capping and resuspension on HOC and metal release from contaminated sediment. We simulated frequent resuspension by ship traffic in a 2-month laboratory experiment using intact sediment cores from a contaminated harbor. We measured sediment-to-water release and pore-water concentrations using a two-factorial design, static (non-resuspended) or resuspended condition, and four thin-layer capping treatments: (1) GAC mixed with clay, (2) PAC mixed with clay, (3) clay only, or (4) uncapped sediment.

To our knowledge, this is the first study that investigates the effects of resuspension on activated carbon thin-layer capping under controlled laboratory conditions and one of the few studies to assess effects on both organic contaminants and metals. We expect that sediment resuspension increases the release of HOCs and metals to overlying water and that activated carbon thin-layer capping reduces contaminant release. We expect thin-layer capping with activated carbon to be more effective than capping with clay only and for thin-layer capping to be more effective with PAC than with GAC.

MATERIALS AND METHODS

Study area and field sampling

Sediment cores were collected from the outer basin of Oskarshamn harbor, Sweden (Figure 1). Oskarshamn is one of the most contaminated harbors in Sweden, owing to historic industrial emissions from a copper processing plant (in operation 1918–1969), a battery factory, and municipal wastewater, all of which were released into the inner harbor until more strict environmental regulations came into force in 1969. The harbor is an active freight port with an oil terminal and connects passenger ferries to the Baltic Sea and several Swedish islands.

The Oskarshamn harbor sediment is known to contain PAHs, PCBs, polychlorinated dibenzodioxins/dibenzo furans, organotin compounds (e.g., tributyltin), and metals (As, Cd, Cu, Hg, Pb, and Zn). Swedish environmental quality criteria show that concentrations of PAHs and PCBs are among the highest
measured in Swedish sediment (exceeding 75th and 95th percentiles of Swedish sediment samples, respectively), and metals in the harbor very strongly deviate (exceed 95th percentile) from preindustrial concentrations (Sveriges Geologiska Undersökning, 2017; Swedish Environmental Protection Agency, 2000). Swedish guidelines and environmental quality criteria do not relate to toxicity risks, but sediment concentrations of \( \Sigma PAH_{16}, \Sigma PCB_7 \), As, Cd, Cu, Hg, Ni, Pb, and Zn in Oskarshamn harbor exceed Norwegian threshold values for ecological risks (Breedbeld et al., 2018).

Because of the risk of contaminant spread from the harbor to the Baltic Sea and to help reach national environmental objectives of a nontoxic environment, contaminated sediments were dredged from the inner harbor basin in 2016–2018 and deposited at a purpose-built landfill, which made it the largest state-funded sediment remediation project in Sweden (Oskarshamn Municipality; Swedish Environmental Protection Agency, 2012). The outer harbor basin was estimated to contain 25% of the total contaminant load of the harbor, but it was not remediated. Greater water depth and higher sediment volume make dredging of the outer harbor basin challenging and expensive; however, storms and other erosional events, as well as resuspension from ship traffic, may pose risks of contaminants spreading from the harbor into other areas of the Baltic Sea.

In May 2017, we collected three sediment grab samples using a van Veen sampler to analyze the benthic community composition in the Oskarshamn outer harbor (at sites E2, E3, and E4; Figure 1). A conductivity/temperature/depth sensor was used to measure sediment turbidity caused by ferry traffic over the sampling site (see Supporting Information, Section SI-1). Finally, a GEMINI corer was used to collect 32 intact sediment cores at the E2 station (Figure 1). The cores were handled with care to avoid sediment resuspension, transported to the sediment laboratory at Stockholm University, and stored in a thermo-constant room at 6°C for 8 weeks with constant gentle water aeration to acclimatize the benthic fauna in the cores and to allow sediment compaction. The temperature was gradually raised from 6 to 10°C before the start of the experiment to match summer field conditions.

### Thin-layer capping

The two bituminous coal–based activated carbon (Jacobi Carbons) used in the present study were PAC with a 15–35-µm median particle size (AquaSorb BP2, size PAC-S) and GAC in the 0.425–0.850-mm range (AquaSorb 2000, size 20 × 50). The thin-layer capping treatments were (1) control (no cap), (2) cap with only clay, (3) cap with clay and GAC, and (4) cap with clay and PAC. The use of an activated carbon–clay blend follows our previous work, where higher capping efficiency and fewer adverse effects on benthic macroinvertebrates were observed when activated carbon was mixed with clay in comparison to applying activated carbon only or covering activated carbon with a layer of sand (Cornelissen et al., 2011; Samuelsson et al., 2015). Glacial clay collected from an offshore reference site at 112 m depth in the Baltic Sea (WGS84 57°24′00″N, 19°20′98″E) was sieved through 0.5 µm to remove any macrofauna and then used as capping clay for the experiment.

The dose of each capping material (600 g m\(^{-2}\); Table 1) was chosen to reduce the release fluxes of contaminants but

| Static          | Resuspended |
|-----------------|-------------|
| Sedimentary clay (g m\(^{-2}\)) | 0 600 600 600 | 0 600 600 600 |
| Activated carbon (g m\(^{-2}\)) | 0 0 600 600 | 0 0 600 600 |
| Replicates (n)  | 4 4 4 4 | 4 4 4 4 |
| Treatment pairing | A B C D | A B C D |

A dose of 600 g m\(^{-2}\) corresponded to a dose of 3.02 g per sediment core.

*Shared letters indicate pairing of twin sediment cores.

GAC = granular activated carbon; PAC = powdered activated carbon.
to be thin enough to allow for measurable contaminant release over the 2-month experiment duration. The capping materials were mixed together with 50 ml of brackish seawater, and a homogenous suspension was gently poured into the water column. The sediment cores were allowed to settle for 7 days before the experiment started. References to the sediment surface refer to the boundary between overlying water and solid material: Thin-layer capping raised the position of the sediment surface by 3–5 mm above the natural sediment.

**Simulating resuspension**

The GEMINI core grabber retrieved two cores at a time, and each twin pair was amended with the same thin-layer capping treatment. The twin cores were then separated into the two resuspension treatments: One core was resuspended, and one core was kept in static condition with no resuspension (Table 1). The water column was maintained at 23 cm height (1.15 L water volume), and sediment resuspension was produced with a stainless-steel paddle (47 × 12 mm) mounted on a stainless-steel rod (8 mm) placed 2 cm above the sediment surface. The paddle rotation was controlled by an electric motor (RH158: 30:1 12 V; Micro Motors) set to 100 rpm, which was operated for 15 min twice daily. The setup is shown in Figure 2.

The speed of the rotor paddle was adjusted to obtain similar turbidities in all cores. Suspended particles were measured during resuspension by retrieving water samples (25 ml) from the center of the water column of each sediment core. The water sample was then vacuum-suctioned onto a GF-C filter and dried at 60 °C overnight to determine suspended matter concentration (grams dry wt per milliliter).

