



Capping fiberbank sediments to reduce persistent organic pollutants (POPs) fluxes: A large-scale laboratory column experiment[☆]

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ABSTRACT

Deposits of contaminated wood fiber waste (*fiberbanks*), originating from sawmills and pulp and paper industries, have been found in the aquatic environment in boreal countries. *In-situ* isolation capping has been proposed as a remediation solution because it has the potential to prevent dispersal of persistent organic pollutants (POPs) from this type of sediment. However, knowledge about the performance of such caps when placed on very soft (unconsolidated), gaseous organic rich sediment is scarce. We investigated the effectiveness of conventional *in-situ* capping to limit POPs fluxes to the water column from contaminated fibrous sediments that produce gas. A controlled, large-scale laboratory column (40 cm diameter, 2 m height) experiment was performed over 8 months to study changes in sediment-to-water fluxes of POPs and particle resuspension before and after capping the sediment with crushed stones (≥ 4 mm grain size). Two different cap thicknesses were tested (20 and 45 cm) on two types of fiberbank sediment with different fiber type composition. Results showed that capping fiberbank sediment with a 45 cm gravel cap reduced the sediment-to-water flux by 91–95% for *p,p'*-DDD, *o,p'*-DDD, by 39–82% for CB-101, CB-118, CB-138, CB-153, CB-180 and by 12–18% for HCB, whereas for less hydrophobic PCBs, capping was largely ineffective (i.e. CB-28 and CB-52). Although cap application caused particle resuspension, the long-term effect of the cap was reduced particle resuspension. On the other hand, substantial sediment consolidation released large volumes of contaminated pore water into the overlying water body. Importantly, both sediment types produced large amount of gas, observed as gas voids forming inside the sediment and gas ebullition events, which increased pore water advection and affected the structural integrity of the cap. This may limit the practical applicability of this method on fiberbank sediments.

1. Introduction

Deposits of contaminated wood fiber waste (*fiberbanks*) originating from sawmills and pulp and paper industries have been found in lakes and along coastal areas of Sweden (Norrlin and Josefsson, 2017). These wood fiber deposits are the legacy of an industry that used to release large amounts of fiber material with their wastewater (Ali and Sreekrishnan, 2001; Swedish-EPA, 1995). The thickness of the banks range up to several meters and they cover large areas (Snowball et al., 2020). In Sweden, fiberbanks have been identified as coastal contamination hot spots as they often are heavily contaminated with persistent organic pollutants (POPs) (Dahlberg et al., 2020). These contaminants have been shown to be remobilized from the sediment and reach other parts of the aquatic environment through various mechanisms, such as diffusion,

advection (particle resuspension) and bioaccumulation (Dahlberg et al., 2021; Goransson et al., 2021). Compared to reference sites, significantly elevated levels of polychlorinated biphenyls (PCBs) were recently found in perch (*Perca fluviatilis*) sampled near several fiber-contaminated sediments (Karlsson et al., 2023). Natural recovery over time may occur, but is uncertain because a majority of the investigated fiberbanks (62%) showed no sign of over-sedimentation (Norrlin and Josefsson, 2017). A reason for this observation is that the fiber material often has deposited in areas where minerogenic material does not usually accumulate. At sites where natural recovery is unlikely to take place, remediation actions might be deemed needed.

Isolation capping is an *in-situ* remediation technique that aims to provide a structural barrier by placement of a subaqueous cap of clean material on top of the contaminated sediment. It is an alternative to

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dredging, with the benefits of being less expensive and less invasive as it does not involve sediment excavation, off-site treatment and disposal of the contaminated sediment (Lbianca et al., 2022). The aim of the *in-situ* cap is to physically hinder biota to come in contact with the contaminated sediment, stabilize the sediment and prevent resuspension of contaminated particles, and reduce diffusion from sediment-to-water (Lbianca et al., 2022; Palermo et al., 1998). The simplest (conventional) cap designs consist of unreactive material, such as clean sediment, sand and gravel, which acts as a physical (passive) barrier for the contaminants. Isolation capping has been used successfully in, for example, USA, Canada and Japan (Palermo et al., 1998). However, knowledge about the performance of isolation caps when placed on very soft (unconsolidated), organic-rich sediments, such as fiberbanks, is essentially lacking in the scientific literature even though contaminated fiber deposits are found in many countries e.g. Finland (Kokko et al., 2018), Canada (Biberhofer, 2011) and USA (WSDE, 2012).

A cap must keep its structural integrity over time to function properly. In sediments, anaerobic degradation of organic material by methanogens leads to biogenic production of methane and carbon dioxide (Bastviken, 2009). Extreme gas production has been measured in fiberbank sediments (Lehoux et al., 2021), and a majority (76%) of the surveyed fiberbanks in Sweden also show signs of gas ebullition in the form of pockmarks on the sediment surface (Norrlin and Josefsson, 2017). Given the high content of organic material in fiberbank sediment, there is a concern that gas ebullition might disturb an isolation cap placed on this type of sediment (Jersak, 2016). Gas ebullition can increase contaminant dispersal from sediment through increased resuspension of contaminated particles (Viana et al., 2012; Yuan et al., 2007), increased sediment pore water advection during ebullition (Klein, 2006) and by partitioning of contaminants from pore water into gas bubbles (Fendinger et al., 1992). Previous studies that have explored the effect of gas ebullition on sediment cap suggest, however, that a sand cap can still be an effective barrier for hydrophobic contaminants (Yuan et al., 2007; Yuan et al., 2009) and reduce particle resuspension (Kavcar and Wright, 2009). These previous studies were performed by artificially introducing gas bubbles into a capped sediment column.

The aim of this study was to investigate the effectiveness of conventional *in-situ* capping to limit POPs fluxes to the water column when applied on contaminated fibrous sediment known to produce extensive amounts of natural gas (Lehoux et al., 2021). Previous studies on the impact of gas ebullition on sediment caps have so far been limited to bench-scale laboratory experiments. Here, we designed a controlled large-scale laboratory experiment to explore the changes in sediment-to-water fluxes of POPs and particle resuspension before and after capping the sediment with crushed stones. Two different cap thicknesses were tested (20 and 45 cm) and changes in sediment and water levels were monitored for two types of fiberbank sediments with different wood fiber composition.

2. Materials and methods

2.1. Fiber sediment

Fiber sediment from two fiberbanks located in Ångermanälven River estuary (Väja N 637,814,0905, E 6985862,666 and Sandviken N 640,790,26, E 6983664,56 in SWEREF99 TM system) in north eastern Sweden was sampled and used in the laboratory experiments. The Väja fiberbank consists mainly of cellulose fibers with a cotton like texture, whereas the Sandviken fiberbank consists mainly of several centimeter-large wood chips and wood shavings. Due to the unconsolidated nature of fiber sediments, no intact sediment cores could be recovered. Instead, the upper 50 cm of each fiberbank were collected using grab samplers (Orange Peel Bucket and Ekman). The sediment was stored in plastic buckets in darkness at +4 °C prior to use.

