Pilot project

Biochar based capping of polluted sediment

Biokolbaserad reaktiv barriär för täckning av förorenade sediment

Luleå tekniska universitet

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Appendix 1: Literature report
Appendix 2: Site characterisation
Appendix 3: Laboratory diffusion tests
Appendix 4: Recipe elaboration
Appendix 5: Pilot project, field report – June 2021
Appendix 6: Master thesis: Biochar-based thin-layer capping of contaminated sediment in Burefjärden, Northern Sweden. Assessment of biochar mixed into four structural materials for preventing release of trace elements from sediment to water.

Summary

A 500 m^2 biochar based thin-layer capping was placed above the sea bottom outside Bureå in June 2021. The sea sediment is polluted with PAH and trace elements e.g. As, Cu, Zn, Pb, and Hg. The capping was composed of a mix of biochar, bentonite, salt and water, mixed in a concrete truck and pumped to the sea, above the pilot area. The efficiency of the capping to hinder PAH-flux to the sea was measured at two occasions in September 2021 and June 2022 using a diffusion chamber and SPMD-membrane. Parallel to the field experiment, laboratory investigations took place to develop a recipe for the blend and to assess the efficiency of different cover mixes to reduce the flux of PAH and trace elements.

The monitoring of the pilot capping showed an efficient reduction of the PAH-flux from the sediment to the sea water. The capping led to a significant reduction of the flux of PAH-compounds, between 80-100%, measured one year after the capping. Capping is a long-term reclamation strategy as it is supposed to last for several decades until natural sedimentation has built on the capping. Therefore, a long-term evaluation of the technology is necessary. Further work is also needed to assess the effect of the capping on redox-sensitive pollutants such as arsenic and the formation of methylmercury.

The laboratory experiments confirmed the ability of the capping to reduce pollutant fluxes. The production of the capping material, the slurry, was successful. However, the pilot experiment was not designed to assess the logistic of the technology as the mixing method was not relevant for the full-scale application. Further work is needed to scale up the method to full-scale and assess the feasibility for capping of large sediment areas. The replacement of bentonite with other structure material e.g., sediment or rock dust is also needed to reduce further the environmental footprint of the method and alternative should be further investigated from both a technical and environmental perspective. Further work is also needed to evaluate different types of biochar and to find the optimal biochar particle size to optimize chemical effectiveness while minimizing negative secondary impacts on benthic organisms.

Laboratory experiments have limitations, especially when dealing with trace elements, as the water quality does not fully represent the water quality in the sea. To measure fluxes of trace elements in the field, the diffusion chambers would have to be adapted using i.e. a DGT membrane.

1. Introduction

1.1 Background

As part of “Regeringsuppdraget för förorenade sediment”, a pilot project was performed between the autumn of 2020 and august 2022 with the objective

- To perform a pilot capping with a biochar/bentonite blend, of an area of sea bottom, polluted with (Polyaromatic hydrocarbon) PAH and metals e.g., Arsenic (As), Copper (Cu), Zinc (Zn), lead (Pb), and Mercury (Hg).
- To evaluate the function of the capping and its capacity to reduce the flux of pollutant from the sediment to the water body

The project was performed in cooperation between *Norges Geotekniska Institut* (NGI), Skellefteå Kommun and *Luleå tekniska universitet* (LTU). The site used for the pilot experiments is the Bay of Bureå (Skellefteå municipality), where large areas of sediment with elevated concentration of both organic and inorganic contaminants are found.

1.2 The technology: thin layer capping

The technology of thin layer capping is based on the application of a reactive material (biochar) that binds pollutant diffusing through the sediment to the water. For practical reason, i.e., to ensure that the capping is applied over the whole surface, the capping has to be 5-10 centimetres while only a few millimetres of biochar are sufficient. Therefore, biochar is mixed with a structure material e.g., rock dust, sand fraction, clay, dredged sediments. In this project, because of a tight timetable, bentonite powder was used instead of a more natural and economic material for the laboratory and the pilot experiments.

NGI has for the last decades developed the technology with sediment capping. A state of the art of the technology is in Appendix 1.

1.3 Overview of the work done

The project was divided in four main steps:

- Investigation of the site and selection of a test area for the pilot experiments (Appendix 2)
- Laboratory investigations to assess the performance of the capping, performed at NGI (Appendix 3)
- Laboratory investigations to determine a recipe for the slurry with the right consistency, performed at LTU (appendix 4)
- Performance and evaluation of the capping (appendix 5)

Parallel with the project, a master thesis was done at LTU, to compare different types of structure material that could be used as an alternative to bentonite, together with biochar (Appendix 6) [1].

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[1] Nathalie Pantzare (2021). Biochar-based thin-layer capping of contaminated sediment in Burefjärden, Northern Sweden. Assessment of biochar mixed into four structural materials for preventing release of trace elements from sediment to water. Natural Resources Engineering, master's. Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering.