**Passive samplers**

Three types of passive samplers were used in the experiment. Detailed experimental and analytical methods are presented in Supporting Information, Sections SI-2–SI-4.

A semipermeable membrane device (SPMD; 91.4 cm standard purity; Environmental Sampling Technologies) was used to calculate sediment-to-water fluxes of dissolved HOCs (PCBs and PAHs were analyzed). The SPMD was mounted on a stainless-steel holder and hung in the water column using stainless-steel wire. Before use, all stainless-steel materials were placed in 0.1 M HCl overnight and then washed in deionized water to minimize metal leaching. The SPMD functions as an infinite sink for freely dissolved HOCs.

Glass fibers coated with polydimethylsiloxane (PDMS; 12.7 μm thickness on GF10 [Witt et al., 2013]; SPC210/230; Fiberguide Industries) were used to quantify freely dissolved porewater concentrations of PAHs and PCBs. The fibers were precleaned with a series of 15-min supersonic baths in ethyl acetate, then ultrapure water. Fibers were cut to 15-cm length and pushed into each sediment core in triplicate, leaving up to 2 cm of the fiber above the sediment surface. Matrix solid-phase microextraction (SPME) utilizes the whole sediment matrix as a reservoir for equilibrium extraction of freely dissolved HOCs to the PDMS, and based on previous studies, equilibrium for PAHs is reached after 30 days (Witt et al., 2009, 2013).

A diffusive gradient in thin film (DGT) device was placed in the overlying water to collect dissolved metals from the water column. The DGT consists of a Chelex binding layer covered with a 0.8-mm agarose cross-linked polyacrylamide diffusion gel (LSNM type; DGT Research) placed in plastic housing. The device maintains near-neutral buoyancy and was monitored during the experiment to prevent exposure to air. The DGT functions as an infinite sink and was used to measure the cationic metals Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, and Zn.

**Experimental setup**

The experiment started with the placement of passive samplers in the sediment cores, and the twice-daily resuspension events began on the same day. Constant aeration was provided to each core by gentle bubbling of air through glass tubes inserted through the top stoppers (Figure 2). Monitoring consisted of observing temperature (10 °C) and maintaining water column height, resuspension, and passive sampler positions during the experiment.

After 60 days, the passive samplers were retrieved from the water column, and the paddles were removed. Each SPMD was removed from its holder, wiped clean using lint-free tissue wetted with ultrapure water, and stored in a glass container at −20 °C. The DGT was gently washed with a small volume of ultrapure water and then stored moist in a plastic bag at 4 °C.

The overlying water was drained from the sediment core, and the sediment column was pushed to the top of the core liner to retrieve the SPME fibers. The length of the fibers protruding above the sediment surface was measured for each
fiber, after which the fibers were retrieved and wiped clean of particles using wetted lint-free tissue and stored in aluminum foil at −20 °C.

A sediment sample (5 ml) was collected from the sediment surface of each sediment core to determine dry weight, organic matter (loss-on-ignition), total carbon, total organic carbon (TOC), and total nitrogen content. Two sediment core replicates from each treatment were sieved through 1.0-mm mesh to recover macroinvertebrates, and the sieved sediment was discarded.

The sediment from the two remaining replicates of each treatment were sliced in sections (0–1, 1–3, 3–5, 5–7, and 7–10 cm depth) using a thin Teflon sheet. Each section was homogenized and then sampled for sediment dry weight and organic matter content. In addition, vertical profiles of total carbon, TOC, total nitrogen, and sediment metal concentrations were determined by sampling each sediment section in the control treatment.

Finally, sediment sections (surface sediment in all treatments and each sediment depth from controls) were sieved through 1.0-mm mesh using a small volume of ultrapure water to remove macroinvertebrates and allow for sediment HOC analyses. The sieved sediment was dried at ambient temperature under laminar flow and stored at 4 °C for analyses of total sediment concentrations of PAHs and PCBs. The sediment samples retrieved from each treatment are summarized in Supporting Information, Table S1.

Chemical analyses

PAHs and PCBs in overlying water. Analyses of PAHs and PCBs in SPMDs were conducted at the Department of Environmental Science at Stockholm University. The SPMDs were twice extracted in n-hexane, and the extracts were spiked following the methods of Mustajärvi et al. (2017), then split 1:5 for PAH and PCB analyses, respectively. The PAH fraction was cleaned using the methods of Mandalakis et al. (2004) as modified by Mustajärvi et al. (2017), and the PCB fraction was cleaned following the methods of Zebühr et al. (1993). All samples were analyzed by gas chromatography–mass spectrometry (GC–MS), and the targeted analytes were 15 PAHs (standard 16 PAHs excluding acenaphthylene) and the standard seven PCBs. More detailed information on chemical analysis of SPMDs is provided in Supporting Information, Section SI-2.

Method detection limits (MDLs) were calculated as the mean plus 3 times the standard deviation (SD) of all blank values (n = 4). Data below the MDL were removed from further analysis, and analyte concentrations were corrected for the blank mean. The MDLs were 0.02–1.2 ng SMPS⁻¹ for PAHs (except for naphthalene at 42 ng SMPS⁻¹) and 0.004–0.16 ng SMPS⁻¹ for PCBs (except for PCB-53 at 0.73 ng SMPS⁻¹). Mean measured concentrations of PAHs were 1.5–168 times higher than MDLS, and PCBs were 1.8–172 times higher than MDL (excluding naphthalene and dibenz[a,h]anthracene, which were not detected).

The total quantity of each analyte in the SMPS was assumed to correspond to the total sediment-to-water release of the analytes, and fluxes were calculated using the sediment surface area and the experimental duration (flux = SMPS uptake/sediment surface area/sampling time [g m⁻² day⁻¹]).

PAHs and PCBs in sediment porewater. Analyses of freely dissolved concentrations of PAHs and PCBs in porewater were performed at Hamburg University of Applied Sciences. The PDMS-coated glass fibers were cut into five segments to produce a vertical profile of PAHs and PCBs in sediment. The first segment was 0–2 cm above the sediment surface, followed by 0–4, 4–8, 8–12, and >12 cm below the sediment surface. Contaminant concentrations in the PDMS were determined by GC–MS. The PDMS fiber samples were placed in individual GC liners, and an automated liner exchange system (GERSTEL ALEX) was used for automated introduction (GERSTEL Multi-Purpose Sampler) and thermal desorption of the fibers in a cooled injection system following the methods of Witt et al. (2009). Analyte concentrations in fibers were calculated using external standard and fiber geometry information from Witt et al. (2013), and freely dissolved concentrations were calculated using PDMS–water partitioning coefficients (KPDMS) from Witt et al. (2009). Targeted analytes were the standard 16 PAHs and seven PCBs (external standard calibration solutions PAH-Mix 9 and PCB-Mix 3; Dr. Ehrenstorfer). Naphthalene freely dissolved concentration (Cfree) data from porewater were excluded from further analyses because the measured concentrations were inconsistent and highly variable and may have resulted from contamination of PDMS fibers in the laboratory or during transport.