2.2. Description of the experimental design

The column experiment was designed to study changes in sediment-to-water flux and resuspension of particles during capped and uncapped conditions. The experiment was divided into five phases, each monitored for more than one month (35–55 days), respectively (Fig. 1). Phase 0, corresponded to the “setup” phase and was measured after addition of sediment and water to the columns, while Phase 1 measured changes occurring during relatively stable uncapped conditions. Phase 2 showed initial changes after placement of the isolation cap, since it was hypothesized that the capping process could result in increased resuspension of particles. Subsequently, phases 3 and 4 aimed to show the long-term effects of the isolation cap. Details about the column experimental work are given in sections 2.2.1 to 2.2.6. Changes in sediment and water levels were recorded throughout the experiment. The sediment-to-water fluxes were measured by deploying a passive sampler for POPs in each column during each phase of the experiment (i.e. phase 0, phase 1, phase 2, phase 3, phase 4). The passive samplers used are described in more detail in section 2.2.2. Water (1 L) was also collected from each column at the end of each phase to quantify the amount of suspended particles. The water was stored cold (+4 °C) in dark glass bottles prior to filtration at SLU.

2.2.1. Construction of the columns

Four cylindrical columns (40 cm diameter, 2 m height) made of Plexiglas™, were constructed in-house (Uppsala University, Sweden). The columns were placed in a temperature-controlled room (+4 °C) in a laboratory at Uppsala University to mimic field conditions and subdue gas production in the sediment. Each column was filled with sediment to reach a height of ~75 cm (corresponding to 90–95 L sediment). Two columns were filled with fiberbank sediment from Väja (hereafter referred to as column V20 and V45) and two columns with fiberbank sediment from Sandviken (hereafter referred to as column S20 and S45). The sediment was sub-sampled for chemical analysis prior to construction of the columns and stored at +4 °C. Artificial brackish water (prepared according to (Kester et al., 1967) and diluted to reach 5‰ salinity to mimic field conditions, 38 L, Table S1) was added to each column after three days. The artificial brackish water used was sampled for particle determination (1 L) prior to use. After the artificial brackish water had been added, a Teflon™ lined mesh (Biltema, Sweden, diameter 50 cm) was cut to correct size and attached to a 40 cm diameter stainless steel ring with a nylon wire and thereafter placed on top of the sediment (Figure S1). No more water was added to the columns after this stage. The stainless steel ring, which was holding the mesh in place, was attached to the column lid with stainless steel rods to prevent sediment flotation due to the known gas production that can make the sediment buoyant (Lehoux et al., 2021). The columns were left to stabilize for a few days (Väja 2 days, Sandviken 7 days), so that suspended particulate matter (SPM) would have time to deposit on the sediment surface before the passive samplers were deployed. The four columns were visually monitored during this time and changes in sediment and water levels were noted.

2.2.2. Passive samplers for POPs

The sediment-to-water flux was measured by deploying a semi-permeable membrane device (SPMD, Exposmeter, Sweden) in the water of each column during each phase of the experiment. SPMD samplers were also deployed in two field blanks consisting of a plastic box filled with artificial seawater (6 L, 5‰ salinity) prepared from the same batch as used in the columns and was stored in the same temperature-controlled room as the columns. A total of 30 SPMD samplers (0.914 m length, 2.5 cm width, 460 cm² surface area, 75–90 μm thick LDPE), filled with triolein (1 mL) as an absorbing phase, were used in the experiments. The SPMD works as an “infinite-sink” that accumulates dissolved organic pollutants. It absorbs pollutants transported directly from sediment to water through diffusion as well as the dissolved fraction that

	Uncapped fiberbank sediment		Capping	Capped fiberbank sediment		
	Phase 0	Phase 1		Phase 2	Phase 3	Phase 4
Väja	35 d	54 d	4 d	46 d	51 d	48 d
Sandviken	36 d	55 d	4 d	48 d	54 d	48 d

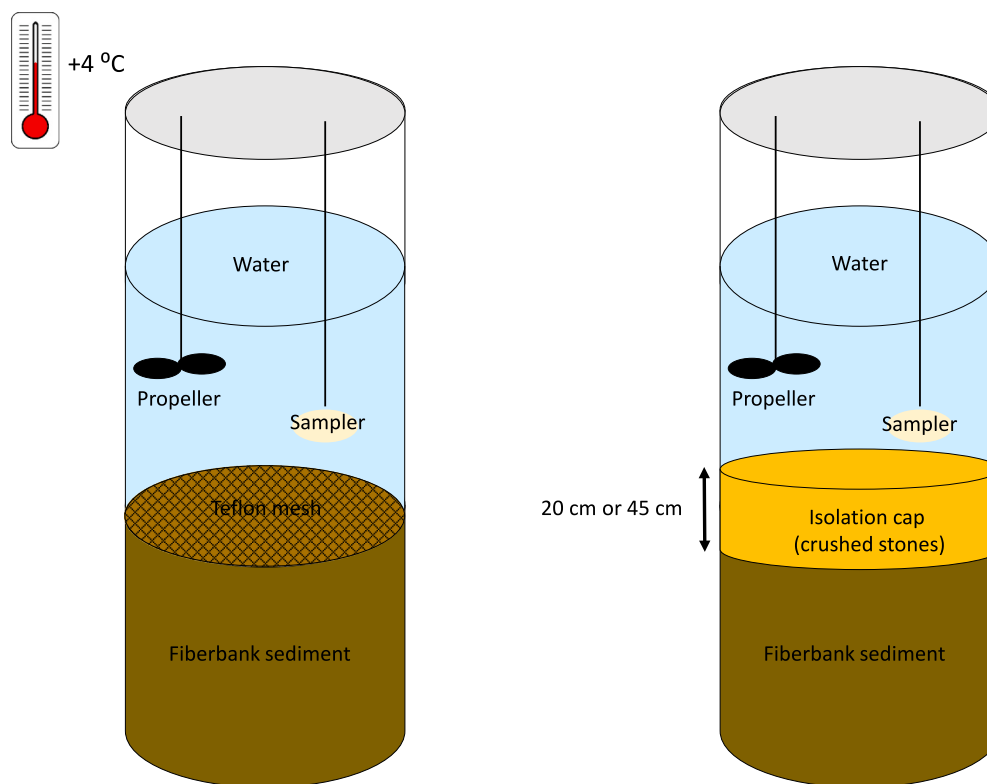


Fig. 1. Schematic illustration of the column and experimental plan in which uncapped sediment conditions (phase 0 and 1) and capped sediment conditions (phase 2, 3 and 4) were studied. The number of days (d) for each phase is presented for both types of fiberbank sediment (Väja and Sandviken).

derives from advective processes, i.e. resuspension and gas ebullition. The SPMD was mounted on a stainless-steel metal spider (diameter: 15 cm) attached to a stainless-steel chain hanging from the lid, which suspended the sampler in the water column approximately 30 cm from the sediment surface. An automatic propeller (diameter: 12 cm, 22.5 rpm) was used to ensure thorough mixing of the water throughout the experiment in each column. After sampling, the SPMDs were stored frozen ($-18\text{ }^{\circ}\text{C}$) in airtight metal containers prior to chemical analysis (SLU, Sweden).

