

REPORT

Sediment capping with activated biochar in Bureå, Sweden

LABORATORY DIFFUSION TESTS

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Summary

In the scope of a larger project where thin-layer capping with bentonite and biochar is being tested as a sustainable remediation strategy for contaminated sediments in the Bureå Bay (Sweden), NGI has conducted laboratory tests. The purpose of these tests was to assess the effect of a capping with bentonite and biochar on the upwards diffusion of contaminants (PAGs and metals, mainly arsenic and mercury) from the sediment to the water column above.

This report summarises the results of these tests and shows that, under conditions where contaminant transport is dominated by diffusion processes, the active thin caps reduced the diffusion of PAHs and most of the metal elements. Capping with bentonite alone reduced the flux of 15-PAHs by 50%, whereas biochar-enriched bentonite reduced this flux by 58%.

The behaviour of arsenic (As) was more complex than that of PAHs and non-redox sensitive elements. The cap limited the upwards diffusion of As under dysoxic conditions, but also the diffusion of iron (Fe). Under more oxic conditions, Fe oxyhydroxides precipitated, and were in the order of magnitude 600-800 μ g/l above capped sediment while they dropped to the detection level above the untreated sediment. Typically, Fe oxyhydroxide precipitates on top of sediment play a dominant role in As sorption in the solid phase. Along with an increasing pH, sediment capping with biochar/bentonite could actually result in increased fluxes of As out of the sediment under field conditions. The results do not allow clear conclusions on the effect(s) of the capping on mercury behaviour. Nevertheless, the results suggest that capping limited the diffusion of mercury during the first weeks, but that the effect of capping becomes more complex at the later stages of the experiment.

We recommend further investigation of the effect of the capping on As and Hg behaviour over time, with a focus on redox and methylation processes. In a more general perspective, thin biochar-based caps can be recommended for the reduction of PAH fluxes from contaminated sediments. Care should be taken about the effect of these caps on the release of redox-sensitive metals such as As and Hg.

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1 Introduction

In the bay of Bureå, *Bure träsliperi och sågverk* (Bure wood grinding and sawmill) operated from 1928 to 1992. The factory manufactured mechanical grinded pulp and between 1948 and 1964 the pulp was treated with the phenylmercury preparation pulpasan to prevent decay of the pulp. As a result of the operation, spreading of fiber sludge (mercury contaminated fibers) has taken place from a sedimentation basin constructed in the bay. From the beginning, the fiber sludge was discharged directly in the bay. With time, embankments were built to contain the sludge and the spreading of fibres decreased gradually. As a result of the operations, a fibre bank was built and affected the surrounding sediment. The sea currents have with time contributed to the spreading of contaminated sediment in the bay and it is assumed that some spreading can continue even today.

Assuming that diffusion is the largest dispersal mechanism from contaminated sediments, covering the contaminated seabed is a possible measure to reduce the spreading of contaminants (Figure 1). Covering large areas becomes unrealistic if the function of the cover only depends on the thickness of the layer. A biochar-based reactive barrier, however, enhances the adsorption that takes place in the sediments at the same time as the need for material is kept down. Biochar can effectively bind substances such as Hg, methyl-Hg, Cu, Zn and PAH.



Figure 1. Vertical dimensions and theoretical water concentration profile of contaminants from a sediment (C_{pw_sed}) through a cap and/or the diffusive bounder layer (DBL) to the bulk water (C_w). Almost constant concentration in the bioturbation zone (C_{cap_bio}) translates the fact that this layer presents smaller resistance to transport. A linear concentration gradient in the DBL and in the bulk cap layer translates the fact that diffusion is the main transport mechanism in these layers. Figure from Eek et al., 2008.

The Geological Survey of Sweden (SGU) funded a demonstration project for the construction of thin capping, carried out by Luleå University of Technology (LTU) in collaboration with the Norwegian Geotechnical Institute (NGI) and Skellefteå Municipality, within the framework of the Government Mission Polluted Sediment. The aim of the method tested is to prevent the spread of contamination (diffusion) from the sediments to the water mass using a thin cover activated by biochar. Biochar has in itself a large adsorption capacity and its addition increases the content of organic carbon at the bottom and adsorbs both organic and inorganic pollutants. The method being tested is a thin reactive barrier (5 cm) which is placed on top of the bottom and which can be used in environments where accumulation conditions prevail.

In the scope of this project, NGI conducted laboratory tests to assess the potential of thin-layer capping with activated biochar for limiting the dispersion of contaminants. The experiment was aimed at addressing the following questions:

- i. Is the upwards diffusion of PAH (Polycyclic Aromatic Hydrocarbons), Hg (mercury) and As (arsenic) limited by a capping layer?
- ii. Does activated biochar limit to a significantly further extent the upwards diffusion of PAH, Hg and As?
- iii. Is As sorbed on biochar, or is it mobilised by locally higher pH?

2 Material and methods

2.1 Sediment material used for the laboratory tests

An area of 30 m² was defined as a test site (testområde) for applying the capping solution, and an area of 30 m² was defined as a reference (referensområde) without capping (Figure 2).

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Figure 2. Localisation of the test area where samples were taken (squares coloured in orange), homogenized and used for the laboratory tests. The histograms shown in top right of the figure show the spatial variation of the concentrations of arsenic, mercury and PAH in the sediment of the individual samples taken at the five different locations. For each location (test site, reference site and reserve site) the five samples were mixed into one sample and homogenized.

Five locations of the test site (T3, T5, T10, T15 and T17 on Figure 1) were sampled and homogenized right after sampling by LTU to obtain one single sample of sediment from the test area. A subsample of the obtained sediment sample was sent to NGI and homogenized again with a cement mixer, right before using it for the laboratory tests.

The concentrations of metal elements and the sum of 16 EPA PAHs in the sediment sample and in the porewater was analysed by an accredited laboratory (ALS). The porewater was sampled in the supernatant of the sediment buckets after phase separation,

and filtered over 0.45 μ m. The mineralogical composition was analysed by X ray diffraction followed by Rietveld refinement, at the laboratory *Xrayminerals* (UK), after drying the sample at 80 °C. Results for the composition of the sediment and its porewater are presented in Tables 1–3.

The Bureå sediments from the test area contain abundant wood pieces in the centimetre size. XRD analyses indicated that the inorganic part of the sediment consists of a majority of silicate minerals as well as a small but significant amount of pyrite (1.5 wt% FeS₂; Table 1). The dark grey colour of the bulk sediment and the thin layer with orange colour observed at the surface of the sediment upon sampling (Figure 3) suggest that the sediment is reduced and oxidizes only at the interface with sea water, where iron oxyhydroxydes precipitated at the surface. The sediments contain concentrations of As and PAH (Table 2) which are considered "bad" and, and Hg concentrations considered "very bad" in the Norwegian classification for sediment (M608-2016).

Table 1: Mineralogical composition of Bureå sediment based on Rietveld analysis of XRD patterns. The sediment was dried at 80°C before analysis

Mineral phase	Rietveld-derived wt%
Illite + Mica	1.6
Chlorite	5.7
Quartz	42.7
K Feldspar	16.3
Plagioclase	29.3
Amphibole	3.0
Pyrite	1.5



Figure 3. Picture of the sediment sampled at the "test area", showing a thin light brown layer indicative of Fe hydroxide precipitates at the surface of dark, reduced sediments.

Table 2: Concentrations of metal elements in the sediment used for the laboratory tests (in mg/kg) and in the corresponding porewater (in μ g/L). Porewater here was sampled in the supernatant of the sediment bucket after phase separation. These concentrations are compared with the concentrations in a water sample collected above the test site in May 2021 ("bay water"). ND= not determined.