1.4 Overview of the methodology

Material from the same sediment sample was used in all the experiments performed in this project. A general composite sample (ca 120 litres) generated of 9 single samples taken from a 30*30 m area was split and used for the laboratory assessment of the capping in jars at NGI, the column tests at LTU and chemical characterisation of the sediment.

The amendments used in the laboratory and field experiment were:

- Activated biochar, CP 1 provided by Jacobi carbon. The biochar is made of coconuts shale. It is powdered (90 % less than 74 µm with an average particle size of 45 µm).
- Bentonite was provided by VIACON. Ashapura bentonite (84 % less than 74 µm).
- Salt (road salt) from a local shop.

Three studies were performed at the laboratory scale

The efficiency of capping was tested at the laboratory scale using jars and columns. Experiment in jars were performed at NGI to assess the effect of biochar dosage in the capping and the effect of biochar mixed to the sediment. Several replicates were prepared and analysed at different interval to follow the evolution of the concentrations in the system.

- For PAH, heptane was placed at the top of the jar, as an infinite sink for PAH-compounds.
- For trace elements, the experiment was done in water which was sampled and analysed.

In parallel experiments performed at LTU, columns (3 litre, height 30 cm) were prepared with capping composed of different structure material. The water was sampled (60 ml) from the same columns at three occasions and analysed for trace elements. The water was not exchanged during the test and the concentrations of trace elements are expected to increase as the result of diffusion.

The consistency of the biochar/bentonite slurry was tested to determine the amount of bentonite and water to add to create a 5 cm thick layer which is thick, to minimize turbidity but also liquid enough to be pumped in a concrete pump.

The field work comprised two activities

- The installation of the capping over a 500 m2 area. The materials were dosed and mixed at a concrete station and transported by concrete truck to the site. The blend was transferred to a concrete pump and distributed above the test are with a hose.
- The efficiency of the capping was measured at two occasions using diffusion chambers and SPMD membrane (infinite sink) the flux of the 16 different PAH-compounds was calculated for the test area and a refence area nearby.

2. Description of the field site

2.1 Site history

The experiment was conducted in a narrow bay, close to the city of Bureå, Skellefteå municipality, Sweden. The site is situated on the shore of an old industrial site. The bay used to be a channel between the mainland and an island. In the 60ies, an embankment was built across the channel and closed the channel.

The area has a long history of industrial activities. 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. The process water, loaded with wood fibres, was discharge in the nearby sea. From the beginning, the fibre sludge was discharged directly in the sea, north of the site (Figure 1). Between 1950 and 1970, embankments were gradually built to contain the sludge and limit the spreading of fibres. The picture from 1972 shows the sedimentation basin north of the industry and a plume of fibre starting at the discharge point of the basin and spreading southward. As a result of the operation, spreading fibre sludge (and to some extent, mercury contaminated fibres) has taken place from the sedimentation basin to the surrounding sediment. During the 60 ies, the embankment to the island was built, which stopped further spreading to site used in this experiment (Figure 2).

During the last decades, after floating of timber has ceased, the area has remained the same. With time more and more vegetation has established (Figure 3).

As a result of the operations, a fibre bank was formed (close to the discharge point) and affected the surrounding sediment (fibre sediment = sediment containing fibres and pollutant). 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.

On the other side of the Skellefteälv estuary, few kilometres north of Bureå, is Rönnskärsverket, a copper smelter, that has been in activity since 1930th. Rönnskärsverket was a huge source of trace elements (arsenic and several heavy metals) to the surrounding land and water. As the bedrock in the region is mineralized, with many mines in the Skellefteå ore field, also rivers (Skellefteälv and Bureälv) transport significant amounts of trace element to the sea.

The area has therefore a complex history of exposure to organic and inorganic contaminants that resulted in a complexed pollution in the sediment in the Skellefteälv estuary, where Bureå bay is a part.

Figure 1 *Bureå bay, 1950. Logs are stored in the Bay outside the industry. The embankment to the island is not built. The process water is discharged in the sea, north of the site.*

Figure 2 *Bureå Bay, 1972. The embankment to the island is built, stopping water movement between the Northern part of the bay and the channel. A sedimentation basin is now built to contain the fibre sludge disposed in the northern part. Excess water is discharged in the sea and a plume with water and sludge is visible, moving southward.*

Figure 3 *Bureå bay 1981. Floating of timber has ceased and the sedimentation basins are visible in the Northern part of the area.*

2.2 Sampling of sediment for site selection and laboratory tests

The first step of the project consisted of the selection of an area where to perform the pilot experiment and to collect sediment to be used for the laboratory investigations. Based on the information available from previous studies, three potential areas were identified i.e. a test area, a reference area and a back-up area.