2.2.3. Uncapped sediment - phase 0 and 1

An SPMD sampler was deployed in the water in each column and field blanks and retrieved after 35 days (Väja) and 36 days (Sandviken) of exposure, representing phase 0 (the setup phase). Since the sediment to water fluxes measured during phase 0 may be influenced by POPs dissolved during the construction of the column, a new passive sampler for POPs (SPMD) was deployed in the water of each column and field blank to monitor sediment to water fluxes of POPs under more stable uncapped conditions. The samplers were retrieved after 54 days (Väja) and 55 days (Sandviken) of exposure, representing phase 1 (stable uncapped conditions).

2.2.4. Capping

To place the isolation cap, the Teflon™ lined mesh was removed and capping material composed of crushed stones ($\geq 4\text{ mm}$ grain size) was added to each column to attain a cap thickness of 5 cm. During the following days, more capping material was added (5–15 cm/day) until a cap thicknesses of 20 cm (columns V20, S20) and 45 cm (columns V45,

S45) were reached. Successive capping layers were applied to limit fiberbank sediment resuspension, and also to provide a succession of grain size gradients (Figure S2, Supporting information). The capping material used was sampled and stored cold ($+4\text{ }^{\circ}\text{C}$) for chemical analysis.

2.2.5. Capped sediment – phase 2, 3 and 4

After capping, a new SPMD was deployed in each column and field blank during phase 2. In column V45 and S45 the passive samplers were deployed the day after addition of the last capping layer, whereas for column V20 and S20 the passive samplers were deployed after 2 days. The samplers were retrieved after 46 days (Väja) and 48 days (Sandviken) of exposure, representing phase 2. Since the capping may have resulted in increased resuspension of particles, a new SPMD was deployed in each column and field blank to monitor sediment to water fluxes of POPs under more stable capped conditions. The samplers were retrieved after 51 days (Väja) and 54 days (Sandviken) of exposure representing phase 3. To evaluate the long-term effectiveness of the isolation cap, new SPMDs were deployed and retrieved after 48 days (for both Väja and Sandviken) of exposure, representing phase 4.

2.2.6. End of experiment

At the end of the experiment, the water was removed by gentle suction using a hose and the cap surface was photographed. Two subsamples were taken from the cap of each column, one sample at the surface of the cap (interface with water) and one sample from the middle of the cap, at 10 cm depth in the 20 cm cap and 22 cm depth in the 45 cm cap for chemical analysis of POPs and to determine the content of total

carbon (TC) and total organic carbon (TOC).

2.3. Chemical analysis

2.3.1. Passive samplers (SPMDs)

The SPMDs ($n = 30$) were extracted with *n*-hexane (150 mL + 150 mL) for 2×24 h while continuously shaken, using a previously described method by (Dahlberg et al., 2021). Isotope- ^{13}C -labelled internal standards (IS, table S2) were added to the first aliquot of extraction solvent. Six procedural solvent blank samples were also included for quality control. The extract was then cleaned up on a multilayer-clean up column composed of activated silica (SiO_2 , 3 g), sulfuric acid treated silica (40% H_2SO_4 : SiO_2 , 6 g) and sodium sulfate (Na_2SO_4 , 3 g), similar to Josefsson et al. (2010). The analytes were eluted with dichloromethane:*n*-hexane (1:4, v/v, 60 mL). The sample volume was reduced under a gentle stream of nitrogen of gas and reconstituted in isooctane. Recover standards (RS, table S2) were added and the sample analyzed on GC-MS/MS.

2.3.2. Sediment pore water

The freely dissolved pore water concentration in sediment ($n = 2$, sampled at the start of the experiment) and cap ($n = 4$, sampled from the middle of the cap at the end of the experiment) was determined by equilibrating wet sediment or capping material with a polyoxy-methylene (POM) strip (76 μm in thickness, CS Hyde, Lake Villa, IL, USA) as previously described by (Dahlberg et al., 2020). All samples were prepared in triplicate and six procedural solvent blank samples were included for quality control. Thus, in total 24 POM strips were used. Each POM strip was extracted with acetone:*n*-hexane (1:1, v/v, 20 + 20 mL) for 2×24 h using an end-over-end shaker. Isotope- ^{13}C -labelled internal standards (IS, table S2) were added in the first aliquot of extraction solvent. The extracted POM strip was retrieved and its weight determined gravimetrically. The extract was reduced under a gentle stream of nitrogen of gas and reconstituted in isooctane. Recover standards (RS, table S2) were added and the sample analyzed on GC-MS/MS.

2.3.3. Sediment and capping material

Freeze dried sediment (2 g, $n = 2$) and capping material (15 g, $n = 5$) were extracted using Soxhlet with acetone:*n*-hexane (200 mL, 1:1, v/v) and cleaned up as previously described by (Dahlberg et al., 2020). The initial sediment and capping material were prepared in triplicate and four procedural blank samples were included for quality control. Thus, POPs were extracted from a total of 17 samples. Isotope- ^{13}C -labelled internal standards (IS, table S2) were added to each sample prior to extraction. Each extract was treated with activated copper to remove sulfur, and then further cleaned up on a multilayer column composed of activated silica (SiO_2 , 3 g), sulfuric acid treated silica (40% H_2SO_4 : SiO_2 , 6 g) and anhydrous sodium sulfate (Na_2SO_4 , 3 g) similar to (Josefsson et al., 2010). The analytes were eluted with dichloromethane:*n*-hexane (1:4, v/v, 60 mL). The sample volume was reduced under a gentle stream of nitrogen of gas and reconstituted in isooctane. Recover standards (RS, table S2) were added and the sample analyzed on GC-MS/MS.

2.3.4. Target compounds

Compounds targeted for analysis in the passive samplers (SPMDs), sediment, pore water and capping material included; twenty polychlorinated biphenyls (CBs-28, -52, -77, -81, -101, -105, -114, -118, -123, -126, -138, -153, -156, -157, -167, -169, -170, -180, -189, -209), dichlorodiphenyltrichloroethane (*o,p'*-DDT and *p,p'*-DDT), dichlorodiphenyldichloroethene (*o,p'*-DDE and *p,p'*-DDE) and dichlorodiphenyldichloroethane (*o,p'*-DDD and *p,p'*-DDD) and hexachlorobenzene (HCB) (Table S3). The abbreviation DDX, occasionally used from here on, refers to all DDT-related compounds. The selected target compounds represent a hydrophobicity range from $\log K_{ow}$ 5.5 up to 7.7 (Table S3).