Compound	Concentration in sediment (mg/kg)	Concentration in porewater (µg/L)	Concentration in the bay water (µg/L)
Fe	28 320	20	1100
Ва	463	46	11
As	240	17	1,4
Pb	196	<0,2	0,5
Zn	183	4,5	11
Cu	93	<1	2,6
V	37	0,2	0,3
Ni	17	1,8	2,5
Со	8,2	0,7	0,4
Hg	1,7	<0,02	<0,02
Methyl-Hg	0,01	ND	ND
Mn	0,43	2120	58

Table 3: Concentrations in mg/kg of PAHs measured in the sediment and in the materials used for capping. The concentrations in sediment are coloured as a function of the quality criteria for sediments defined in the Norwegian standards (M-608): yellow = moderate, orange = bad, red = very bad.

Compound	Sediment	Biochar	Bentonite
Naphthalene	0.72	0.09	< 0,05
Acenaphthylene	0.35	< 0,01	< 0,01
Acenaphthene	<0.10	< 0,01	< 0,01
Fluorene	0.26	< 0,02	< 0,01
Phenanthrene	1.3	0.07	< 0,02
Anthracene	0.63	< 0,01	< 0,01
Fluoranthene	2.72	0.05	< 0,01
Pyrene	2.2	0.04	< 0,01
Benz(a)anthracene	1.19	< 0,01	< 0,01
Chrysene	1.05	< 0,01	< 0,01
Benzo(b)fluoranthene	1.33	< 0,01	< 0,01
Benzo(k)fluoranthene	0.47	< 0,01	< 0,01
Benzo(a)pyrene	1.04	< 0,01	< 0,01
Dibenz(ah)anthracene	0.14	< 0,01	< 0,01
Benzo(ghi)perylene	0.61	< 0,01	< 0,01
Indeno(1,2,3-cd)pyrene	0.63	< 0,01	< 0,01
Sum of 16 EPA PAH	14.6	0.25	<ld< td=""></ld<>

2.2 Capping material used for the laboratory tests

The materials used for the sediment capping were:

- A commercial activated biochar from Jacobi Carbons (Kalmar, Sweden), CP1 powdered, with 80% of particles in a size smaller than 74 μ m (surface area and pore volume are detailed in Table 4)
- Bentonite clay, which is a dry powdered white sodium montmorillonite, saline seal from CETCO and was obtained from FLA Geoprodukter.

Table 4: Surface area (SA) and pore volume (V) of biomass-based activated biochar (CP1), as determined by CO_2 sorption (pore sizes 3.5-15 Å) and N_2 sorption (pore sizes 15-400 Å).

CO ₂ ((273 K)		N ₂ (77 K)	
Pore SA 3.5-15 Å	Pore V 3.5-15 Å	Pore SA 15-400 Å	Pore V 15-400 Å	BET total SA	BET total pore V
$[m^2 g^{-1}]$	$[cm^3 g^{-1}]$	$[m^2 g^{-1}]$	$[cm^3 g^{-1}]$	$[m^2 g^{-1}]$	$[cm^3 g^{-1}]$
977	0.322	61	0.053	1158	0.539

The PAH concentration in these materials was analysed at Ökometric in Bayreuth, Germany, using gas chromatography- mass spectrometry (GC-MS). No PAH could be detected in the bentonite material, and only minor concentrations of a few PAHs were detected in the biochar (Table 3):

- naphthalene (0.09 mg/kg, i.e. 12% of the concentration in the sediment),
- phenanthrene (0.07 mg/kg, i.e. 5% of the concentration in the sediment),
- fluoranthene (0.05 mg/kg, i.e. 2% of the concentration in the sediment) and
- pyrene (0.04 mg/kg, i.e. 2% of the concentration in the sediment).

2.2.1 Concentrations of metals in biochar and bentonite

Table 5: Element concentrations in mg/kg of dry matter measured in the sediment and in the materials used for capping.

Compound	Biochar	Bentonite
Fe	328	95200
Ва	6	164
As	0.1	0.7
Pb	<0.05	8
Zn	3	80
Cu	37	118
V	2	227
Ni	1	35
Со	0.3	45
Hg	<0.04	<0.03
Mn	20	937
S	103	909

The bentonite clay used for capping in this experiment contained significant amounts of Fe, Cu, V, Ni, Co and Mn, i.e. higher concentrations than the sediment (Table 2).

However, these concentrations are significantly lower in the biochar material. In addition, the concentrations of As, Hg and Pb, which are the most problematic metal contaminants at the Bureå Bay, are significantly lower in either of the capping materials compared to in the sediment.

2.2.2 Fe oxidation state in sediment, biochar and bentonite.

Because Fe(III) oxyhydroxides have typically high affinity for metal elements and in particular for arsenic, the concentration of "available" Fe(III) was analysed in the covering materials (bentonite and biochar) and compared with the sediment (Table 6). The method used for Fe(III) analysis was based on acid (0.5 M HCl) extraction of Fe(II) and spectrophotometry on ferrozine-complexed Fe(II). Total Fe was analysed by reducing all Fe and applying the same colorimetry analysis. Fe(III) concentration was then deduced from the difference between total Fe and Fe(II). The detailed method is described in Stookey (1970).

Table 6: Concentrations of total acid-extractible iron (Fe_{TOT}) and Fe(III) in the Bureå sediment and capping materials.

Fe _{tot} (mg/kg DM)		Fe ^(III) (mg/kg DM)	% Fe ^(III) /Fe _{TOT}	
Bentonite	124	110	89	
Biochar	36	4	11	
Sediment	739	0	0	

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Note that the bentonite material contains significant concentrations of available Fe(III) (Table 6). As expected from the dark colour and the pyrite content, most of Fe from the sediment is in the reduced form Fe(II).

2.2.3 pH of biochar and bentonite.

pH of biochar and bentonite was measured in a paste (bentonite) or suspension (biochar) with solid:liquid ratio of 1:2.5 in mass, after shaking and settling during 2h. The pH of bentonite was 9.3 and pH of biochar was 10.0.

2.3 Five treatments tested

Five different treatments were applied to the sediments during the laboratory tests:

- A. No treatment (control)
- B. Only bentonite capping $(2.6 \pm 0.4 \text{ kg/m}^2 \text{ corresponding to } \sim 1.5 \text{ cm cap})$
- C. Only biochar, mixed with the sediment (15 g/jar, i.e. 3 kg/m^2)
- D. Biochar $(0.7 \pm 0.1 \text{ kg/m}^2)$ + bentonite $(2.6 \pm 0.4 \text{ kg/m}^2)$ (~1.5 cm cap)
- E. Biochar $(1.8 \pm 0.1 \text{ kg/m}^2)$ + bentonite $(2.6 \pm 0.4 \text{ kg/m}^2)$ (~1.5 cm cap)



Figure 4. Pictures of the experimental tests with sediment and different treatments. NB: the pictures were taken after sampling of the water phase above.

The surface coverage of biochar was chosen to be in the range of those tested in previous Norwegian sediment capping. For example, in the scope of the *OPTICAP* NFR project, the biochar cover applied in a dioxin-contaminated site in the Grenland fjord corresponded to a surface coverage of 1.6 kg/m^2 .

The amount of bentonite added was chosen so that a paste was obtained, relatively easy to apply as a flat layer. This corresponded to a mass proportion bentonite:water of 20:90.

The water used for the tests was salted with NaCl 3 g/L, in order to represent brackish water.



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Figure 5. Schematic principle of the experimental tests for diffusion of metal elements (left) and PAH (right) through the (capped) sediments.

2.4 Diffusion tests for PAHs

In order to assess the diffusion of PAHs from the sediment to water, the approach chosen was similar to the one used in Eek et al., 2008. Separate glass jars with a diameter of 7.9 cm were prepared for each treatment and each time point tested. Water (miliQ water with 3 g/L NaCl) was placed above a flat surface of sediment, and a heptane phase was placed above the water (Figure 5). Heptane was used as an infinite sink for PAHs diffusing from the sediment to the above water, indeed the affinity of organic solvants for PAHs is on average several orders of magnitude higher than the affinity of water for PAHs (the logarithmic octanol-water partition coefficients of PAHs (log Kow) is typically in the range of 4 to 6 at 25°C; De Maagd et al., 1998).