Method quantification limits (MQLs) and MDLs were calculated as the mean mass in blank fibers plus 3 times the SD for MDL or plus 10 times the SD for MQL and then converted to fiber coating concentrations. The MQLPDMS values were 3.6–8.9 ng ml⁻¹ for PAHs and 3.2–7.2 ng ml⁻¹ for PCBs. The MDLPDMS values were <2.0 ng ml⁻¹ for all target compounds. The MQL values based on freely dissolved concentrations (MQLfree) were lower and decreased with increasing KPDMS. Further details on analyses are provided in Supporting Information, Section SI-3.

Total PAHs and PCBs in sediment. Sediment samples (2–4 g dry wt) were spiked with surrogate standards for PAHs and PCBs and analyzed at Hamburg University of Applied Sciences. Sediment samples were extracted twice with acetone/hexane (40:60 by volume) using an accelerated solvent extractor (ASE 200; Dionex) at 100 °C and 140 bar, followed by cleanup and analyses in GC–MS. Target analytes were the standard 16 PAHs and seven PCBs. The high-performance liquid chromatography cleanup was tested with standard solutions (PAH-Mix 9, PAH-Mix 9 deuterated and PCB-Mix 3, PCB-Mix 3 deuterated; Dr. Ehrenstorfer), which gave final mean standard recoveries from the surrogate and external PAH and PCB target compounds of 95 ± 8% (n = 10). Further details on analytical methods are provided in Supporting Information, Section SI-4.

The analytical quality control for the whole procedure was carried out with a certified reference material for PAHs and PCBs in marine sediments (QPH 058 and QPH 059; QUASIMEME, Laboratory Performance Studies, quasimeme.org).
Surrogate solutions were added to each sample. The mean recovery values ranged between 71% (naphthalene) and 102% \((n = 10)\). The measured concentrations for single compounds were in all cases in the range of certified values (with or without certified uncertainty). Relative SDs of the measured values for the single compounds \((n = 10)\) ranged between 5% and 12%, and mean recovery rates of the surrogate solutions were calculated for all target compounds with 84 ± 5%. The MQLs were estimated to be 0.3–5 \(\mu\text{g kg}^{-1}\) dry weight for PAHs and 0.5–1 \(\mu\text{g kg}^{-1}\) dry weight for PCBs.

**Metals in sediment and overlying water.** Analysis of metals in DGTs and sediment was conducted at ALS Scandinavia. Sediment concentrations of 16 elements were analyzed in sections down to 10 cm depth in the control treatment and in surface sediment in the capping treatments. Targeted analytes in sediment were As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sr, V, and Zn. The DGTs were extracted by drying the diffusive gel and binding layer at 50 °C and leaching the sample in 10% \(\text{HNO}_3\). Sediment samples were dried at 105 °C, ground, and extracted through digestion in 10% \(\text{HNO}_3\). Metal quantification followed SS EN ISO 17294-1:2004 (International Organization for Standardization, 2004) and 17294-2:2016 (International Organization for Standardization, 2016) protocols and a modified US Environmental Protection Agency (USEPA) method 200.8 protocol (USEPA, 1994). Targeted analytes in DGT samples were Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, and Zn. The output was the mean concentration of dissolved species in the overlying water over the experiment duration.

**Statistical analyses**

For statistical analyses, each metal was tested separately, PCBs were tested as \(\Sigma\text{PCB}_7\), and PAHs were separated into two groups and tested because of clear dissimilarities in partitioning. Seven low–molecular weight PAHs (PAH\(_1\)) and nine high–molecular weight PAHs (PAH\(_4\)) were analyzed as independent groups. The classifications of USEPA (2007) were used: PAH\(_1\) consists of naphthalene, acenaphthene, acenaphthylene (not analyzed in all matrices), fluorene, phenanthrene, anthracene, and fluoranthene; and PAH\(_4\) consists of pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-CD]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene.

Statistical analysis was based on null hypothesis significance testing. Pairwise t tests were used to test for differences between static and resuspended treatments within a thin-layer capping treatment. This pairwise comparison assumes that our twin sediment cores are closely related. Tukey's honestly significant difference test was used to evaluate differences between thin-layer capping treatments sharing a resuspension condition (i.e., static treatments were tested separately from resuspended treatments). Quantile–quantile and residual plots were evaluated to assess normality and heterogeneity, and an \(\alpha\) of 0.05 was our criterion to reject the null hypothesis.

**RESULTS AND DISCUSSION**

**Field and experimental conditions**

Water quality parameters measured in bottom water at the site were temperature 8.7 °C, salinity 6.4‰, and dissolved oxygen 11.1 mg L\(^{-1}\). Sediment cores had a water temperature of 10.3 ± 1 °C, salinity of 6.9 ± 0.3‰, and dissolved oxygen of 10.4 ± 0.03 mg L\(^{-1}\) at the end of the experiment.

Sediment resuspension in the cores caused a 15-fold increase in suspended matter content in overlying water, from mean 40 mg L\(^{-1}\) in static cores to mean 611 mg L\(^{-1}\) in resuspended cores (Table 2). Resuspension due to marine traffic has been visually observed in the inner harbor, and severe weather or large vessels may resuspend sediment in the outer harbor (Oskarshamn Municipality, 2019). However, turbidity measurement indicates that no sediment resuspension occurred in the outer harbor following ferry traffic (see Supporting Information, Section SI-1). Resuspension may occur more intermittently or at a lower intensity in the outer harbor than in the present experiment.

### Table 2: Sediment geochemical properties at the end of the experiment (mean of two samples) and suspended particles sampled during resuspension events (mean and standard deviation of three samples)

| Treatment | Depth  | Ctrl-S | Clay-S | GAC-S | PAC-S | Ctrl-R | Clay-R | GAC-R | PAC-R |
|-----------|--------|--------|--------|-------|-------|--------|--------|-------|-------|
| DW (%)    | Surface| 11.5   | 14.1   | 16.8  | 16.9  | 11.6   | 13.1   | 17.9  | 15.7  |
|           | Subsurface| 17.7  | 17.7   | 17.5  | 17.9  | 17.6   | 17.9   | 17.9  | 18.3  |
| LOI (%)   | Surface | 22.9   | 18.8   | 36.6  | 37.4  | 22.6   | 18.8   | 38.4  | 33.7  |
|           | Subsurface| 18.5  | 17.8   | 17.9  | 17.7  | 18.3   | 17.5   | 17.9  | 17.3  |
| TOC (%)   | Surface | 5.9    | 5.7    | 23.9  | 32.0  | 7.5    | 6.4    | 22.6  | 33.8  |
|           | Subsurface| 7.7   | 6.1    | 22.9  | 34.0  | 7.7    | 6.6    | 22.8  | 31.6  |
| TC (%)    | Surface | 0.95   | 0.67   | 0.63  | 0.60  | 0.90   | 0.73   | 0.59  | 0.52  |
|           | Subsurface| 0.89  | –      | –     | –     | 0.84   | –      | –     | –     |
| TN (%)    | Surface | 8.53   | 8.67   | 35.9  | 55.3  | 8.19   | 8.75   | 36.1  | 62.6  |
|           | Subsurface| 8.10  | –      | –     | –     | 8.10   | –      | –     | –     |
| Suspended particles (mg L\(^{-1}\)) | Water | 42.9 ± 13.7 | 64.8 ± 21.6 | 30.8 ± 16.9 | 21.5 ± 18.6 | 725 ± 436 | 583 ± 169 | 500 ± 268 | 638 ± 126 |