2.3.5. GC-MS/MS analysis

The instrumental analysis was performed using a gas chromatograph (GC; Agilent Technologies, 7890 A) coupled to a triple quadrupole mass spectrometer (Agilent Technologies, 7010, GC-MS/MS Triple Quad). The mass spectrometer was operated using multiple reaction monitoring (MRM) mode, in which two transitions were monitored for each compound. Detailed information about the instrumental settings have been presented previously (Dahlberg et al., 2020). The software Agilent MassHunter Quantitative Analysis (for QQQ) was used for data evaluation.

2.3.6. Quality assurance and quality control (QA/QC)

The limit of detection (LOD) was set at a signal to noise ratio of 3, whereas the limit of quantification (LOQ) was set as the lowest calibration solution that could be detected reliably by the GC-MS/MS instrument. The recovery of the internal standards was on average; $48 \pm 10\%$ for HCB, $91 \pm 17\%$ for PCB, $122 \pm 35\%$ for DDX in SPMDs; $80 \pm 26\%$ for HCB, $104 \pm 31\%$ for PCB, $111 \pm 34\%$ for DDX in sediment; $48 \pm 23\%$ for HCB, $93 \pm 11\%$ for PCB, $104 \pm 27\%$ for DDX in cap; $55 \pm 16\%$ for HCB, $92 \pm 15\%$ for PCB, $94 \pm 19\%$ for DDX in pore water.

The triplicate sediment samples analyzed showed low relative standard deviations (RSD) for both Väja; 19% (HCB), 2.6% ($\Sigma_{20}\text{PCBs}$), 2.7% ($\Sigma_6\text{DDX}$) and Sandviken; 12% (HCB), 11% ($\Sigma_{20}\text{PCBs}$), 8.0% ($\Sigma_6\text{DDX}$). The triplicate pore water samples also showed acceptable method variability with higher RSD for Väja; 19% (HCB), 29% ($\Sigma_{20}\text{PCBs}$), 26% ($\Sigma_6\text{DDX}$) compared to Sandviken; 6.6% (HCB), 7.7% ($\Sigma_{20}\text{PCBs}$), 7.9% ($\Sigma_6\text{DDX}$). The cap material analyzed in triplicate also showed low RSD of 0.71% (HCB), 0.71% ($\Sigma_{20}\text{PCBs}$), 14% ($\Sigma_6\text{DDX}$).

2.3.7. TOC analysis

An aliquot of wet sediment and capping material was used to gravimetrically determine the dry weight (dw) of each sediment sample after heating (105 °C for 24 h). Dry combustion (1350 °C) and elemental analysis using a TruMac instrument (Leco corporation, St Joseph, USA) was also used to determine the sediment content of total carbon (TC) and total organic carbon (TOC), following the Swedish standard procedure SS-ISO 10694.

2.3.8. Suspended particulate matter (SPM)

Water samples ($n = 22$, 500 mL) were filtered through pre-weighed GF/F glass microfiber filters (0.7 μm , Whatman, UK) for gravimetric determination of the mass of particles after drying the filters at 105 °C. Six procedural blanks using Milli-Q water were included for quality assurance. Prior to filtration, the filters had been cleaned by filtrating 500 mL Milli-Q water and then dried at 400 °C.

2.4. Calculations

The sediment to water flux of each target compound (F_{COMPOUND} ; $\text{ng m}^{-2} \text{day}^{-1}$) was calculated using Eq. (1), where M_{SPMD} is the amount of the target compound accumulated in the SPMD (ng), A_{SED} is the sediment surface area (m^2) and $t_{\text{DEPLOYMENT}}$ is the sampling time (days).

$$F_{\text{COMPOUND}} = (M_{\text{SPMD}}) / (A_{\text{SED}} \times t_{\text{DEPLOYMENT}}) \quad (1)$$

For calculation of mean and sum, values below LOD and LOQ were assigned a value of LOD/2 and LOQ/2, respectively.

3. Results and discussion

3.1. Changes in sediment consolidation and water surface levels before, during and after capping

Given the unconsolidated nature of fiberbank sediment, it was hypothesized that fiberbank sediment would consolidate significantly under the load of the cap and that there would be enhanced pore water

movement due to the extreme gas formation in this type of sediment (Lehoux et al., 2021). Therefore, vertical changes in sediment, cap and water levels were monitored throughout the experiment to study changes in sediment compression and pore water upwelling (Fig. 2).

In the two columns composed of fiberbank sediment from Vāja, the surface water level increased rapidly initially and continued to increase slowly until capping (days 1–95, Fig. 2) although no additional water had been added. In column V20, the increase in surface water level corresponded to an increase of an apparent overlying water volume of 33 L and in column V45 of 39 L. The initial increase in surface water level prior to phase 0 is explained by the numerous gas voids that formed inside the sediment after a few days (Figure S3). As the gas voids rapidly grew in size and numbers, they pushed out pore water from the sediment into the overlying water. The water level continued to increase during phase 0 and 1 and did not stabilize before capping. During and after capping, the soft sediment compressed over time in both columns (days

95–244, Fig. 2). In column V20, the sediment compressed by –22 cm and in column V45 by –32 cm. After capping, the apparent overlying water volume increased with 22 L in column V20 and with 33 L in column V45 (days 99–244). The rate of sediment consolidation, however, decreased with time, although stable conditions were not reached within the time frame of the experiment.

In the two columns composed of fiberbank sediment from Sandviken, a slow increase in the surface water levels was observed until capping (days 1–99, Fig. 2). In column S20, the increase in surface water level corresponded to an apparent overlying water volume increase of 19 L and in column S45 with 13 L. Gas voids were also observed to form in this sediment during phase 0, but the increase in water level was much lower compared to Vāja, and more stable conditions were observed already after a month. These results are in line with the previous experimental study, which also showed a higher rate of methane gas production in Vāja than in Sandviken sediment (Lehoux et al., 2021).