Figure 6. Theoretical PAH concentration profile in water and capping layer in the microcosm test (blue dashed lines) assuming steady-state molecular diffusion. Concentration in water in contact with heptane (C_w), concentration in sediment pore water (C_{pw_sed}), diffusive layer thickness (δ_e) and cap thickness (h_{cap}) are indicated. (a) Test with uncapped sediment (treatments A and C), (b) test with capped sediment (treatments B, D and E).

The procedure for setting up the diffusion tests was the following:

- The sediment was homogenized using a cement mixer, then 150 g was placed in each glass jar using a pastry pouch. Caution was taken to avoid air pockets in the sediment or traces of sediment on the walls and to obtain a flat surface.
- The treatments A-E were applied to all the glass jars.
 - For the A samples, 150 mL of milliQ water with NaCl 3 g/L was added slowly to the top with a plastic pipette.
 - For the B samples, a paste was made with bentonite and milliQ water with NaCl 3 g/L, in a mass proportion bentonite:water of 20:90, and then 50 mL of the paste was applied above the sediment using a syringe, which resulted in a cap layer of approximately 1.5 cm thickness.
 - For the C samples, 15 g of biochar was mixed with the sediment and the mix was flattened. The walls of the jars were cleaned to ensure a flat interface between solid and liquid.
 - For the D and E samples, a paste was made with bentonite, biochar and milliQ water with NaCl 3 g/L, in a mass proportion bentonite:biochar:water of 20:5:90 and 20:15:94, respectively for the D and E treatments. Then, 50 mL of the paste was applied above the sediment using a syringe, which resulted in a cap layer of approximately 1.5 cm thickness.
- All the jars were placed under a fume hood and 60 mL of heptane (containing the internal standard) was added above the water phase.
- The weight of the remaining pastes after the capping application was used to calculate the amount of capping material applied to each jar.



Figure 7. Preparation of the test samples for diffusion of PAHs from sediment to water.

For each time point, the heptane phase was collected using methanol-washed Pasteur pipettes and glass test tubes, then the volume of heptane was reduced to 0.5 ML to 1 mL using a rotational vacuum concentrator equipped with a cold trap (®CHRIST, model RVC 2-25 CDplus). The samples were stored under -18 °C before analysis. The masses of 15 EPA PAHs, i.e. acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, benz(a)anthracene, fluoranthene. pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene and dibenz(ah)anthracene, were then analysed in the heptane phase by Ökometric in Bayreuth, Germany, using gas chromatography- mass spectrometry (GC-MS). The sum of 15 EPA PAHs was calculated and is noted hereafter 15-PAH. An internal standard, consisting of deuterated Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Fluoranthene, Benz(a)anthracene, Benz(a)pyrene and Dibenz(ah)anthracene in nonane, was used in the heptane phase, in order to correct PAH concentrations for eventual losses of heptane during the sampling procedure.

PAH concentrations were also analysed in the solid phase (sediment and capping) for a selection of samples after 100 days and 386 days of diffusion.

2.5 Diffusion tests for metal elements

In order to assess the diffusion of metal elements from the sediment to water, the approach chosen was similar to the one for the tests for PAH diffusion, but the metal concentrations were measured directly in the water phase due to the lack of a properly tested infinite sink method for metal removal from the water phase. In this case, the diffusion regime was not a steady state with infinite sink. Instead, in principle the flux decreases as concentrations in the water phase increase, until an equilibrium is reached between the porewater in sediment and the water phase above the sediment.

Past experience at NGI showed that it is more difficult to capture the metal fluxes from sediment to water in the case of metal elements, compared to PAHs, especially in the case of redox-sensitive elements. Indeed, oxidation in the water phase can lead to the precipitation of Fe minerals and coprecipitation or sorption of trace elements to these minerals. With the aim of limiting these precipitation processes, the tests for metal diffusion were conducted under inert atmosphere in glovebags filled with nitrogen. The oxygen concentrations measured above the sediment in test samples during the first two weeks were between 0.2 mg/L and 1 mg/L, which corresponds to dysoxic conditions (Tyson and Pearson, 1991). At the Bureå site, the oxygen conditions measured above the sediment were between 1 mg/L and 2 mg/L, which overlaps between dysoxic (0.2-2 mg/L O₂) and oxic (2-8 mg/L O₂) conditions (Tyson and Pearson, 1991). In addition, oxygen concentrations are expected to fluctuate with time (e.g., seasonally) under environmental conditions. Oxic conditions were also represented in the experimental tests after two weeks, when the glovebags were not anymore refilled with nitrogen and oxygen concentrations increased above 2 mg/L.

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Figure 8. Glovebags used to set up the metal diffusion tests under oxygen-limited conditions.

The procedure for setting up the diffusion tests was the following:

- The sediment was homogenized using a cement mixer, then 150 g was placed in each glass jar using a pastry pouch. Caution was taken to avoid air pockets in the sediment or traces of sediment on the walls and to obtain a flat surface.
- The jars were placed in glovebags, which were then purged with nitrogen. Oxygen consumers were opened in the glovebags to ensure a low oxygen concentration at start of the experiment.
- The following day, the treatments A-E were applied to all the glass jars in the N₂-filled glovebags.
 - For the A samples, 150 mL of N₂-sparged milliQ water with NaCl 3 g/L was added slowly to the top with a plastic pipette.
 - \circ For the B samples, a paste was made with bentonite and N₂-sparged milliQ water with NaCl 3 g/L, in a mass proportion bentonite:water of 20:90, and then 50 mL of the paste was applied above the sediment using a syringe, which resulted in a cap layer of approximately 1.5 cm thickness.
 - For the C samples, 15 g of biochar was mixed with the sediment and the mix was flattened. The walls of the jars were cleaned to ensure a flat interface between solid and liquid.
 - \circ For the D and E samples, a paste was made with bentonite, biochar and N₂-sparged milliQ water with NaCl 3 g/L, in a mass proportion bentonite:biochar:water of 20:5:90 and 20:15:94, respectively for the D and E treatments. Then, 50 mL of the paste was applied above the sediment using a syringe, which resulted in a cap layer of approximately 1.5 cm thickness after swelling.
- All the jars were then closed in zip-lock bags until the water above was sampled.



- The weight of the remaining pastes after the capping application was used to calculate the amount of capping material applied to each jar.
- Oxygen concentrations in equilibrium with water were monitored at the start and during water sampling, in a jar filled with water placed in the same glovebag.
- For each time point, a new jar was sampled. A plastic syringe was used to take the water above the sediment, then water was filtered at 0.45 μ m using Whatmann PES filters and stored in plastic bottles with nitric acid in a final concentration of 1 wt%. Every other time point was sampled in triplicates (Table 7). A selection of water samples was also stored in dark glass bottles with 1% nitric acid for Hg analyses.
- Before each sampling, the pH of the water above sediment was measured using a pH paper with a precision of ± 0.5 .
- For a selection of time points, the solid phase was also sampled, and in the case of capped samples the cap layer was separated from the underlying sediment before freezing.

The water samples were stored at 4 °C or -18 °C and sent to the Norwegian university of life sciences (NMBU) for metal analyses. In addition, seven samples were sent to the Norwegian institute for water research (NIVA) for total mercury analysis using a method which provides a detection limit of 0,1 ng/l and a typical quantification limit of 0.3 ng/l, which is 100-fold lower than the limits for the procedure used at NMBU.