For each location, a grid (mesh: 10x10 m) was established. The test areas were 30 x 30 m and sampling was done in half of the cells according to Figure 4, to collect sediment representing the bottom conditions at each location.

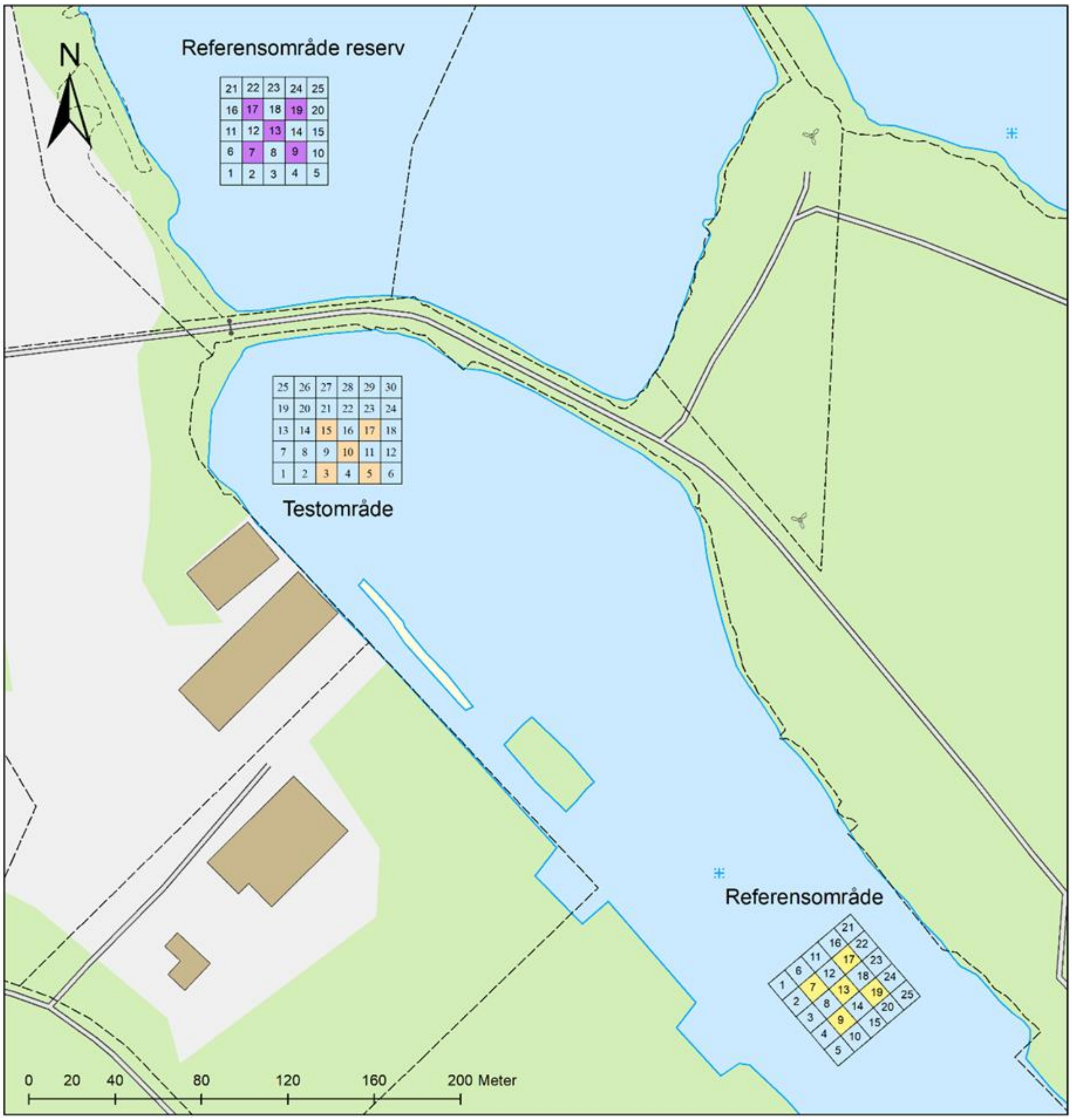

Figure 4 *Map of the Bureå bay with the three sampling locations: The reference area (yellow grid), the test area (orange grid), and the backup area (purple grid) (Ramboll, 2021).*

The sediment samples were collected with a Van Veen grab, which was rinsed with sea water in between each sampling. The collected sediment was poured into a rinsed plastic container and stirred with a shovel to homogenize the material (Figure 5). Sediment from each location within the respective area was first sampled in one plastic jar and one glass jar for metals and PAH analysis. The remaining sediment in the plastic container was then evenly distributed into eight buckets of 15L, and 1 scoop of sediment was collected in a smaller bucket (Figure 6) to generate a general composite sample for each area analysed for metal and PAH.