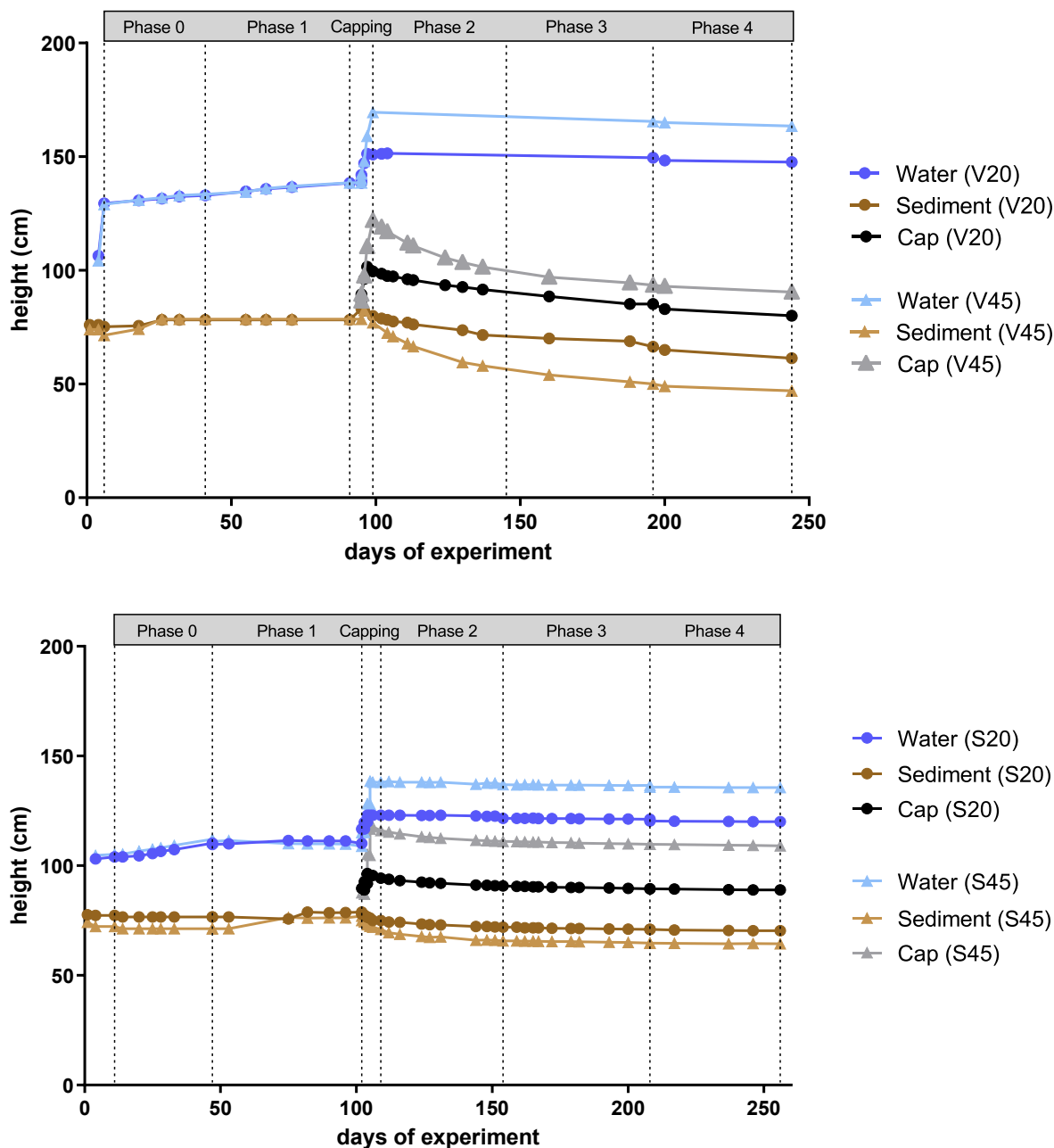


Fig. 2. Changes in sediment, cap and water surface levels (cm) before, during and after capping. Upper figure represents column V20 and V45 and lower figure represents column S20 and S45.

During and after capping, the sediment compressed over time in both Sandviken columns (days 102–256, Fig. 2). In column S20, the sediment compressed by 8.4 cm and in column S45 by 13 cm. After capping, the apparent overlying water volume increased with 4 L in column S20 and with 9 L in column S45 (days 106–256). The rate of sediment consolidation decreased with time, and stable conditions were reached after approximately 1 month after capping. The lower degree of consolidation of the Sandviken fiberbank sediment was expected given that the Sandviken fiberbank is composed of coarser wood material (i.e. wood chips), whereas Väja fiberbank is composed of cellulose fibers with expected higher compressibility.

3.2. Effect of gas ebullition on cap structure

The gas formed in the sediment led to gas ebullition events in all four columns. It was apparent that upwards gas migration formed semi-permanent conduits through the isolation cap, which facilitated further gas release and also vertical pore water transport through the cap and formation of gas craters (pockmarks) on the cap surface (Figs. S4 and S5). Similar gas-mediated formation of macropore network has been observed in natural sediment (Liu et al., 2018) and suggested to facilitate pore water movement in the sediment (Yuan et al., 2007). At the end of the experiment, several pockmarks were visible on the cap surface of all four columns (Figure S4). The extensive gas production in fiberbank sediment negatively affects the structural integrity of the cap, potentially resulting in poorer long-term performance.

3.3. Initial concentration of POPs in sediment, pore water and capping material

The sediment concentrations at the start of the experiment were in the order $\Sigma_6\text{DDX} > \Sigma_{20}\text{PCBs} > \text{HCB}$ in Väja, with levels at $\Sigma_6\text{DDX}$: 146 ± 4.0 ng/g dw, $\Sigma_{20}\text{PCBs}$: 41 ± 1.1 ng/g dw and HCB: 0.44 ± 0.085 ng/g dw (Figure S6-S8). In Sandviken, the concentrations were different and in the order $\Sigma_{20}\text{PCBs} > \Sigma_6\text{DDX} > \text{HCB}$, with levels at $\Sigma_{20}\text{PCBs}$: 121 ± 14 ng/g dw; $\Sigma_6\text{DDX}$: 16 ± 1.3 ng/g dw and HCB: 0.36 ± 0.044 ng/g dw (Figure S6-S8). The levels of PCBs and DDX in Väja are classified as very high levels (category V) according to the Swedish environmental assessment criteria for organic pollutants in sediment (Josefsson, 2017), whereas the levels of HCB in both sediments are classified as moderate levels (category 3). The levels of the targeted POPs are similar to those reported earlier from these fiberbanks with the exception of the (24 times) higher level of DDX found in Väja in this study. This difference might be due to the fact that the sediment collected for this study was taken from deeper sediment layers (0–50 cm) than in the previous study, which indicates a heterogeneous distribution of contaminant levels in the fiberbank. Both Väja and Sandviken fiberbank sediments had high TOC contents (Väja 31%, Sandviken: 43%). TOC normalized concentrations are presented in Figure S9-S11.

In Väja, the sediment PCB congener profile was dominated by CB-101 (17% of $\Sigma_{20}\text{PCBs}$), CB-138 (29%), CB-153 (22%), whereas the DDX congener profile was dominated by *o,p'*-DDD (84% of $\Sigma_6\text{DDX}$) and *p,p'*-DDD (13%) (Figure S6-S7). The Sandviken profile was similar with CB-101 (18%), CB-138 (23%), CB-153 (24%), *p,p'*-DDD (61%) and *p,p'*-DDE (25%). The congener profiles are in accordance with those reported earlier from these fiberbanks (Dahlberg et al., 2020).