	Triplicates	Single sample	
А	6h, 3d, 16d, 64d	3h, 24h, 7d, 32d	
В	2d, 8d, 32d, 99d	4d, 16d, 64d	
С	6h, 3d, 16d, 64d	3h, 24h, 7d, 32d	
D	2d, 8d, 32d, 99d	4d, 16d, 64d	
Е	2d, 8d, 32d, 99d	4d, 16d, 64d	

Table 7: Time points with triplicates or unique samples for the various treatments

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3 Results and interpretation

3.1 Diffusion tests for PAHs

3.1.1 Diffusion of PAHs from untreated sediments (samples A)



Figure 9. Cumulative amounts of PAHs analysed in the heptane phase of tests with untreated sediment (A samples) as a function of time. NB: error bars are shown only for samples for which triplicate analyses are available, i.e. for 2, 15 and 50 days, and for 386 days in the case of A, B, D samples for PAH compounds with Kow > Kow_pyrene. Only two of the triplicate samples for 200 days could be analysed and averaged, therefore the standard deviation was not calculated. A linear regression is shown in dashed line. Only examples of individual PAHs are shown, but these examples were chosen to represent various affinities for organic solvants (The octanolwater partitioning coefficient K_{ow} for acenaphtylene, anthracene, fluoranthene, chrysene and benso(ghi)perylene are respectively 3.80, 4.73, 5.34, 5.95 and 7.24 according to Smedes, 2019).

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In the case of untreated sediment (A samples), the concentration of most PAH compounds analysed in heptane increased over time (Figure 9). Low concentrations compared to quantification limits in a few samples, as well as experimental error due to for example floating of sediment particles up to the transition between water and heptane in some of the samples, led to large standard deviations among triplicate samples, and inconsistently high concentrations in some of the samples. Nevertheless, the general trend is a linear increase of PAH concentrations in heptane over time. Because the heptane is behaving as an infinite sink for PAHs present in the water layer (Figure 6) a linear increase of PAH concentration in heptane indicates a constant concentration in the water phase. This linear trend is consistent with a steady-state diffusive flux from sediment through a diffusive boundary layer (DBL) and can be expressed as follows (Jørgensen and Revbech, 1985):

$$J_{i\,\text{sed}} = \frac{D_i}{\delta_{\text{DBL}}} (C_{i\,\text{pw}} - C_{i\,\text{w}}),$$
^[1]

With J_{ised} the diffusive flux, D_i the diffusion coefficient for a given compound in cm²/cm, δ_{DBL} the diffusive boundary layer in cm, $C_{i pw}$ the pore water concentration and $C_{i w}$ the concentration in the water layer.

3.1.2 Diffusion from capped sediments (samples B, D and E)

In the case of treated sediments, the concentrations of PAHs detected in the heptane phase are generally lower than in the case of untreated sediment, and the reduction was stronger in the case of capping with both biochar and bentonite (D and E samples) than in the case of capping with bentonite alone (B samples) (Figure 10, Figure 11).



Figure 10. Cumulative amounts of 15-PAH analysed as a function of time in the heptane phase of tests with (A) untreated sediment, (B) sediment capped with only bentonite, (D and E) sediment capped with bentonite mixed with respectively low and high amounts of biochar. Results for C treatment are not shown for a better readability; indeed, 15-PAH were not available for all of the time points.

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Despite large experimental uncertainties (Figure 11), a tendency is that PAHs detection in the heptane phase of the covered samples is <u>delaved</u> compared to the untreated A samples. Indeed, for a number of PAH compounds, including acenaphtylene, benso(a)anthracene and chrysene, a delay of 50 to 100 days is observed for increase of PAH concentrations over time in capped samples, compared to the untreated samples (Figure 11). This delay is partly due to the additional thickness of clean capping that the contaminants are diffusing through (h_{cap} in Figure 6). Indeed, when contaminated sediments are capped with clean materials, contaminants from the sediment diffuse into the pore water in the cap and adsorb to the cap material. When the dissolved concentration in the pore water in the cap is in equilibrium with the adsorbed concentration in the cap, a new steady state is reached (Figure 1; Eek et al., 2008). The time to reach steady state and the breakthrough time of contaminants is dependent on the sorption capacity of the capping material.

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Figure 11. Cumulative amounts of PAHs analysed as a function of time in the heptane phase of tests with (A) untreated sediment, (B) sediment capped with only bentonite, (C) sediment mixed with biochar, (D and E) sediment capped with bentonite mixed with respectively low and high amounts of biochar. NB: error bars are shown only for samples for which triplicate analyses are available, i.e. for 2, 15 and 50 days, and for 386 days in the case of A, B, D samples for PAH compounds with Kow > Kow_pyrene. Only two of the triplicate samples for 200 days could be analysed and averaged, therefore standard deviation was not calculated. A linear regression is shown in dashed line. Only examples of individual PAHs are shown, but these examples were chosen to represent various affinities for organic solvents (The octanol-water partitioning coefficient K_{ow} for acenaphtylene, anthracene, fluoranthene, chrysene and benso(ghi)perylene are respectively 3.80, 4.73, 5.34, 5.95 and 7.24 according to Smedes, 2019). Time points are joint with dashed line for distinguishing the different treatments, but each time point corresponds to a distinct sample that is sacrificed for sampling.

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The diffusion fluxes with and without capping can be approximated by the slopes of PAH increase from the time of PAH breakthrough. For example, the diffusion flux of 15-PAH through the bentonite cap was 2-fold smaller than the diffusion flux of 15-PAH without cap (Figure 12). This result is consistent with the fact that, after the new steady-state flux from the capped sediment has been reached, the flux is in principle lower than the steady-state flux without capping. This is a result of an increased diffusive path length above capped sediments, as explained above (Figure 6) – the diffusive path length is now the whole thickness of the cap instead of just around 1.7 mm in the case of uncapped sediment, increasing δ_{DBL} in eq. 1 by around a factor of ten.



Figure 12. Slope calculation corresponding to fluxes of the sum of 15 EPA PAHs with a bentonite cover (B, orange) and a bentonite+biochar cover (E, black) compared to without cover (A, green). The flux above B samples is calculated after 100 days and the flux above E samples after 200 days because results of individual PAHs indicate that breakthrough through the bentonite cap was not reached before (Figure 10).

The remediation effectiveness (RE) of a capping layer can be expressed as the reduction of the steady state contaminant transport from the sediment after capping (Jicap) relative to the transport from the sediment before capping (Jised) (Eek et al., 2007):

$$\mathbf{RE} = 1 - \frac{J_{i\,\mathrm{cap}}}{J_{i\,\mathrm{sed}}}$$

In the case of the bentonite cap, RE= 1-6/12 = 0.5, meaning that the diffusive flux of dissolved PAHs was reduced by 50% by introducing a 1-cm undisturbed capping layer of bentonite. In the case of the biochar-enriched bentonite cap (E sample), RE = 1-5/12 = 0.58, meaning that the diffusive flux of dissolved 15-PAHs was reduced by 58% by introducing a 1-cm undisturbed capping layer (a factor of 2.4). The reduction factor was lower than the theoretical one of a factor of ten, but this can be explained by uncertainties in the thickness of the diffusive boundary layer in the uncapped sediment.

For a number of PAH compounds like acenaphtylene, acenaphtene and chrysene, phenanthrene and anthracene, the concentrations measured in heptane were significantly lower for samples capped with bentonite and high amounts of biochar $(1,8 \pm 0,1 \text{ kg/m}^2)$ than for samples with bentonite and lower amounts of biochar $(0,7 \pm 0,1 \text{ kg/m}^2)$, which was lower than for samples capped with only bentonite (Figure 11). These lower PAH concentrations for sediment covered with more biochar are interpreted as being at least partly due to **sorption** of PAH on biochar. Indeed, PAHs have a high sorption affinity for biochar (Chen and Yan, 2011) and sorption processes in the cap delays and limits diffusion of contaminants to the water above (Viana et al 2008). The biochar effect on breakthrough delay could also be influenced (although to a lesser extent) by the effect of particles of biochar on porosity (ϵ , dimensionless) and tortuosity (τ , dimensionless) (equation {2}). Indeed, diffusive flux through the cap under the new steady-state can be approximated by equation {2} (Eek et al., 2008),

$$J_{i \operatorname{cap}} = \frac{\varepsilon \cdot D_i}{\tau \cdot (h_{\operatorname{cap} d} + \delta_{\operatorname{DBL}})} (C_{i \operatorname{pw}} - C_{i \operatorname{w}})$$

$$\{2\}$$

where h_{capd} is the thickness of the (undisturbed part of the) capping layer in cm, δ_{DBL} the diffusive bonder layer in cm, ϵ is the porosity and τ is the tortuosity. ϵ and τ are dimensionless (Boudreau, 1997). In the laboratory tests there was no visual bioturbation so the whole cap was assumed to be undisturbed.