Surface indicates 0–1 cm depth, and subsurface indicates the mean of samples from 1–3, 3–5, 5–7, and 7–10 cm depth.

*Measured in one replicate.

- S = static; GAC = granular activated carbon; PAC = powdered activated carbon; \(-R\) = resuspended; DW = dry weight; LOI = loss-on-ignition; TOC = total organic carbon; TC = total carbon; TN = total nitrogen.
In the cores, the resuspended particles settled on the walls and other surfaces, including the surface of the SPMD passive sampler. This deposition consisted primarily of contaminated sediment in the control treatment, glacial clay in the clay and GAC treatments (because the GAC was not resuspended), and a mix of activated carbon and glacial clay in the PAC treatment. A photograph displaying particle deposition in resuspended cores is presented in Supporting Information, Figure S1.

Sediment cores were visually examined to assess sediment conditions at the end of the experiment. The lower section of sediment was black, indicating euxinic (i.e., anoxic and sulfidic) conditions. Above this was a section of brown sediment, which had a lighter brown color and presumably fully oxygenated, with a mean thickness of 4.7 mm. Photographs of these sediment layers are presented in Supporting Information, Figure S2.

Thin-layer capping affected sediment properties at 0–1 cm depth but not deeper in the sediment (Table 2). Surface sediment dry weight slightly increased in the clay treatment and further increased in the GAC and PAC treatments. Clay somewhat reduced organic matter content, total carbon content, and TOC content in surface sediment, whereas GAC and PAC strongly increased them. This indicates that the activated carbon fraction was captured in organic matter, total carbon, and TOC analyses. The total nitrogen content of surface sediments was reduced by all thin-layer capping treatments, a result that shows that the sediment contains more natural organic matter than the thin-layer caps amended with activated carbon. The activated carbon materials used in the present study consisted of approximately 90% carbon and no nitrogen (Bonaglia et al., 2019).

### Benthic community

Macroinvertebrate burrows were formed in the sediment cores during the experiment. The most abundant species in both field samples and sediment cores were the gastropod genus *Hydrobia*, the bivalve *Limecola balthica* (previously *Macoma*), aquatic larvae of the midge family Chironomidae, and the polychaete *Hediste diversicolor* (previously *Nereis*). We identified seven species in sieved sediment cores and 10 species in field samples. These sampling efforts represent relatively low sediment surface areas, illustrated by the presence of unique species in both samplings. We found the polychaete *Brygides sarsi* in sediment cores but not in the field, and we found four species in the field that were not present in the sediment cores at the end of the experiment (see taxonomic data in Supporting Information, Table S2).

In the present study, assessing effects on benthic organisms was not a primary goal. However, the high survival rate of benthic invertebrates in the experiment demonstrates that sediment parameters and environmental conditions remained tolerable for the observed species in thin-layer capping and resuspension throughout the experiment. The heterogeneity of the community made statistical analysis of differences in species composition between treatments and comparison to the initial benthic community unfeasible, but a simple comparison of organism abundances was made. This comparison reveals that GAC maintained the same organism abundance as control, roughly twice as high as in the PAC and clay treatments. Organism abundance was reduced by resuspension in all treatments except for GAC; resuspended GAC had higher abundance than resuspended control (Supporting Information, Table S2).

Activated carbon amendment may cause adverse biological effects on benthic invertebrates, and it has been observed that fine activated carbon particles may have a stronger adverse impact on benthic organisms than coarser particles (Janssen & Beckham, 2013). In the present study, it also appears that PAC had an adverse effect on species abundance of macroinvertebrates, whereas GAC supported a higher organism abundance even during intense resuspension (see Supporting Information, Table S2). Biological responses to thin-layer capping were recently reported to depend on activated carbon particle size, where only ingestible activated carbon caused adverse biological responses in two deposit feeders (Rämö et al., 2021); but further research would be necessary to assess the impact of resuspension on such responses.

### Organic contaminants

#### Sediment concentrations

Sediment total concentrations (C<sub>total</sub>) were measured in vertical profiles in the control treatments, which showed that $\Sigma$PCB<sub>7</sub> and $\Sigma$PAH<sub>1</sub> concentrations were relatively stable to a 10-cm depth, whereas $\Sigma$PAH<sub>1</sub> was higher in subsurface sediment than at the surface (Supporting Information, Figure S3). Generally, control in the resuspended condition had lower C<sub>total</sub> of individual PCBs and PAHs than control in the static condition (Supporting Information, Table S4).

Surface sediment C<sub>total</sub> was measured in all treatments to assess dilution effects of thin-layer capping. Mean $\Sigma$PCB<sub>7</sub> was reduced by 19% in clay, 43% in GAC, and 52% in PAC compared to surface sediment in uncapped control (Figure 3; Supporting Information, Table S3). This corresponds to the dilution expected from thin-layer capping: 600 g m<sup>−2</sup> for clay and 1200 g m<sup>−2</sup> for the activated carbon treatments.

### Discussion

In many aquatic systems, sediments may be biologically highly productive ecosystems that are rich in carbon and organic matter. As such, they may act as a source of organic carbon and nutrients to the overlying water. However, increased sediment resuspension can also stimulate the release of contaminants to the overlying water, potentially leading to increased environmental impact. In the present study, assessing effects on benthic organisms was not a primary goal. However, the high survival rate of benthic invertebrates in the experiment demonstrates that sediment parameters and environmental conditions remained tolerable for the observed species in thin-layer capping and resuspension throughout the experiment.

The heterogeneity of the community made statistical analysis of differences in species composition between treatments and comparison to the initial benthic community unfeasible, but a simple comparison of organism abundances was made. This comparison reveals that GAC maintained the same organism abundance as control, roughly twice as high as in the PAC and clay treatments. Organism abundance was reduced by resuspension in all treatments except for GAC; resuspended GAC had higher abundance than resuspended control (Supporting Information, Table S2).