The pore water concentrations at the start of the experiment were in the order $\Sigma_6\text{DDX} > \Sigma_{20}\text{PCBs} > \text{HCB}$ in both Väja and Sandviken (Figure S12-S14), with Väja levels at $\Sigma_6\text{DDX}$: 1800 ± 490 pg/L, $\Sigma_{20}\text{PCBs}$: 38 ± 11 pg/L and HCB: 12 ± 2.3 pg/L and Sandviken levels at $\Sigma_6\text{DDX}$: 112 ± 5.0 pg/L, $\Sigma_{20}\text{PCBs}$: 34 ± 2.6 pg/L and HCB: 1.4 ± 0.094 pg/L. In Väja, the PCB congener profile was dominated by CB-28 (6% of $\Sigma_{20}\text{PCBs}$), CB-52 (18%), CB-101 (44% of), CB-138 (18%) and CB-153 (5%), whereas the DDX congener profile was dominated by *o,p'*-DDD (68% of $\Sigma_6\text{DDX}$) and *p,p'*-DDD (32%). In Sandviken, the PCB congener profile was dominated by CB-52 (29%) and CB-101 (31%), whereas the

DDX congener profile was dominated by *p,p'*-DDD (87%), *o,p'*-DDE (9%) and *p,p'*-DDE (4%). Except for the much higher (19 times) levels of DDX in Väja pore water, the congener profile and levels were similar to those previously reported (Dahlberg et al., 2020). It is apparent that DDD dominated the DDX profile in Väja and Sandviken pore waters. DDD is less hydrophobic ($\log K_{ow}$ 5.5–6.0) than most PCBs ($\log K_{ow}$ 5.7–8.2) and is therefore expected to have a higher partitioning to the pore water. The difference in fiber type could also influence the partitioning because cellulose fibers (Väja) might be a poorer sorbent for POPs than coarser wood material (Sandviken) as noted in our previous study (Dahlberg et al., 2020).

At the start of the experiment, the crushed stones used as capping material (≥ 4 mm grain size) was found to contain only small amounts of POPs ($\Sigma_6\text{DDX}$: 0.430 ± 0.060 ng/g dw, $\Sigma_{20}\text{PCBs}$: 0.072 ± 0.00052 ng/g dw and HCB: 0.00019 ± 0.0000014 ng/g dw).

3.4. Sediment to water fluxes of POPs – before and after capping

One of the aims of *in-situ* isolation capping is to reduce diffusion from the contaminated sediment to the overlying water column. The calculated sediment-to water fluxes of HCB and PCBs are presented in Fig. 3 and those of DDX in Fig. 4.

The flux of HCB showed similar or slightly higher fluxes before capping (phases 1) than after the sediment had been capped (phases 4). In column V20, V45 and S45 the flux of HCB reduced by 15%, 18% and 12%, respectively after capping, whereas no decrease was observed for HCB in column S20. HCB is less hydrophobic ($\log K_{ow}$ 5.5) and more prone to diffuse into overlying water and be transported by advection with upwelling pore water than more hydrophobic PCBs.

Among the PCB congeners, the least hydrophobic compound CB-28 showed increasing flux more or less throughout the experiment in all four columns. CB-28 was the only *tri*-CB measured and is less hydrophobic (mono-*ortho* substituted, $\log K_{ow}$ 5.67) than CB-52 (di-*ortho*, tetra-CB, $\log K_{ow}$ 5.84), which showed similar fluxes before and after capping. In the two columns with the thickest cap (column V45 and S45), CB-101 (di-*ortho*, penta-CB, $\log K_{ow}$ 6.38), CB-138 (di-*ortho*, hexa-CB, $\log K_{ow}$ 6.38) and CB-153 (di-*ortho*, hexa-CB, $\log K_{ow}$ 6.92) showed increasing or steady fluxes in the uncapped sediment over time but decreased after capping, reaching 70–82% lower fluxes in phase 4 compared to phase 1. A decrease in flux after capping by 49–77% was also noticed for CB-77 (non-*ortho*, tetra-CB, $\log K_{ow}$ 6.36), CB-118 (mono-*ortho*, penta-CB, $\log K_{ow}$ 6.74), CB-156 (mono-*ortho*, hexa-CB, $\log K_{ow}$ 7.18), CB-167 (mono-*ortho*, hexa-CB, $\log K_{ow}$ 6.74), CB-180 (di-*ortho*, hepta-CB, $\log K_{ow}$ 7.36) in column V45. In column S45, fluxes of CB-118, CB-156 and CB-180 decreased after capping by 23–49% (phase 4 compared to phase 1). For the two columns capped with a 20 cm thick cap (column V20 and S20) a lower flux after capping was only observed for CB-101 (46–54%) and CB-118 (15–32%) in both columns. In column S20, a 19–30% decrease in the fluxes of CB-167 and CB-156 were noted. In addition, CB-77, CB-169 (non-*ortho*, hexa-CB, $\log K_{ow}$ 7.42), CB-189 (mono-*ortho*, hepta-CB, $\log K_{ow}$ 7.71), and CB-209 (tetra-*ortho*, deca-CB, $\log K_{ow}$ 8.18) show reduced flux after capping, whereas no such trend was observed in column V20. Since the flux of these PCB congeners were very low prior to capping and decreased to below the detection limit after capping in column S20, the change in percentage was not calculated for these congeners.

The results indicate that hydrophobicity and the three-dimensional structure of the PCB molecule play a role for their mobility. Planar PCBs (non-*ortho* substituted) are known to show stronger sorption to sedimentary (soot-like) particles (known to be present in the aquatic environment) than medium planar PCBs (mono-*ortho* substituted) and nonplanar PCBs (poly-*ortho* substituted) (Jonker and Koelmans, 2002; Josefsson et al., 2011), thus they are harder to mobilize from the sediment. In our study, it was di-*ortho* substituted PCBs (i.e. CB-101, CB-138, CB-153, CB-180) and some mono-*ortho* substituted PCBs (i.e. CB-118, CB-156) that showed the largest reduction in flux after capping in