Figure 13. Concentrations of PAHs in the cap layers after 100 days and 386 days of experiment. Note that the vertical scale is logarithmic. Error bars are shown only for samples available in triplicate, i.e. the B and E caps after 386 d.

Analyses of PAHs in the capping layer after 100 and 386 days of experiment show that part of the PAHs diffused into the capping layer. The PAH concentrations are found in increasing levels for the capping with only bentonite (B samples) < bentonite and small amount of biochar (D samples) < bentonite and high amount of biochar (E samples). The very low concentrations of PAHs present in biochar (Table 3) cannot explain the difference in PAH concentration in biochar-bearing caps compared to bentonite-only

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cap. This suggests a higher retention of PAHs in the capping layers containing biochar, due to sorption on biochar.

3.2 Diffusion tests for metal elements

3.2.1 Diffusion of redox-inactive elements



Figure 14. Concentrations of Mg, Si, Ca and K over time in the water phase. Error bars are calculated as standard deviation of triplicate results for samples taken after 1.5h, 6h, 3d, 16d, 64d in the case of A and C samples; and for samples taken after 2d, 8d, 32d, 99d in the case of B, D and E samples. When triplicates were not available, error bars shown are the maximum relative errors for a given treatment and a given element, based on time points where triplicates are available.

3.2.1.1 Diffusion of redox-inactive elements from untreated sediment

The concentrations of Mg, Si, Ca and K in water increased over time, at a rate that decreased with time, and reached a stable concentration. This behaviour is consistent with diffusion processes for systems in equilibrium in a closed system, where the flux is controlled by the difference between the concentration in water (C_w) and the concentration in porewater (C_{pw}). Over time, this difference decreases and the concentration reaches a plateau.

In order to verify whether the concentration of these elements was controlled by diffusion processes, a steady-state diffusion model was compared with experimental

concentrations. This model was based on equation $\{1\}$, and the following parameters were used:

- Di: Diffusivity coefficients at 25°C referenced in Yuan-Hui and Gregory (1974) were used.
- δ_{DBL} : A diffusivity bounder layer of 0.17 cm was considered, based on previous measurement (0.17 ±0.02 cm) on similar laboratory tests done following the alabaster method Eek et al (2008).
- Ci_{pw}: Porewater concentrations of Mg, Ca and K reported in Table 2 were used.
- Ci_w: The water concentration at a time *i* was calculated by adding to the concentration at time *i*-1 the mass of element diffused from sediment at time *i*-1, which is the flux J_{i-1sed} (in μg/cm²/s) multiplied by the surface area of the sediment/water interface and by the time laps between *i*-1 and *i*. A time step of 0.1 days was used).
- A surface area of 49 cm², based on the manual measurement of the inner diameter of the glass jars, was considered for calculation of concentrations C_{iw}.



Figure 15. Comparison of measured concentrations of Mg, Ca and K with concentrations predicted by a model supposing only a steady-state diffusion from the untreated sediment to the water above (see text). Errors shown are calculated similarly to those in Figure 15.

In the case of uncovered sediment (samples A), the maximum concentration reached in water for Ca is close to the initial concentration in porewater (110 mg/L; Table 2), suggesting that the porewater concentration is controlled by equilibrium with the solid phase. The maximum concentration of Mg (around 60 mg/L) is smaller than that measured initially in the porewater (82 mg/L; Table 2), suggesting that the porewater

concentration is not (only) controlled by equilibrium with the solid phase, and Mg from the initial porewater was being depleted. In the case of potassium (K), the maximum concentration (23 mg/L, Figure 15) is slightly smaller but close to initial porewater concentration in the water above uncovered sediment (A samples) (29 mg/L; Table 2). The slight discrepancy is likely due to depletion of easily available K in the upper layer of the sediment. However, this maximum concentration is much higher than the initial porewater concentrations in the water above sediment treated with biochar (C, D and E samples). Indeed, the biochar used in the capping, similar to other biochars, contains high amounts of K (13 g/kg of dry matter), and thus the equilibrium concentration in the water phase is controlled by K released from the biochar.

The fact that concentrations of these major elements was, as expected, controlled by diffusion processes, and that consistent release curves were observed, validates the sampling procedure. Comparison with the more complex behaviour of redox-sensitive elements (as shown in the next section) suggests that for those elements, discrepancy with only-diffusion control is caused by redox and pH effects and not experimental artefacts.

3.2.1.2 Diffusion of redox-inactive elements from capped sediments

The difference of initial diffusion flux (i.e. the slope at initial state) indicates a diffusionlimiting effect of the capping layer (Figure 6).

I addition, the difference of concentration at steady state translates a sorption effect of the added material. Indeed, in our closed system without an infinite sink removing desorbed metals, in principle the maxima at steady state would be the same with and without cap if diffusion was the only process controlling transport. On the contrary, the maximum concentration of Mg and Ca reached in water in the case of capped sediments (B, D and E samples) was significantly smaller than in untreated samples (Figure 14). This was also the case for Si during the first 14 days.

This maximum concentration was also slightly smaller in the case of biochar-mixed sediment (samples C) than in the case of untreated sediments (samples A), suggesting that biochar either sorbed some Mg, Si and Ca, or that biochar addition changed the diffusive properties (e.g. porosity and tortuosity) of the sediment. However, the maximum concentrations of Mg, Si and Ca were not significantly different in the case of the capping enriched in biochar (samples E and D) compared to the capping with only bentonite (samples B), suggesting that biochar does not have a significant sorption effect on Mg, Si and Ca compared to bentonite-only. This is in accordance with previous observations that biochar does not show strong direct sorption of these elements (Xu et al., 2013.

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Figure 16. Comparison of measured concentrations of Mg and Ca, with concentrations predicted by a model supposing only a steady-state diffusion from i) the capped sediment to the water above (dashed black line) vs. ii) the untreated sediment to the water above (dashed green line). Errors shown are calculated similarly to those in Figure 15.

In order to further analyse the diffusion limitation due to the capping layer, a diffusion model was calculated, where steady-state diffusion is considered as the only process controlling Fe concentrations. This model was based on equation $\{2\}$ with similar parameters to the model presented in paragraph 3.2.1.1. Additional parameters used were:

- The cap thickness, h_{cap d}, was approximated to 1.5 cm which is a statistically good approximation of the cap experimentally obtained.
- The porosity ε was approximated to 0.5.
- The tortuosity τ was approximated to $\varepsilon^{-1/3}$ (Boudreau, 1997)

The diffusion-only models show that:

- Diffusion limitations caused by the cap layer explain part of the reduction of concentrations above the capped sediments compared to the sediment alone.
- In addition, other effects seem to be involved, for example sorption effects.

The remediation effectiveness (RE) of a capping layer can be expressed as the reduction of the steady state contaminant transport from the sediment after capping (J_{icap}) relative to the transport from the sediment before capping (J_{ised}) , following equation {3} (Eek et al., 2007):

$$RE = 1 - \frac{J_{i \operatorname{cap}}}{J_{i \operatorname{sed}}} = 1 - \frac{\varepsilon \cdot \delta_{\mathrm{DBL}}}{\tau(h_{\operatorname{cap} d} + \delta_{\mathrm{DBL}})}$$
^[3]

Where h_{capd} is the thickness of the (undisturbed part of the) capping layer in cm, δ_{DBL} the diffusive bonder layer in cm, ε is the porosity and τ is the tortuosity. ε and τ are dimensionless (Boudreau, 1997).

The RE was calculated for Mg and Ca, even though these elements are not contaminants, to give an idea of the initial remediation effect the capping can have in the absence of redox effects.

The diffusion flux of Ca was calculated by measuring the slope of the concentration in water as a function of time at the initial state, i.e. when the water concentration is negligible (equation $\{1\}$).