Figure 5 Sediment collected with the Van Veen grab and mixed in a plastic container (left) and picture of the upper part of the sediment with a typical oxidized top layer (light brown) and some organic material (Flodin, 2020).

Figure 6 Preparation of eight composite samples for laboratory experiments (Flodin, 2020).

The undisturbed sediment had a dark brown/black colour and some of the samples had a light brown coloured layer on the top (see appendix 2). The material varied in texture between the locations, where some of the samples had a firmer texture while others were looser with visible branches and organic material.

The chemical characterisation of the sediment was performed by ALS Scandinavia AB in Luleå. In total, 10 samples were collected from each area (9 single samples from each 10x10 m mesh and 1 composite sample), whereas 6 samples from each area were sent to analysis (5 single samples and 1 composite sample). The analyses performed were:

- OJ-1 PAH (EPA-PAH, 16 st)
- MG-1 (metals)
- MeHg (methylmercury)

2.3 Pollution situation at the test site

Figure 7 presents the average concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn for the three areas. Observe that the figure has a logarithmic scale. The average values do not include the composite samples (REF-SAM, TEST-SAM, B-SAM).

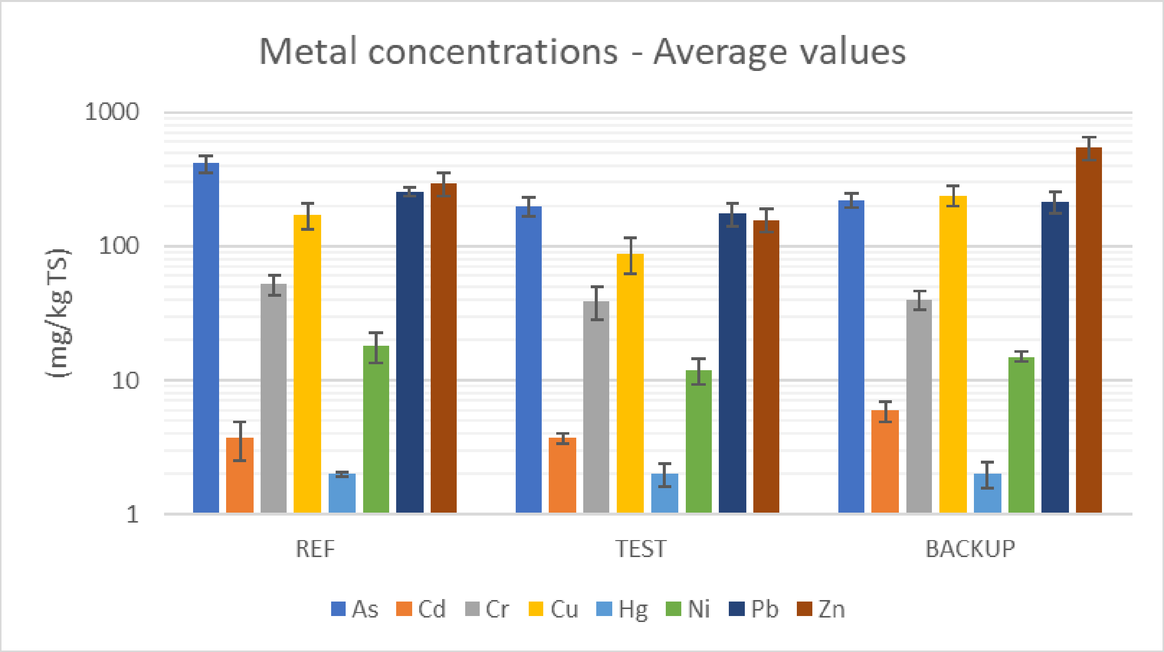

Figure 7 *Average values of arsenic, cadmium, chromium, copper, mercury, nickel, lead, and zinc (mg/kg dry substance) with standard deviation for the three areas, logarithmic scale.*

The average concentrations of arsenic, lead, chromium, and nickel are higher in the *reference area* compared to the other areas, while the concentrations of cadmium, copper, and zinc are higher in the backup area. The average level of mercury is approximately the same in all areas (around 2 mg/kg TS). The test area shows the lowest concentrations of copper, arsenic, lead, nickel, and zinc.

According to the *Assessment criteria for inorganic elements in sea sediment, report 4914* (Naturvårdsverket, 1999[2]), in all three area, the concentrations of As, Cd, Hg, and Pb exceeds *very high* concentrations, and Ni is found in *very low* concentrations. In the *reference area*, Cu and Cd are found in *high* to *very high* concentrations, and Cr is found in *low/mediate* to *high* concentrations. In *the test area*, Cu shows *high* to *very high* concentrations, and Cr *low* to *mediate* concentrations. *The backup area* has very high concentrations of Cu and very low to low concentrations of Cr.