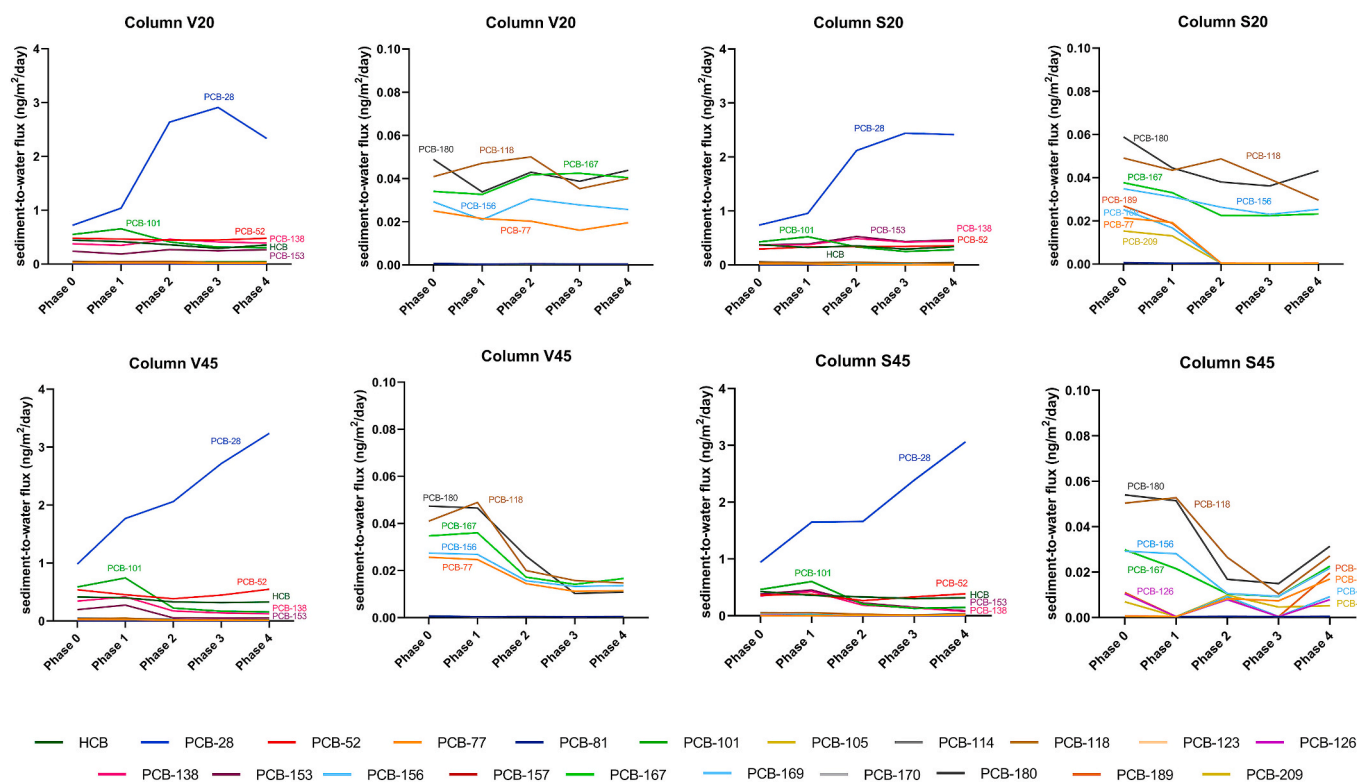


Fig. 3. Sediment-to-water fluxes ($\text{ng}/\text{m}^2/\text{day}$) of HCB and PCBs during uncapped (phase 0 and 1) and capped sediment conditions (phase 2, 3 and 4) in column V20, V45, S20, S45.

both column V45 and S45. Whereas the least hydrophobic mono-*ortho* PCB (CB-28) and di-*ortho* PCB (CB-52) were not affected by the cap. Others have also observed differences in diffusive transport for PCBs across passive caps (gneiss and limestone), with breakthrough of CB-28 and CB-52 in particular (Eek et al., 2008).

Large decreases in fluxes were also observed after capping for *o,p'*-DDD ($\log K_{ow}$ 6.00) and *p,p'*-DDD ($\log K_{ow}$ 5.50) in both columns with sediment from Våja (column V20 by 76–78% and V45 by 91–95%). A decrease in flux of *p,p'*-DDD after capping was also observed in the two columns with sediment from Sandviken (column S20 by 72% and S45 by 92%). Note that the flux of *o,p'*-DDD and *p,p'*-DDD decreased to lower levels when a thicker cap (45 cm) was used compared to a thinner cap (20 cm).

3.5. Suspended particle – before and after capping

The amounts of suspended particles in the overlying water column during the uncapped phases of the experiment (phase 0 and 1) were found to be higher in the columns containing Sandviken sediment (S20, and S45) than those containing Våja sediment (column V20 and V45), Figure S15 adapted from (Lehoux et al., 2023). After capping (phase 2), the amount of suspended particles decreased in S20 and S45. However, for column V45 an increase in suspended particles was observed after capping (phase 2), which then slowly decreased. At the end of the experiment (phase 4), the amount of suspended particles was fairly similar in all four columns. A second aim of *in-situ* isolation capping is to stabilize the sediment and thereby hinder resuspension. Our results indicate that although the placement of the cap can result in increased resuspension initially, one long-term effect of the cap is reduced particle resuspension.

3.6. Concentration of POPs in the cap at the end of the experiment

A third aim of *in-situ* isolation capping is to create a barrier of clean

material that prevent biota coming into contact with the contaminated sediment. It is apparent that some of the suspended sediment particles resettled on the cap, which increased the TC and TOC content in the material sampled from the cap surface (0–1 cm) compared to the initial capping material (Figure S16). Almost twice as high TC content was measured in the cap surface sampled from column V45 (0.20% TC) compared to V20 (0.11% TC), whereas S20 and S45 showed fairly similar levels (S20: 0.16% TC; S45 0.15% TC).

At the start of the experiment, the cap material used was found to contain low amounts of POPs ($\Sigma_6\text{DDX}$: 0.430 ± 0.060 ng/g dw, $\Sigma_{20}\text{PCBs}$: 0.072 ± 0.00052 ng/g dw and HCB: 0.00019 ± 0.0000014 ng/g dw). These concentrations are classified as low or very low according to Swedish environmental assessment criteria for organic pollutants in sediment (Josefsson, 2017). At the end of the experiment, slightly higher levels of HCB were observed in the surface cap of column S20 (0.045 ng/g dw) and S45 (0.042 ng/g dw) (Figure S17). The highest concentrations of $\Sigma_{20}\text{PCB}$ were measured in the surface cap in column V45 (0.11 ng/g dw) and S20 (0.092 ng/g dw), whereas V20 and S45 showed only slightly higher concentrations as measured initially in the cap (Figure S18). Compared to initial levels, similar or lower concentrations of $\Sigma_6\text{DDX}$ were measured in the cap surface at the end of the experiment (Figure S19). The PCB concentrations in the cap surface of the different columns show a similar pattern as observed for TC, which indicate that resettling of PCB contaminated sediment particles caused increased PCB levels in the cap. In general, the concentrations measured in the surface cap material at the end of the experiment are classified as low or very low according to the Swedish environmental assessment criteria for sediment (Josefsson, 2017). Since these values are similar to background concentrations in offshore sediments in Sweden, the risk to sediment dwelling organisms that come in contact with contaminated sediment particles is greatly reduced by applying the cap on the sediment.