Activated carbon amendment may cause adverse biological effects on benthic invertebrates, and it has been observed that fine activated carbon particles may have a stronger adverse impact on benthic organisms than coarser particles (Janssen & Beckham, 2013). In the present study, it also appears that PAC had an adverse effect on species abundance of macroinvertebrates, whereas GAC supported a higher organism abundance even during intense resuspension (see Supporting Information, Table S2). Biological responses to thin-layer capping were recently reported to depend on activated carbon particle size, where only ingestible activated carbon caused adverse biological responses in two deposit feeders (Rämö et al., 2021); but further research would be necessary to assess the impact of resuspension on such responses.

### Supporting Information

**Table 3**: Mean efficacy (percentage) of thin-layer caps at reducing contaminant release from sediment to overlying water compared to untreated control under static and resuspended conditions.

| Contaminant | Clay | GAC | PAC | Clay | GAC | PAC |
|-------------|------|-----|-----|------|-----|-----|
| $\Sigma$PCB<sub>7</sub> | 15 | 6 | 57 | 20 | 17 | 91 |
| $\Sigma$PAH<sub>H</sub> | 22 | -13 | 76 | 30 | 47 | 99 |
| $\Sigma$PAH<sub>L</sub> | 17 | 30 | 45 | 38 | 42 | 88 |
| Cd | 0 | 34 | 68 | -13 | 4 | 53 |
| Cu | -20 | 72 | 91 | -2 | 42 | 96 |
| Ni | 81 | 71 | 90 | -18 | -2 | 34 |
| Pb | 10 | -145 | 34 | 68 | 69 | 55 |
| Zn | 13 | 28 | 63 | -58 | -47 | 41 |

Underlying data are provided in the Supporting Information (Tables S1-3 and S1-S5). Positive values indicate a reduced release of contaminants.

GAC = granular activated carbon; PAC = powdered activated carbon; PCB = polychlorinated biphenyl; PAH<sub>H</sub> = high-molecular weight polycyclic aromatic hydrocarbon; PAH<sub>L</sub> = low-molecular weight polycyclic aromatic hydrocarbon.
Resuspension had a small but statistically significant effect in reducing surface sediment $C_{\text{total}}$ of $\sum \text{PCB}_7$ in the clay treatment but not in the other treatments.

Surface sediment $C_{\text{total}}$ of PAHs was also studied. The GAC and PAC treatments reduced $C_{\text{total}}$ of $\sum \text{PAH}_H$ by 96% and 88%, respectively; and both activated carbon treatments reduced $\sum \text{PAH}_L$ by 94%. These reduced $C_{\text{total}}$ values of PAHs in the activated carbon treatments far exceeded the effect of dilution observed for PCBs, suggesting that reduced PAH concentrations cannot be attributed to dilution alone. Resuspension caused a small but significant reduction of $\sum \text{PAH}_H$ in PAC but not in GAC. The clay treatment reduced $\sum \text{PAH}_H$ by 51% in the static condition only, and no significant effects were observed for $\sum \text{PAH}_L$ in clay.

A possible explanation for the loss of PAH $C_{\text{total}}$ in activated carbon-amended sediment is reduced extraction due to strong PAH sorption onto activated carbon. Jonker and Koelmans (2002a, 2002b) have reported poor extraction of PAHs from soot and sediment containing soot-like particles such as activated carbon. Planar compounds, such as PAHs, have been observed to sorb more strongly to activated carbon than nonplanar compounds (Cornelissen et al., 2005; Jonker & Koelmans, 2002a, 2002b). Strong sorption was also observed in the seven PCBs, where the mono-ortho coplanar PCB 28 and

---

**FIGURE 3:** Sediment concentrations of $\sum \text{PCB}_7$, $\sum \text{PAH}_H$, and $\sum \text{PAH}_L$ at 0–1 cm depth. Crossbar boxes indicate mean and bootstrapped 95% confidence limits. Shared letter indicates similar treatments (Tukey’s honestly significant difference, $\alpha = 0.05$). Asterisks denote a statistical difference between static and resuspended treatments (paired t test, *p < 0.05). PCB = polychlorinated biphenyl; DW = dry weight; GAC = granular activated carbon; PAC = powdered activated carbon; $\text{PAH}_H$ = high–molecular weight polycyclic aromatic hydrocarbon; $\text{PAH}_L$ = low–molecular weight polycyclic aromatic hydrocarbon.

**FIGURE 4:** Vertical profiles of mean freely dissolved concentrations of $\sum \text{PCB}_7$, $\sum \text{PAH}_H$, and $\sum \text{PAH}_L$ in porewater (freely dissolved concentrations) with 95% confidence intervals. Absence of confidence interval represents $n = 1$. Horizontal line indicates the sediment surface. Open dots represent individual observations. Note the different units of $\sum \text{PCB}_7$ and the PAHs. PCB = polychlorinated biphenyl; $\text{PAH}_H$ = high–molecular weight polycyclic aromatic hydrocarbon; $\text{PAH}_L$ = low–molecular weight polycyclic aromatic hydrocarbon; GAC = granular activated carbon; PAC = powdered activated carbon.
PCB 118 were reduced by 68% on average in the activated carbon treatments, while nonplanar di-ortho-indicator PCBs were reduced by 39% on average. The effect of activated carbon amendment on the total extractable fraction of PAHs and coplanar PCBs in sediment should be further investigated.

**Porewater concentrations.** Vertical profiles of $C_{\text{free}}$ were measured to assess the influence of thin-layer capping on PAHs and PCBs in porewater at different depths. There was no general effect of sediment depth, but some treatments proved noticeable exceptions (Figure 4). Porewater concentrations of $\sum \text{PCB}_2$ were not different between treatments in the resuspended condition, but the static control had elevated $\sum \text{PCB}_2$ concentrations relative to the thin-layer capped sediments. Depth profiles of individual compounds (Supporting Information, Figure S4) reveal elevated concentrations of PCBs 28 and 52. An outlier in 0–4 cm porewater concentration of $\sum \text{PCB}_2$ (Figure 4) was attributed to PCBs 118, 138, 153, and 180 (Supporting Information, Figure S4).

Porewater concentrations of $\sum \text{PAH}_{\text{H}}$ were generally similar at the different depths, but the static control and resuspended PAC had elevated $\sum \text{PAH}_{\text{H}}$ in at least one depth. In the static control, high $C_{\text{free}}$ values were observed between 0 and 12 cm depth. This was caused by high concentrations of every PAH in at least 0–4 cm depth, whereas pyrene caused elevated concentrations at 4–12 cm depth (Supporting Information, Figure S4). In the resuspended PAC treatment, elevated $C_{\text{free}}$ of $\sum \text{PAH}_{\text{H}}$ in the 0–4 cm depth was attributed to every PAH except pyrene.