For the *reference area,* the measured concentrations of PAH within the area shows high spatial variability. The *test- and backup area* shows a smaller, but still large, spatial variability within the areas compared to the reference area. For all three areas the difference is also large between the composite sample concentrations and the calculated average concentrations. Table 1 shows that all areas have *high concentrations* to *very high concentrations* of PAHs.

Table 1 *PAH analysis result for the three areas. The red cells indicate very high concentrations of PAHs, and the orange cells indicate high concentrations of PAHs.*

Reference area

Element (mg/kg TS)	REF-7	REF-9	REF-13	REF-17	REF-19	REF-SAM	Average	Dev % from average	Diff % REF-SAM/Average
PAH, sum 16	14	50	14	24	68	18	34	70.7	-46
PAH, sum L	1	4	1	2	5	1	3	64.5	-46
PAH, sum M	7	29	7	12	35	8	18	72.7	-55
PAH, sum H	5	17	6	10	28	9	13	72.1	-33

Test area

Element (mg/kg TS)	B-7	B-9	B-13	B-17	B-19	B-SAM	Average	Dev % from average	Diff % TEST-SAM/Average
PAH, sum 16	32	35	12	15	15	15	22	49.6	-33
PAH, sum L	4	4	1	1	1	1	2	63.7	-52
PAH, sum M	17	21	6	8	9	7	12	54.1	-41
PAH, sum H	12	10	5	6	5	6	8	40.0	-16

Backup area

Element (mg/kg TS)	TEST-15	TEST-17	TEST-10	TEST-3	TEST-5	TEST-SAM	Average	Dev % from average	Diff % B-SAM/Average
PAH, sum 16	12	14	15	10	26	8	15	40.6	-49
PAH, sum L	3	4	5	3	8	3	5	44.7	-43
PAH, sum M	6	7	7	5	14	4	8	45.0	-43
PAH, sum H	3	3	3	2	4	1	3	26.0	-74

Figure 8 shows the average values for the different sums of PAH for the three areas (SUM 16, SUM L, SUM M, and SUM L). The *reference area* appears to have the largest average concentration of PAH Sum 16, PAH sum M, and PAH sum H. However, the standard deviation is large, especially for the calculated PAH sum 16 for the *reference area*, which indicates a large spatial variation. The backup area shows the lowest concentrations of PAHs, except for PAH sum L.

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[2] Naturvårdsverket. (1999). Naturvårdsverkets bedömningsgrunder för miljökvalitet – Kust och Hav, NV rapport 4914, 1999 (senare uppdaterad

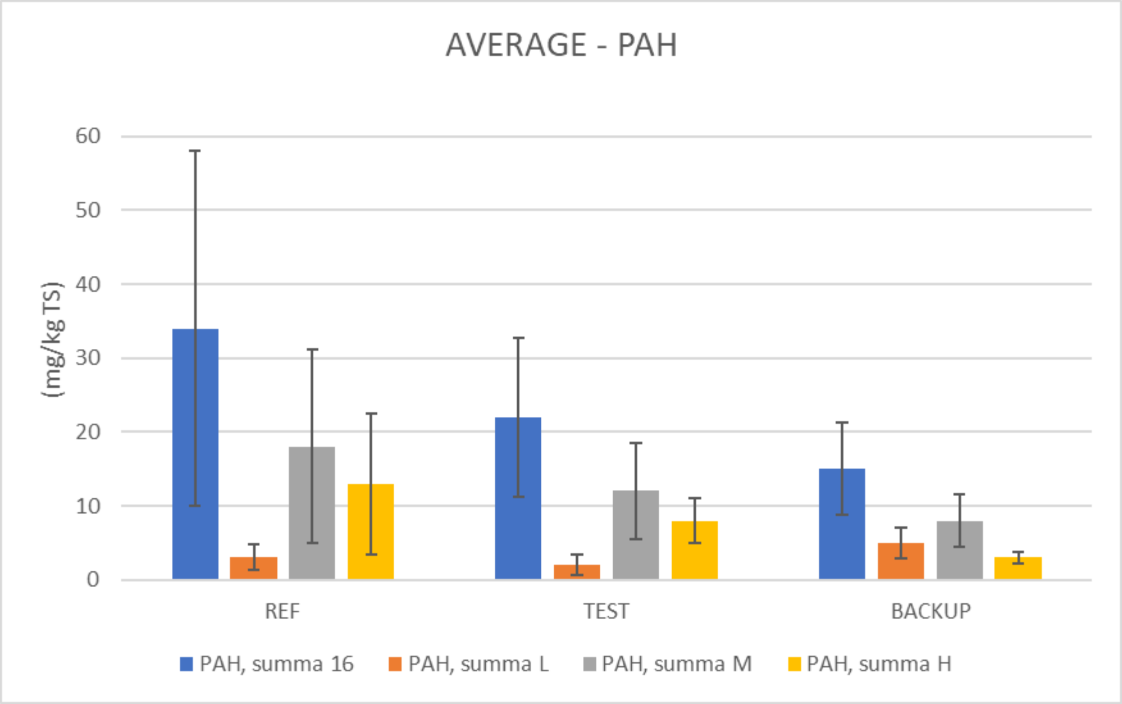

Figure 8 *Average values for PAH (mg/kg dry substance) for the three areas. Highest concentrations are found in the reference area.*