The pore water concentration was measured in the middle of the cap at the end of the experiment (Figure S20 and S21). The highest levels of $\Sigma_6\text{DDX}$ were measured in V20 (130 pg/L) and V45 (32 pg/L), whereas in

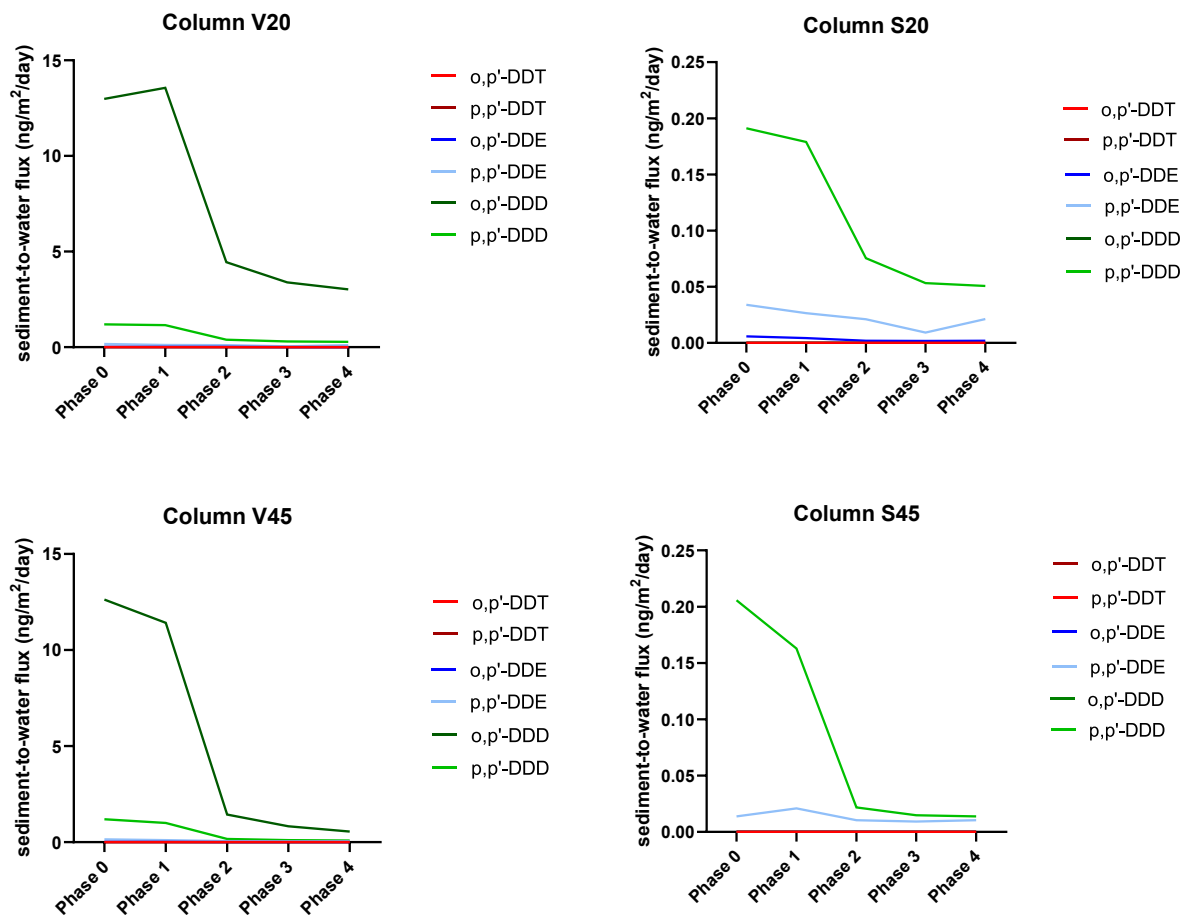


Fig. 4. Sediment-to-water fluxes ($\text{ng/m}^2/\text{day}$) of DDX during uncapped (phase 0 and 1) and capped sediment conditions (phase 2, 3 and 4) in column V20, V45, S20, S45.

S20 and S45 all DDXs were below detection. This is also in agreement with the higher flux of DDX measured in V20 and V45 in phase 4 (Fig. 4). Similar levels of PCBs were found in the middle of the cap of V20 ($\Sigma_{20}\text{PCBs}$: 3.1 $\mu\text{g/L}$) and S20 (5.3 $\mu\text{g/L}$), whereas in V45 and S45, all PCB congeners were below detection. HCB was not detected in the cap's pore water in any of the four columns. Compared to the initial sediment pore water concentration (Figure S12-S14), the levels of contaminants in the cap's pore water were substantially lower. Since the pore water constitutes the freely dissolved and the more bioavailable fraction of contaminants, the exposure for sediment burrowing organisms is more reduced by applying a thicker cap.

4. Conclusions

This study showed that capping fiberbank sediment with a 45 cm gravel cap reduced the sediment-to-water fluxes for most of the studied POPs, while no post-capping reduction in sediment-to-water flux was observed for the less hydrophobic compounds (i.e. CB-28 and CB-52). On the other hand, the cap placement caused consolidation of the soft fiberbank sediment, resulting in a transport of contaminated pore water to the overlying water column. Hence, it is important that the cap is designed to reduce the effects of consolidation-induced advective transport of contaminants. Importantly, gas formation and gas ebullition events in the sediment columns was shown to increase pore water advection and negatively affect the structural integrity of the cap. In our laboratory set-up lateral movement of the gas was restricted by the column walls, while the boundary conditions in the field are likely to be different. Although increased resuspension was observed initially when applying the cap, the long-term effect of the cap was reduction of

particle resuspension, and at the end of the experiment, the levels of suspended particles were similar (Väja) or lower (Sandviken) than prior to capping. The POP concentrations in the cap at the end of the experiment are classified as low. Hence, the risk for benthic biota to come in contact with contaminated sediment particles is greatly reduced by applying a cap. Furthermore, our study demonstrates the implications of extensive gas production in this type of sediment and how it results in increased pore water advection. It also shows how gas migration through the cap disturbs its structural integrity and, therefore, potentially reduces the long-term efficiency of conventional isolation-caps, which may limit its practical applicability. Given the number of fiberbanks currently present, it is important to find suitable remediation solutions for this type of sediment. Although this study is based on a limited number of columns, the results from our large-scale column set up and long-term monitoring of fluxes in a controlled environment provide useful and novel information that will be beneficial for decision makers and consultants working in the field of sediment remediation.

Credit author statement

Capping fiberbank sediments to reduce persistent organic pollutants (POPs) fluxes: A large-scale laboratory column experiment.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.122019>.

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