Finally, porewater concentrations of $\sum \text{PAH}_{\text{H}}$ were higher in the static control treatment than in any thin-layer capped treatment (Figure 4). This was attributed to every PAH occurring at higher concentrations in the control (Supporting Information, Section SI-4). No clear differences in PAH$C_{\text{free}}$ in porewater were observed in the resuspended condition.

The static control appeared to have higher porewater $C_{\text{free}}$ of PAHs and PCBs than thin-layer capped treatments, but PDMS fibers from the static control were successfully retrieved and analyzed in one replicate only. On the other hand, the resuspended control had multiple replicates and did not clearly differ from thin-layer capped treatments, which may suggest that no clear effects of treatments were observed in PAH and PCB porewater concentrations.

Stringer et al. (2014) used SPME passive sampling and reported that effects of activated carbon amendment were measurable within only a few centimeters from the treatment. The present study analyzed porewater concentrations in 4-cm fiber segments, and a higher vertical resolution would have been necessary to capture the effects of thin-layer capping on freely dissolved porewater concentrations. The effects of activated carbon thin-layer capping on porewater concentrations are also expected to increase over time as the activated carbon is distributed into the bioactive sediment through bioturbation: activated carbon mixed into sediment is effective at reducing PCP porewater concentrations.

**Sediment-to-water fluxes.** The flux of $\sum \text{PCB}_2$ from sediment to water was reduced by 57% in static PAC and by 91% in resuspended PAC compared to control, whereas clay and GAC treatments did not reduce $\sum \text{PCB}_2$ fluxes (Figure 5). In the static condition, the sediment-to-water fluxes largely consisted of PCBs and PAHs with low log $K_{\text{OW}}$ (Figure 6), which is to be expected because more hydrophobic substances are to a higher degree sorbed to particles. Most of the resuspended treatments had increased fluxes of PCBs with log $K_{\text{OW}} > 7.0$, likely due to desorption from sediment particles suspended in the water column. However, the PAC treatment further reduced fluxes of PCBs with high log $K_{\text{OW}}$, demonstrating strong sorption and higher capping efficiency of PAC relative to clay and GAC treatments.

Release fluxes of $\sum \text{PAH}_{\text{H}}$ were not significantly affected by capping in the static condition; but resuspended clay and GAC treatments reduced fluxes of $\sum \text{PAH}_{\text{H}}$ by 30% and 47%, respectively, and resuspended PAC reduced fluxes of $\sum \text{PAH}_{\text{H}}$ by 99.4%. Thin-layer capping had no effect on $\sum \text{PAH}_{\text{H}}$ fluxes in the

![FIGURE 5: Sediment-to-water release fluxes of $\sum \text{PCB}_2$, $\sum \text{PAH}_{\text{H}}$, and $\sum \text{PAH}_{\text{L}}$ measured using semipermeable membrane devices. Crossbar boxes indicate mean and bootstrapped 95% confidence limits. Shared letter indicates similar treatments (Tukey’s honestly significant difference, $\alpha = 0.05$). Asterisks denote a statistical difference between static and resuspended conditions (paired t-test, *p < 0.1, **p < 0.05, ***p < 0.01). Note that the lowest release fluxes of both polychlorinated biphenyls and polycyclic aromatic hydrocarbons are found in the powdered activated carbon treatment. PCB = polychlorinated biphenyl; PAH$C$ = high-molecular weight polycyclic aromatic hydrocarbon; PAH$L$ = low-molecular weight polycyclic aromatic hydrocarbon; GAC = granular activated carbon; PAC = powdered activated carbon.](image-url)
static condition, but the resuspended PAC treatment reduced the $\Sigma_{PAH}$ flux by 88% compared to the control. The resuspended control, clay, and GAC treatments had higher $\Sigma_{PAH}$ fluxes than the static condition (Figure 5), which is caused by an increased release of PAHs with log $K_{OW}$ of approximately 5–6 (Figure 6). In contrast, resuspension of the PAC treatment instead further reduced fluxes of PAHs with a log $K_{OW}$ of approximately 4, resulting in very low PAH fluxes in resuspended PAC.

A comparison of sediment-to-water fluxes to porewater concentrations of PCBs and PAHs shows slight correlation in the static, but not in the resuspended, condition (Figure 7). Linear regression models for PAHs and PCBs (fitted to all observations of respective contaminant class) had generally poor explanatory power in static conditions (mean $R^2 = 0.35$) and even lower explanatory power in resuspended conditions (mean $R^2 = 0.06$). The lack of correlation in the resuspended treatments is to be expected because fluxes from sediment to water in these treatments are governed by additional variables, such as turbidity and sorption properties of suspended particles. Volatilization of low-molecular weight compounds (PAHs) from water to air may have taken place during the experiment; however, the observed high sediment $C_{total}$ and porewater $C_{free}$ values were expected to have compensated for potential losses from water to air.

Sediment resuspension significantly increased the release fluxes of $\Sigma_{PCB}$ and $\Sigma_{PAH}$ in all treatments, except in the PAC treatment, where resuspension reduced fluxes of both $\Sigma_{PCB}$ and $\Sigma_{PAH}$ (Figure 5). The reverse effect on contaminant release in PAC can be explained by sorption of contaminants onto suspended activated carbon particles. Nonetheless, the capping efficiency of PAC may be overstated in the present study compared to the field, where resuspended particles are lost in advective transport from the site. In addition, resuspended PAC particles were observed coating surfaces of sediment cores and passive samplers (Supporting Information, Figure S1), which may have increased sequestration of PCBs and PAHs from the water phase. The effect of the PAC fouling on SPMDs was not quantified in the present study. However, fouling by biofilm formation on samplers has been reported to reduce contaminant sampling rates by up to 50% (Richardson et al., 2002), and activated carbon is known to be a stronger sorbent than natural organic matter.

Another point to consider is that in field conditions resuspension and subsequent advection are likely to lead to off-site transport of PAC, reducing the effective dose of the PAC materials at the site of application. In comparison, we did not observe GAC resuspension in the present study. The apparent densities of PAC and GAC are comparable (450–520 and 390–600 kg m$^{-3}$, respectively), whereas clay particles have higher density than activated carbon and were still readily resuspended. Larger particles require higher fluid velocity (i.e., higher shear stress) to suspend (Graham et al., 2013), implying that resuspension events achieved the required sheer forces to suspend PAC and clay particles but did not achieve the forces required to suspend GAC particles. The clay component of the thin-layer caps was resuspended in both treatments, which meant that GAC was covered by clay particles over the course of the experiment. Although GAC was only effective at

---

FIGURE 6: Fluxes of individual polychlorinated biphenyls and polycyclic aromatic hydrocarbons as measured in semipermeable membrane devices plotted against their log $K_{OW}$ values, shown in static and resuspended treatments, respectively. The R function `ggplot2::geom_smooth()` was used to fit a local polynomial regression with 95% confidence intervals. PCB = polychlorinated biphenyl; PAH = polycyclic aromatic hydrocarbon; $K_{OW}$ = octanol–water partitioning coefficient; GAC = granular activated carbon; PAC = powdered activated carbon.
reducing fluxes of $\Sigma$PAH in the present experiment, increased sorption efficiency over time has been reported in other studies (Choi, Cho, Werner, & Luthy, 2014b; Kupryianchyk et al., 2013b; Werner et al., 2006), indicating that GAC may represent a better capping option for long-term remediation because of its higher retention rate relative to PAC. However, an increased dose of GAC would be necessary to obtain sorption efficiencies comparable to PAC in the short term.