Table 8: Initial fluxes of Ca and Mg based on the slope of concentrations as a function of time during the first two days of experiment, as well as corresponding remediation effectiveness RE = $1-(J_{icap}-J_{ised})$.

	А	В	С	D	E	Model sed	Model cap
Ca							
Initial Slope (mg.L ⁻¹ .d ⁻¹)	88	1	40	1	1	126	5
Initial flux (µg. cm ⁻² .s ⁻¹)	3.1E-03	3.5E-05	1.4E-03	3.5E-05	3.5E-05	4.5E-03	1.8E-04
RE (%)		99		99	99		96
Mg							
Initial Slope (mg.L ⁻¹ .d ⁻¹)	95	0.8	26	0.6	0.7	126	5
Initial flux (µg. cm ⁻² .s ⁻¹)	3E-03	3E-05	9E-04	2E-05	2E-05	4E-03	2E-04
RE (%)		99		99	99		96

3.2.2 Changes of pH as a function of time

The pH values above uncapped sediment (samples A) were relatively stable around pH 5.5-6.0 (± 0.5) (Figure 17). However, during the first 2-3 days after treatment with bentonite and/or biochar, the pH increased in the water above sediment and capping (Figure 17). This is consistent with the observations that pH of biochar was 10.0 and pH of bentonite 9.3. After this first period of time, pH decreased significantly and reached a value of pH 7 (± 0.5) in the case of sediment covered with bentonite and/or biochar (Figure 17); a pH decrease of <0.5 unit is possible within the same period, but this change would be within the error of analysis. The pH decrease could suggest the occurrence of precipitation of Fe (oxyhydr)oxydes and water hydrolysis. Fe concentrations measured in the water above the treated samples were small, especially in comparison with untreated samples (Figure 20), but it cannot be excluded that Fe diffused to the water phase and immediately precipitated. For the untreated samples, Fe concentrations increased during the first 7 days, suggesting diffusion of Fe (II), and decreased after this period of time, suggesting indeed precipitation of Fe in the solid phase (Figure 20).



Figure 17. pH evolution over time. The light blue rectangle indicates typical ranges of pH values in sea water.

Note that in the open sea, the pH in water would be buffered by the sea water. Nevertheless, the systems used for this study provide information relevant to the porewater in the capping material.

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3.2.3 Diffusion of redox-sensitive elements





Figure 18. Left panel shows concentrations of Fe, As and Mn in the water phase during the first day, from which a linear regression is calculated and the slope is used as an approximation of the "worst case scenario" flux if no precipitation occurred (under anoxic conditions). Right panel shows concentrations measured after up to 64 days and compares measured concentrations with concentrations predicted by a model supposing only a steady-state diffusion from the untreated sediment to the water above. Errors shown are calculated similarly to those in Figure 15.

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Fe and S concentrations increased during the first days above the uncovered sediment, to an extent that is consistent with diffusion transport from sediment porewater to the water above (Figure 18). But after 7 days, Fe concentrations decreased in the case of uncovered sediments, while S concentrations steadily increased. This geochemical behaviour clearly deviates from diffusion-controlled processes as described in the previous section. An explanation for this deviation is that oxygen concentrations increased in the systems (see part 2.5), with downwards infiltration of O₂ leading to oxidation and precipitation of Fe hydroxides, with SO_4^{2-} remaining in solution. Oxidation of pyrite (FeS₂) from the sediment can explain that S concentrations reached values that were higher than the model considering only diffusion from sediment porewater. A precipitation of Fe hydroxides would be consistent with the slight (and barely significant) decrease in pH observed above uncapped sediments (Figure 12).



Figure 19. A sample with untreated sediment after 64 days of experiment, showing an orange layer at the surface interpreted as Fe oxyhydroxide precipitate.

Arsenic (As) concentrations above the uncapped sediment also increased during the first days, and followed the fate of Fe, with a simultaneous decrease after seven days. Arsenic typically exhibits a high affinity to Fe oxyhydroxides (Gulledge et al., 1973; Amstaetter et al., 2010), therefore it is likely that As adsorbed on the Fe precipitates or coprecipitated with Fe, explaining the decrease in As concentrations after > 10 d, when oxygen levels rose in the systems and iron oxyhydroxides were formed.

Manganese (Mn) concentrations above the uncapped sediment quickly increased up to 1300 μ g/L during the first days, after which the concentrations did not follow a clear trend, with a wide variation of results, even though the values were significantly higher than the quantification limit of the analysis. Manganese is a redox sensitive element,

occurring under three different redox states under common natural conditions, Mn(II), Mn(III) and Mn(IV), among which Mn(II) is typically most soluble. In contact with oxygen, it is possible that Mn(II) oxidized to less soluble Mn(IV) species or coprecipitated with Fe(III) (Lan et al., 2017), which would explain that the concentration of Mn was no longer controlled by diffusion processes after more than 7 days.

In order to test the hypothesis that the concentrations of Fe, As and Mn were controlled by diffusion processes during the first days of experiment, the same diffusion model as in the previous discussion on the non-redox sensitive elements was applied, and compared with experimental concentrations (Figure 18). Porewater concentrations of Fe, As, Mn and Mo reported in Table 2 were used as Ci_{pw}.

The diffusion model was observed to fit well with the concentrations of Fe, As and Mn observed during the first day, and relatively well with the concentrations of Fe and Mn observed until the seventh day. The interpretation proposed is that diffusion processes controlled the concentrations of these redox-sensitive elements during the first day(s), as long as oxygen-limited conditions were maintained in the system, but other processes like precipitation and adsorption started to dominate later on upon entry of oxygen into the system. Arsenic is particularly sensitive to oxidation, especially in presence of Fe(II) (Ona-Nguema et al., 2010), explaining the relatively early deviation from diffusion-dominated observed for this element.

Low O₂-conditions (< 1 mg/L O₂) occurring during the first days provide insights in the "worst case" diffusion fluxes of metal elements migrating from the sediment to the water column, when dysoxic conditions prevail above the sediment. Such dysoxic conditions are relevant to the Bureå field site, indeed O₂ concentrations measured above the Bureå sediment were between 1 mg/L and 2 mg/L in April 2021, and colder conditions or other spatial or temporal variations likely yield lower O₂ concentrations at other places or time.

Higher O₂-concentrations occurring during the following weeks provide insights in the precipitation controls on the speciation of metal elements, and these processes are relevant in a shallow bay environment (2-3m deep) with seasonal fluctuating temperatures and water mixes during e.g. storm events. Precipitation of iron hydroxides at the surface of sediments do occur at the Bureå site, indeed a brown ochrous layer is observed on top of the sediment (Figure 3). Precipitation processes will scavenge metal elements like As in the sediment phase and limit their flux into the water column. However, such processes will concentrate metal elements at the surface of the sediment compared to the deeper layer. Benthic life is mostly active in the upper centimeters of the sediment, therefore surface concentration and speciation changes of toxic elements are important to consider in the remediation assessment.

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3.2.3.2 Diffusion of redox sensitive elements from treated sediments

Figure 20. Concentrations of Fe, S, As and Mn in the water phase as a function of time for the sample tests with (A) only sediment, (B) sediment covered with only bentonite, (C) sediment mixed with biochar, (D and E) sediment capped with bentonite mixed with respectively low and high amounts of biochar. Errors shown are calculated similarly to those in Figure 15.

Effect of capping on Fe behaviour

Fe concentrations measured above capped sediments (samples B, D and E) were very low and barely significant in comparison with concentrations measured above uncovered sediments, during the 99 days of experiment (Figure 20).

Lower concentrations of Fe above covered sediments are in agreement with the theoretical effect of a cap on diffusion fluxes. In order to illustrate this principle, the same diffusion model was applied once again (Figure 21), where steady-state diffusion was considered as the only process controlling Fe concentrations.

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Figure 21. Comparison of measured concentrations of Fe, As and Mn with concentrations predicted by a model supposing only a steady-state diffusion from the capped sediment to the water above (dashed black line). Errors shown are calculated similarly to those in Figure 15.