2.4 Selection of the test site Pollution situation at the test site

Comparing the PAH, methylmercury, and inorganic element concentrations in the sediment, the two most interesting locations for performing the cover test are the **reference area** and the **test area**. The two areas show similar concentrations of trace elements, PAHs, and methylmercury. Regarding suitability for performing the covering test, the **test area** is the most suitable location since it shows high concentrations of inorganic elements and PAH, and since it is located in the bay relatively close to the shore (see Figure 4).

The water depth is the comparable at both sites. The sediment contains certain amount of wood and fibres. However, both areas are not in the vicinity of the fibre bank, and gas production is not expected to disturb the bottom condition at both areas.

A crane lorry was used for pumping the biochar-mixture and therefore it was therefore an advantage to perform the covering in close access to land. The selection of the test area took into account the pollution situation at each location, as an outcome of the sediment characterization, and practical consideration such as accessibility for the trucks and distance from the shore. Based on those considerations, the **test area** was selected for the pilot experiments.

The orange and yellow marked cells in figure 4 are 10*10 meters each and indicate the cells that were sampled and analysed. The central cell of the test area indicates the middle of the area that was capped. A square (3x3 cells, with cell 10 in the middle*, see* Figure 4*)* was used for the pilot capping experiment with a biochar-bentonite mixture, while the outer part of the grid delineate the capped area. The monitoring of turbidity was done on the outer limits of the capped area.

Both the test area and the reference area were monitored with diffusion chambers to measure transport of organic compounds to the water and assess the efficiency of the capping.

3. Laboratory investigations prior to the field test

3.1 NGI – Absorption efficiency

The assessment of the capping efficiency was done in laboratory experiments, prior to the pilot experiments. The sediment used in the experiments was a compositive sample of the 9 cells sampled during 2020. As a consequence, the sediment was mixed and homogenised before testing. The experiment was done in jars that were analysed at different time intervals (Figure 9). The experiment included the measurement of both PAH and trace element fluxes from untreated sediment (A), sediment amended (B) with biochar (which was note tested in the field) and capped sediment (D and E). Several replicats were generated at the starting point and were sampled at regular interval to calculate the flux through the capping.

The method and the results from the experimental work done at NGI is presented in appendix 3.

The PAH compounds migrating through the cap are captured in the heptane layer that act as an infinite sink, thanks to the high affinity of PAH in heptane. A compilation of the measured fluxes is presented in Figure 10. The fluxes i.e., the slope of the dotted lines, 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 of the B samples was calculated after 100 days and the flux above E samples after 200 days, after the breakthrough through the cap.

According to the experiments, the thin cap with bentonite and biochar could reduce significantly the flux of PAH diffusing to water, with a capping efficiency depending on PAH compounds. Capping with bentonite alone had a significant efficiency for most of PAH compounds. This positive effect of bentonite capping can for a large part be explained by the increase of diffusion boundary layer (Eek et al., 2008[3]). But it is also possible that bentonite sorbs to some extent PAHs.

The bentonite cap had a remediation efficiency RE= 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 = 0.58, meaning that the diffusive flux of dissolved 15-PAHs was reduced by 58% by introducing a 1-cm undisturbed capping layer. 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 ±0,1 kg/m^2) than for samples with bentonite and lower amounts of biochar (0,7 ±0,1 kg/m^2), which was lower than for samples capped with only bentonite (see Appendix 3). 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)[4] and sorption processes in the cap delays and limits diffusion of contaminants to the water above (Viana et al 2008)[5].

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[3] 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.

[4] 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.

[5] 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.

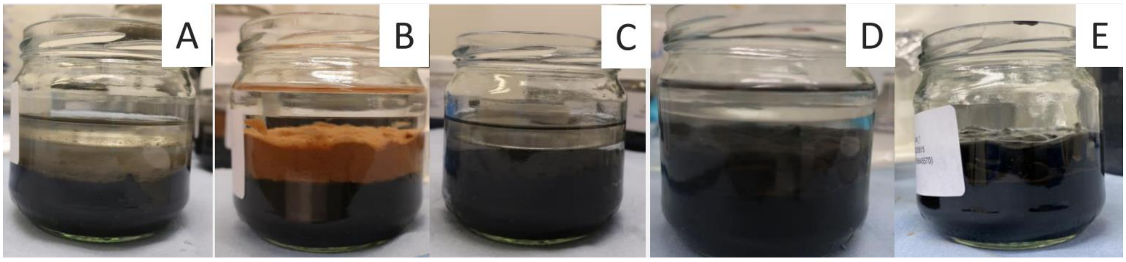


Figure 9 *Pictures of the experimental tests with sediment and different treatments. NB: the pictures were taken after sampling of the water phase above.*