**Metals**

**Sediment concentrations.** The $C_{\text{total}}$ values of metals in control were compared to Swedish environmental quality criteria (Swedish Environmental Protection Agency, 2000). This places As, Cd, Cu, Pb, and Zn in Class 4 to Class 5, indicating that sediment concentrations far exceed preindustrial levels.

Surface concentrations of As, Cd, Cu, Pb, and Zn also follow the dilution pattern that was observed for $\Sigma$PCB: the highest concentrations in control, followed by reduced concentration in clay, and the lowest concentrations in GAC and PAC treatments (Figure 8). An additional 11 metals were measured in sediment and conformed to this pattern of dilution, with the exception of Be which increased from 1.2 to 2.4 mg kg$^{-1}$ dry weight in the GAC treatment (Supporting Information, Figure S5). Resuspension did not significantly affect $C_{\text{total}}$ of these 16 metals in surface sediment.
Vertical profiles of \( C_{\text{total}} \) in the control treatments show that concentrations of most elements were constant or increased with depth, but six metals (As, Ba, Fe, Mn, P, and Sr) had elevated concentrations in surface sediment in both static and resuspended control treatments (Supporting Information, Figure S5). The cause of this is not well understood because only small quantities could have leached from our prewashed stainless-steel devices. A possible mechanism for the accumulation of certain metals near the sediment surface may be transport from deeper anoxic sediment to the oxygenated surface sediment.

**Water concentrations.** The DGT passive samplers provide a time-weighted average of the \( C_{\text{free}} \) of metals. The metals of concern in Oskarshamn harbor showed varied responses to resuspension and thin-layer capping (Figure 9). Release of Cd was reduced by GAC and PAC treatments in the static condition, and PAC reduced Cd release in the resuspended condition. Resuspension reduced Cd release in control, clay, and GAC treatments but not in PAC-treated sediment. Both activated carbon treatments appeared to reduce Cu release compared to control and clay, but the effect could not be established statistically because of multiple outlier values. Resuspension appears to have had no effects on the release of Cu.

Water concentrations of Pb increased in GAC and were reduced in PAC, with resuspension causing only a small increase in clay. However, the Pb measurements also contain outliers that interfered with statistical analysis. Concentrations of Zn were reduced by resuspension in control and clay, and PAC reduced Zn concentrations under static conditions, although outliers again interfered with statistical analysis. Results for additional metals are presented in Supporting Information, Figure S6 and Table S5.

In general, resuspension did not lead to a higher sediment-to-water release of dissolved metals. There were 11 metals quantified in DGTs, but Al and Cr were only detected in one and two sediment cores, respectively, and were not further assessed. Based on nine metals and eight treatments, there were 72 possible metal–treatment combinations. Resuspension increased dissolved metal concentrations in one metal–treatment combination and reduced concentrations in 12 combinations (Figure 9; Supporting Information, Figure S7), which suggests that resuspension had a much lower effect on metal release from sediment to overlying water than we expected.

The overall response to resuspension may be due to interactions between dissolved metals and resuspended sediment or thin-layer capping materials. Apler et al. (2019) reported that in situ resuspension of a contaminated sediment in the Baltic Sea increased particle-bound concentrations of metals in overlying water but decreased their dissolved concentrations and concluded that this may be due to sorption of dissolved metals onto resuspended particles (a particle scavenging effect).

Overall, activated carbon treatments performed better than clay at reducing overlying water concentrations of five metals of concern, and PAC was somewhat more effective than GAC. The precise mechanism of action of activated carbon on metal sequestration is not known, but effects may be caused by nonspecific binding of metals onto activated carbon, dilution of the surface sediment, elevated pH in the activated carbon thin-layer cap, or a shift of the oxygenated sediment zone into the...
thin-layer cap, as was reported by Bonaglia et al. (2019). In addition, altered microbial processes following thin-layer capping with activated carbon (Bonaglia et al., 2020) may affect speciation of metals and their bioavailability and toxicity (Azeez et al., 2006; Chapman et al., 1998).

CONCLUSIONS

Thin-layer capping using a mixture of PAC and clay reduced sediment-to-water fluxes of PAHs and PCBs, and its performance improved under resuspended conditions (Table 3). However, the capping efficiency of PAC may be overestimated because advection of suspended PAC particles would reduce the effective dose and decrease the long-term efficacy of the treatment. Our results show that thin-layer capping with GAC, though less efficient at reducing contaminant fluxes in the present study, offers an alternative to PAC in turbulent waters because it is less prone to resuspension and more likely to persist through frequent and repeated resuspension events. Benthic infauna abundance decreased in PAC treatments, whereas GAC maintained infauna abundance at levels similar to or higher than those in control sediment. Additional studies with a wider range of particle sizes are necessary to identify optimal trade-offs between activated carbon particle size, thin-layer cap persistence, and contaminant retention in resuspended sites.

Supporting Information—The Supporting Information is available on the Wiley Online Library at https://doi.org/10.1002/etc.5292.

FIGURE 9: Water concentrations of As, Cd, Cu, Pb, and Zn as determined by diffusive gradient in thin film uptake. Crossbar boxes indicate mean and bootstrapped 95% confidence limits. Shared letter indicates no statistical difference between treatments (Tukey’s honestly significant difference, α = 0.05). Asterisks denote differences between static and resuspended conditions (paired t test, *p < 0.05). GAC = granular activated carbon; PAC = powdered activated carbon.

ACKNOWLEDGMENT—The authors thank O. Svensson, C. Raymond, S. Tobiasson, P. Bruce, and the crew aboard M/S Fyrbyggaren who assisted with field sampling; J. Honkanen and A. Poulsen who assisted with the experiment; J. Wikström for graphic illustrations; M. Arndt, J. Ericsson, and K. Vannerberg at Jacobi Carbons for providing the activated carbons; and L. Bäcklin of the Central Workshop at Stockholm University for assistance with the experimental setup. The present study was managed by J. Gunnarsson at the Department of Ecology, Environment and Plant Sciences, Stockholm University, with funding from the TUFFO Program, Swedish Geotechnical Institute, project CAPTIVE (grant no. 1.1-1602-0106).