Comparison of the diffusion model for capped sediment (dashed black line) vs. for the uncapped sediment (green dashed line) shows that lower concentrations of Fe are indeed expected in the case of covered sediment. However, the Fe concentrations measured experimentally remained low during the 99 days of experiment, while the diffusion model for capped sediment predicts an increase in Fe concentrations over time.

During the first day(s), when Fe concentrations increase above the uncovered sediments and oxygen was limited in the systems, it is likely that the low concentrations observed above covered sediments are explained by a retardation effect due to placement of the capping material and time to reach a new steady state, as well as potential sorption of Fe on the capping material. Fe sorption on biochar would be consistent with the observation that Fe concentrations were also very low in the case of sediments mixed with biochar, where no cap was applied.

Later on, when, according to interpretations made for Fe concentrations above uncovered sediments, oxygen entered the system, additional processes like Fe(III) oxyhydroxide precipitation could explain the discrepancy with the model and steadily low Fe concentrations.

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Effect of capping on S behaviour

During the first days of experiment, S concentrations were higher above covered sediments (B, D and E samples) than above uncovered sediments (A and C samples). This could be due to the significant concentrations of S present in bentonite (910 mg/kg S in the bentonite used).

Later on, S concentrations were significantly lower above covered sediment than above uncovered sediments. A hypothesis to explain this observation is that reducing conditions were better maintained under capping and pyrite (FeS_2) oxidation to sulfate followed by dissolution did not occur, resulting in lower sulfate releases to the sediment porewater over time.

Effect of capping on arsenic (As) behaviour

During the first days of experiment, As concentration increased above the capped sediments, at a rate that was lower than that of As above uncovered sediments (Figure 14). During these first days, the interpretation made above is that the conditions were anoxic (or dysoxic) and that diffusion controlled metal concentrations. A model for steady-state diffusion of As through a 1.5 cm cap was calculated and compared with concentrations measured above the capped sediment (Figure 21). This model suggests that As concentrations measured above covered sediments were smaller than those predicted with the steady-state diffusion-only model. As for Fe, this is likely due to sorption to the capping material and a resulting time delay of the breakthrough. Sorption of As on biochar is consistent with the fact that As concentrations above the sediment mixed with biochar (C samples) increased more slowly than those above untreated samples (samples A) (Figure 20). Therefore, the proposed interpretation of the results obtained during the first days is that the cover limits As diffusion from the sediment to water, and the biochar is slightly enhancing the diffusion limitation.

Importantly, Arsenic concentrations continued to increase above the sediments treated with biochar and/or bentonite after 7 days, while this was not the case for the untreated sediment (Figure 20). In addition, even though As concentrations decreased after 24 days in the case of capped sediment and after 16 days in the case of biochar-mixed sediments, As concentrations remained significantly higher above the treated samples than above the untreated samples during the remainder of the experiment (Figure 14). This is an important observation as it indicates that capping, while beneficial for organic compounds and many positively charged metal ions, can have negative effects on the spreading of As contamination.

It is not straightforward to explain the observed increase in As release from the capped/treated sediments. A possible explanation is related to the pH effect of the capping materials. Anionic As is more mobile at higher pH, and both biochar and bentonite increase the pH of the sediment porewater. Therefore, it is possible that the higher concentrations of As are partly explained by mobilisation of As from the sediment in contact with high pH porewater, and a less effective immobilisation in the capping at

higher pH. This explanation is consistent with the fact that pH and As concentrations both follow increasing values in the case of samples B>D>E (Figure 17, Figure 20).

The decrease of As concentrations occurs later above capped sediments (B, D and E samples), and to a smaller extent than As concentrations above sediment mixed with biochar (C samples). An explanation for this could be that under the cap, reducing conditions are maintained and less pyrite is dissolved, leading to lower amounts of Fe diffused to the water phase and less sorption sites for As. This hypothesis would be consistent with the low S concentrations above capped sediments (B, D and E samples) compared to uncapped sediments (A and C samples). Another explanation for the higher As concentrations above covered sediment could be that the cover sorbs Fe and thus smaller amounts of Fe oxides precipitate at the interface sediment/water, yielding smaller surface for As sorption.

Effect of capping on Mn behaviour

The Mn concentrations above capped sediment were significantly lower than above uncapped sediments (Figure 20), and significantly lower than concentrations predicted by the steady-state diffusion model considering a cap layer (Figure 21). The discrepancy with the model suggests that processes other than simple retardation through the capping thickness are limiting the diffusion of Mn. Indeed, the model does not take into account Mn sorption on biochar, and this process is likely important in this system. It is also possible that a part of Mn is diffusing through the capping but is sorbing or coprecipitating with Fe oxyhydroxydes formed after 14 days, though less Fe is diffusing to the water phase in capped systems according to interpretations proposed for Fe and S behaviour. It is also possible that some Mn sorbs on bentonite in the capping, which would explain that Mn concentrations were lower above sediments treated with bentonite or both bentonite and biochar, compared to biochar alone (Figure 20).

Diffusion fluxes under dysoxic conditions ("worst case diffusion")

Initial fluxes of Fe, Mn and As were calculated (Table 8) and used as an indication of "worst case" metal diffusion from sediment to water, in a scenario of dysoxic conditions ($< 1 \text{ mg/L O}_2$).

Table 9: Initial fluxes of Fe, Mn and As based on the slope of concentrations as a function of
time during the first two days of experiment, as well as corresponding remediation effectiveness
$RE = 1 - (J_{icap} - J_{ised}).$

	Α	В	D	E	Model sed	Model cap
<u>Fe</u>						
Initial flux (µg.cm ⁻² .s ⁻¹)	9E-03	1E-04	1E-04	7E-05	8E-03	7E-04
RE (%)		95	95	97		96
<u>Mn</u>						
Initial flux (µg. cm ⁻² .s ⁻¹)	3E-02	1E-05	1E-05	7E-06	3E-02	3E-03
RE (%)		100	100	100		90
As						
Initial flux (µg. cm ⁻² .s ⁻¹)	1E+00	2E-02	9E-02	9E-02	3E+00	3E-01
RE (%)		100	100	100		88

Under conditions where diffusion controls element transport from the sediment to water (initial conditions), the caps were very effective at limiting the transport of As and Mn (Table 9). The observed effectiveness of capping on As flux is even better (RE=100%) than predicted with the model (88%) which did not consider sorption to bentonite and biochar.

However, as discussed above, the effects of the capping on As transport are more complex when O_2 concentrations fluctuate and pH increases, actually leading to potential increase and negative remediation effectiveness.

3.2.3.3 Elements with very low concentrations

The concentrations of Ba, Ni, Co, Zn, Al and were relatively low in the water phase, and the concentrations of Hg were under the detection limit (0.039 μ g/L) for all of the samples analysed. Therefore, it was difficult to discern trends and identify transport mechanisms for these elements.

A subset of 6 water samples were analysed for total Hg with another instrument with a lower detection limit (0.1 ng/L). The results suggest that total Hg concentrations were lower above covered sediment than above uncovered sediment 16 days after cap placement (Figure 22). After 64 days, the concentration above the biochar-covered sample was still significantly lower than above the uncovered sediment; however, the effect of the bentonite capping was less clear after 64 days, and a larger dataset with triplicate analyses would be needed to draw more firm conclusions on the behaviour of Hg.



Figure 22. total Hg concentrations analysed in a subset of 6 water samples corresponding to the water above uncovered sediment (A), sediment covered with only bentonite (B) and with biochar-enriched bentonite (E), for two diffusion times, i.e. 16 d and 64 d. Note that Hg concentration measured above biochar-capped sediment after 16 days was < LOD.

4 Implications and further research needs

The experiments presented in this report were designed to provide information on the potential of a biochar- and bentonite-based capping for limiting the diffusion of contaminants from Bureå sediments to the bay water.