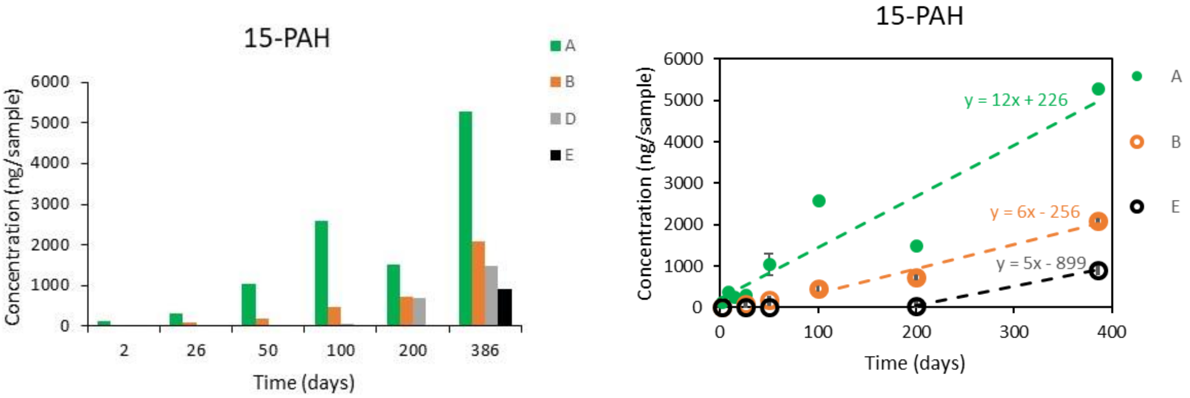


Figure 10 *Cumulative amounts of 15-PAH analysed as a function of time in the heptane phase of tests with (A) untreated sediment, (B) sediment capped with only bentonite, (D and E) sediment capped with bentonite mixed with respectively low and high amounts of biochar. Results for C treatment are not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

In similar experiments, the effect of the capping on trace element diffusion was assessed. As a result of diffusion through the capping, the concentration of respective elements increases gradually in the water, until it reaches a plateau. The behaviour of Mg was consistent with pure diffusion from sediment to water in a closed system, i.e. where water is a finite sink. Indeed, concentration of Mg in water above uncapped sediment increased fast at start, then slower with time, tending to pore water concentration. The concentration of Mg increased significantly slower above capped sediment than above uncapped sediment. The fact that capping limited Mg diffusion is qualitatively consistent with the diffusion model (Figure 11), indeed Mg diffusion is limited by a longer diffusion boundary layer. However, biochar addition to the bentonite cap did not significantly limit Mg diffusion, even though biochar mixing with sediment hindered it slightly (see appendix 3 for further details).