DISCLAIMER—Activated carbon was provided as a research collaboration free of charge from Jacobi Carbons. Chemical analyses at ALS Scandinavia were performed through a contract with the Oskarshamn harbor remediation group.

DATA AVAILABILITY STATEMENT—Data, associated metadata, and calculation tools (e.g., R scripts used to produce statistics and figures) are available from the corresponding author (robert.ramo@su.se) and the principal investigator (jonas.gunnarsson@su.se).

REFERENCES

Abel, S., & Akkanen, J. (2018). A combined field and laboratory study on activated carbon-based thin layer capping in a PCB-contaminated boreal lake. Environmental Science & Technology, 52, 4702-4710. https://doi.org/10.1021/acs.est.7b05114
Menzie, C. A., Amos, B., Driscoll, S. K., Ghosh, U., & Gilmour, C. (2016). Evaluating the efficacy of a low-impact delivery system for in situ treatment of sediments contaminated with methymercury and other hydrophobic chemicals (Final Report. Project ER-200835). Environmental Security Technology Certification Program, US Department of Defense.

Millward, R. N., Bridges, T. S., Ghosh, U., Zimmerman, J. R., & Lathy, R. G. (2005). Addition of activated carbon to sediments treated with activated carbon: A demonstrated sediment cleanup technology. Integrated Environmental Assessment and Management, 11, 195–207. https://doi.org/10.1002/ieam.1589

Netzer, A., & Hughes, D. E. (1984). Adsorption of copper, lead and cobalt by activated carbon. Water Research, 18, 927–933.

Oskarshamn Municipality (2019). Saneringen av Oskarshamns hamnbassäng (In Swedish). https://www.oskarshamn.se

Patmont, C. R., Ghosh, U., LaRosa, P., Menzie, C. A., Lathy, R. G., Greenberg, M. S., Cornelissen, G., Eek, E., Collins, J., Hull, J., Hjartland, T., Glaza, E., Bieler, J., & Quadrini, J. (2014). In situ sediment treatment using activated carbon: A demonstrated sediment cleanup technology. Environmental Toxicology and Chemistry, 33, 3465–3477.

Rämö, R. A., Honkanen, J., Nybom, I., & Gunnarsson, J. S. (2021). Biological effects of activated carbon on benthic macroinvertebrates are determined by particle size and ingestibility of activated carbon. Environmental Toxicology and Chemistry, 40(12), 3466–3477.

Richardson, B. J., Lam, P. K. S., Zheng, G. J., McClellan, K. E., & De Luca-Abbott, S. B. (2002). Biofouling confounds the uptake of trace organic contaminants by semi-permeable membrane devices (SPMDs). Marine Pollution Bulletin, 44, 1372–1379. https://doi.org/10.1016/s0025-326x(02)00263-1

Samuelsson, G. S., Hedman, J. E., Elmquist Knusa, M., Gunnarsson, J. S., & Cornelissen, G. (2013). Capping in situ with activated carbon in Trondheim harbor (Norway) reduces bioaccumulation of PCBs and PAHs in marine sediment fauna. Marine Environmental Research, 109, 103–112. https://doi.org/10.1016/j.marenvres.2015.06.003

Schaanning, M. T., Beylich, B., Gunnarsson, J. S., & Eek, E. (2021). Long-term effects of thin layer capping in the Grenland fjords, Norway: Reduced uptake of dioxins in passive samplers and sediment-dwelling organisms. Chemosphere, 264, Article 125844. https://doi.org/10.1016/j.chemosphere.2020.125844

Stringer, R. D., Burken, J. G., Elmore, A. C., & Reible, D. D. (2014). Using in situ solid phase microextraction (SPME) for depth profiling in sediments treated with activated carbon. Journal of Soils and Sediments, 14, 1013–1020. https://doi.org/10.1007/s11368-014-0857-9

Sun, X., & Ghosh, U. (2007). PCB bioavailability control in Lumbiriculus variegatus through different modes of activated carbon addition to sediments. Environmental Science & Technology, 41, 4774–4780. https://doi.org/10.1021/es062934e

Sveriges Geologiska Undersökning. (2017). Klassning av halter av organiska föroreningar i sediment (In Swedish). http://resource.sgu.se/producter/sgrupper/s1712-rapport.pdf

Swedish Environmental Protection Agency. (2000). Environmental quality criteria: Coasts and seas (Report 5052).

Swedish Environmental Protection Agency. (2012). Beslut om bidrag för åtgärder i Oskarshamns hamnbassäng (In Swedish).

Tomaszewski, J. E., & Lathy, R. G. (2008). Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. Environmental Science & Technology, 42, 6086–6091.

Tomaszewski, J. E., Werner, D., & Lathy, 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. Environmental Toxicology and Chemistry, 26, 2143–2150. https://doi.org/10.1002/etc.1797.07-197.r1

US Environmental Protection Agency. (1994). Method 200.8: Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry.

US Environmental Protection Agency. (2007). Ecological soil screening levels for polycyclic aromatic hydrocarbons (PAHs) (Interim final. OSWER Directive 9285.7-78).

Van Sprang, P. A., & Janssen, C. R. (2001). Toxicity identification of metals: Development of toxicity identification fingerprints. Environmental Toxicology and Chemistry, 20, 2604–2610.

Werner, D., Ghosh, U., & Lathy, R. G. (2006). Modeling polychlorinated biphenyl mass transfer after amendment of contaminated sediment with activated carbon. Environmental Science & Technology, 40, 4211–4218.

Witt, G., Lang, S. C., Ullmann, D., Schaffrath, G., Schulz-Bull, D., & Mayer, P. (2013). Passive equilibrium sampler for in situ measurements of freely dissolved concentrations of hydrophobic organic chemicals in sediments. Environmental Science & Technology, 47, 7830–7839. https://doi.org/10.1021/es400395t

Witt, G., Liehr, G. A., Borck, D., & Mayer, P. (2009). Matrix solid-phase microextraction for measuring freely dissolved concentrations and chemical activities of PAHs in sediment cores from the western Baltic Sea. Chemosphere, 74, 522–529. https://doi.org/10.1016/j.chemosphere.2008.09.073

Zebühr, Y., Näf, C., Bandh, C., Broman, D., Ishaq, R., & Pettersen, H. (1993). An automated HPLC separation method with two coupled columns for the analysis of PCDD/Fs, PCBs and PACs. Chemosphere, 27, 1211–1219.

Zimmerman, J. R., Ghosh, U., Millward, R. N., Bridges, T. S., & Lathy, R. G. (2004). Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physicochemical tests. Environmental Science & Technology, 38, 5458–5464.

Zimmerman, J. R., Werner, D., Ghosh, U., Millward, R. N., Bridges, T. S., & Lathy, R. G. (2005). Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. Environmental Toxicology and Chemistry, 24, 1594–1601.