Results clearly showed that a thin biochar/bentonite cap has the potential to significantly limit the diffusion of PAH contaminants to water. Under the conditions of the experiment, the diffusive flux of dissolved 15-PAHs was reduced by 50% by capping with a 1-cm bentonite layer, and by 58% by capping with a 1-cm biochar-enriched bentonite layer. This conclusion is in agreement with many references of successful remediation operations based on classical capping (Eek et al., 2008) and capping with activated carbon (Patmont et al., 2015). Efforts to study the effect of thin capping with biochar for PAH contaminants have been initiated recently (Silvani et al., 2017, Bianco et al., 2021; Yang et al., 2021), and this study provides important argumentation for discussing the interest of the method.

However, results also show that the behavior of redox-sensitive contaminants such as arsenic (As) and mercury (Hg) is more complex than that of PAHs, and more complex than only diffusion. Capping with biochar/bentonite was proven successful for limiting the diffusion of As and Hg under dysoxic conditions, however other processes than simple diffusion controlled the behavior of these elements upon oxic conditions. In fact, under oxic conditions in the second phase of our experiment, the biochar/bentonite capping had negative remediation effects on As. Dysoxic conditions are relevant to field conditions at the Bureå bay when the water surface is frozen, as observed in April 2021, but oxic conditions are expected to prevail under warmer conditions in these shallow waters. Therefore, it is important to understand the relative importance of diffusion, redox reactions, co-precipitation and sorption processes under field conditions when the redox conditions fluctuate in situ. We thus recommend to further investigate the effect of capping on redox- and pH- driven processes affecting the As speciation (sorbed to sediment vs. dissolved) and fluxes, as well as Hg speciation (sorbed to sediment vs. dissolved, methylation).

In this controlled experimental set up, a lower number of parameters influenced contaminant behavior compared to field-conditions, allowing for an easier interpretation of the results and to some extent, processes understanding. However, under field conditions other processes like bioturbation or wave- or current-induced physical disturbances could influence the remediation effects of the proposed thin capping. In addition, the experimental systems used in this study were closed and pH was controlled by equilibrium with the solid phase (i.e., more acidic in the case of sediment alone, and more basic in the case of bentonite or biochar). This experimental bias can constitute a limitation in the translation of the laboratory results to field conditions, where more open systems are encountered and pH is buffered to values around 7-8. Also, in the case of the experiment assessing the diffusion of metal contaminants, the sink for metal diffusion was finite, while it can be considered an infinite sink under field conditions.

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For this reason, the diffusion rates observed in the first days of the experiments are more representative of the in situ situation than those later on.

Therefore, for full understanding of the system, it is recommended to combine the results of this laboratory experiment with those obtained under field conditions during the in situ part of the project. In addition, field analyses of As and Hg behavior could be recommended – the challenge however is that currently no reliable methods exist for the measurement of in-situ sediment-to-water fluxes of heavy metals.

Another challenge for translating the experiment results in the scope of field upscaling, is the fact that bentonite is an expensive resource and it is unlikely to be used for large full scale applications. Bentonite was chosen for the experiment because of the originally tight schedule for the project which did not allow testing of other bearing material. Bentonite itself was very efficient as a diffusion barrier and therefore, the biochar effect was likely underestimated.

To conclude, a biochar/bentonite capping seems promising for remediating PAH contamination from the Bureå Bay, but the effect on As and Hg should be further investigated, as it could be the opposite. In case of positive chemical effects for all elements, this approach with thin biochar-based capping would likely consume fewer resources than traditional capping and yield a lower global atmospheric and environmental impact than dredging solutions.

5 References

Amstaetter, K., Borch, T., Larese-Casanova, P., & Kappler, A. (2010). Redox transformation of arsenic by Fe (II)-activated goethite (α -FeOOH). *Environmental science & technology*, 44(1), 102-108.

Bianco, F., Race, M., Papirio, S., Oleszczuk, P., & Esposito, G. (2021). The addition of biochar as a sustainable strategy for the remediation of PAH–contaminated sediments. *Chemosphere*, *263*, 128274.

Boudreau, B.P., 1997. Diagenetic Models and Their Implementation. Springer, Berlin, p. 414.

Chen, B., & Yuan, M. (2011). Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *Journal of Soils and Sediments*, *11*(1), 62-71.

De Maagd, P. G. J., ten Hulscher, D. T. E., van den Heuvel, H., Opperhuizen, A., & Sijm, D. T. (1998). Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. *Environmental Toxicology and Chemistry: An International Journal*, 17(2), 251-257.

Eek, E., Cornelissen, G., Kibsgaard, A., & Breedveld, G. D. (2008). Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurement and modelling. *Chemosphere*, *71*(9), 1629-1638.

Eek, E., Godøy, O., Aagaard, P., Breedveld, G.D., 2007. Experimental determination of efficiency of capping materials during consolidation of metal-contaminated dredged material. Chemosphere 69, 719–728.

Gulledge, J. H., & O'Connor, J. T. (1973). Removal of arsenic (V) from water by adsorption on aluminum and ferric hydroxides. *Journal-American Water Works Association*, 65(8), 548-552.

Jørgensen, B.B., Revsbech, N.P., 1985. Diffusive boundary layers and the oxygen uptake of sediments and detritus. Limnol. Oceanogr. 30, 111–122

Lan, S., Wang, X., Xiang, Q., Yin, H., Tan, W., Qiu, G., ... & Feng, X. (2017). Mechanisms of Mn (II) catalytic oxidation on ferrihydrite surfaces and the formation of manganese (oxyhydr) oxides. *Geochimica et Cosmochimica Acta*, *211*, 79-96.

M608-2016

Moses, C. O., Nordstrom, D. K., Herman, J. S., & Mills, A. L., 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochimica et Cosmochimica Acta*, 51(6), 1561-1571.

Ona-Nguema, G., Morin, G., Wang, Y., Foster, A. L., Juillot, F., Calas, G., & Brown Jr, G. E. (2010). XANES evidence for rapid arsenic (III) oxidation at magnetite and ferrihydrite surfaces by dissolved O2 via Fe2+-mediated reactions. *Environmental science & technology*, *44*(14), 5416-5422.

Patmont, C. R., Ghosh, U., LaRosa, P., Menzie, C. A., Luthy, R. G., Greenberg, M. S., ... & Quadrini, J. (2015). In situ sediment treatment using activated carbon: a demonstrated sediment cleanup technology. *Integrated environmental assessment and management*, *11*(2), 195-207.

Silvani, L., Di Palma, P. R., Riccardi, C., Eek, E., Hale, S. E., Viotti, P., & Papini, M. P. (2017). Use of biochar as alternative sorbent for the active capping of oil contaminated sediments. *Journal of environmental chemical engineering*, *5*(5), 5241-5249.

Smedes, F. (2019). SSP silicone–, lipid–and SPMD–water partition coefficients of seventy hydrophobic organic contaminants and evaluation of the water concentration calculator for SPMD. *Chemosphere*, *223*, 748-757.

Stookey L.L. 1970. Ferrozine - a new spectrophotometric reagent for iron. Analytical Chemistry 42: 779-781

Tyson, R. V., & Pearson, T. H. (1991). Modern and ancient continental shelf anoxia: an overview. *Geological Society, London, Special Publications*, 58(1), 1-24.

Viana, P. Z., Yin, K., & Rockne, K. J. (2008). Modeling active capping efficacy. 1. Metal and organometal contaminated sediment remediation. *Environmental science & technology*, *42*(23), 8922-8929.

Xu, G., Wei, L. L., Sun, J. N., Shao, H. B., & Chang, S. X. (2013). What is more important for enhancing nutrient bioavailability with biochar application into a sandy soil: Direct or indirect mechanism?. *Ecological engineering*, *52*, 119-124.

Yang, Y., Ye, S., Zhang, C., Zeng, G., Tan, X., Song, B., ... & Chen, Q. (2021). Application of biochar for the remediation of polluted sediments. *Journal of Hazardous Materials*, 404, 124052

Yuan-Hui, L., & Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et cosmochimica acta*, 38(5), 703-714.

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