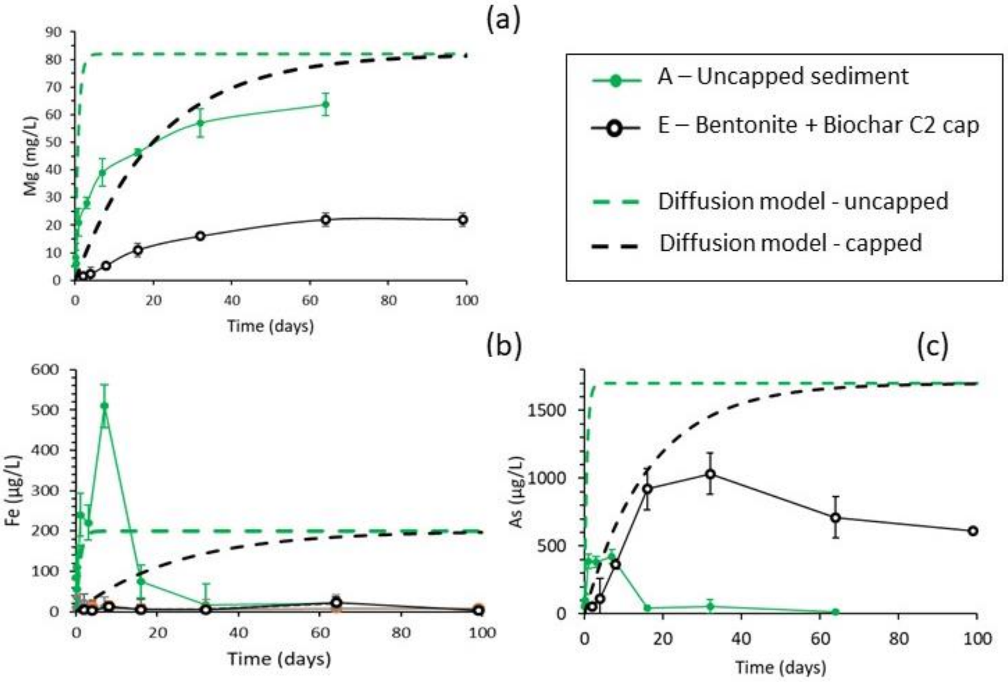


Figure 11 *Comparison of concentrations of Mg (a), Fe (b) and As (c) measured in A and E samples (plain lines) with concentrations modelled (dashed lines) considering equations {1} and {3}, respectively for uncapped an capped sediments.*

Biochar-enriched thin cap not only limited the diffusion of metal elements, but also changed the pH and redox conditions in the experimental system, and consequently the mobility of different elements. The Fe concentrations reflect the evolution of oxygen concentrations in the water above sediment. One effect of changing redox conditions is believed to indirectly limit the surface of Fe oxides available for sorption of trace metal elements.

During the first seven days, Fe concentrations built up above the uncapped sediment, indicating diffusion of Fe (likely Fe(II)) as predicted by the model (Figure 11). On the contrary, Fe concentration dropped between 7 days and 16 days, indicating oxidation of Fe(II) to Fe(III) and precipitation. Consistently, an orange precipitate was observed at the surface of uncapped samples. This phenomenon is assumed to be the consequence of oxygen diffusion form the air to the jar. In addition to lower redox conditions, capping led to higher pH values i.e. biochar (pH 10) and bentonite (pH 9). Indeed, pH values were higher above capped sediment than above uncapped sediment, especially right after application of the cap.

As concerns redox conditions, the first two weeks of experiment mimicked dysoxic conditions (0.2-2 mg/L O_2) while the following phase represented oxic conditions (2-8 mg/L O_2). Both conditions are relevant to the environment at the Bureå bay, where 1 to 2 mg/L O_2 were measured in April and seasonal variations are expected. However, the changes in pH caused by the capping are only relevant for the conditions in the pore water and not in the water column.

Our results suggest that capping can have antagonistic remediation effects for redox sensitive metal elements like As. Even though capping was efficient for limiting As diffusion under dysoxic conditions, it led to higher As mobility, likely due to pH increase and favouring of reducing conditions. Under field conditions, the system would not be closed, therefore pH in the shallow cover would be to some extent buffered by sea water and pH effects on metal mobility would likely be less predominant.

Capping could decrease the As concentration at the sediment surface where benthic organisms live, at least for some time. Indeed, in the field, the surface of the sediment is covered by a layer of Fe oxides before the capping is applied. This layer of Fe oxides provides a natural sorption trap for As, concentrating As at the surface where benthic organisms live, and capping could protect these organisms from older As-enriched Fe oxide layer. Because Fe diffusion would be limited by the cap, the deposition of a new As-enriched Fe oxide layer would be slower.

3.2 LTU – Development of the mixing field recipe

The capping is applied as blend of biochar, water and a structure material to ensure an even distribution of the biochar above the sea bottom. For the pilot experiment, dry bentonite was used as structure material as it swells and is expected to keep the biochar in place. To ensure the blend had appropriate technical properties, a recipe was developed in laboratory conditions.

The objective of the work was to develop a recipe for a slurry that could be used in the pilot experiment. The main requirements set for the blend were:

- A blend with a consistency as thick as possible to limit turbidity and facilitate sedimentation
- A slurry that is easily pumped from the cement truck and does not swell and clog the system
- Ensure that the blend sink and stay at the bottom
- Contain enough material to result in the formation of a 5-10 cm thick layer, at the bottom.

The dosage was set to 3 kg/m^2 of biochar, to ensure a capping layer of at least 1.6 kg/m^2, which is the amount that has been used in laboratory experiments performed by NGI (see appendix 3).

The blending tests were performed at LTU's geotechnical laboratory, at different scales. Most tests were performed in a 3-litre mixer. As the mixing at small scale is more intensive than mixing at pilot or industrial scale, with e.g. cement blenders, tests with 16 resp. 200 litres to investigate the scale effect (Figure 12). The objectives of the tests were to define the blending time and the dosage (see appendix 4).

(a) Cake mixer with 3 litre bowl

(b) Laboratory mixer with 16 litre bowl

(c) Laboratory mixer with 200 litre bowl

Figure 12 Different laboratory mixer used in the laboratory investigation (Al Jabban, 2021).

The sedimentation velocity was assessed in series of column tests to determine the thickness of the layer and control the turbidity of the water phase. Salt was added to increase the density of the blend (enhance sedimentation) and limit the swelling of bentonite. Addition of 1-2 % salt (NaCl) to the blend effectively reduced the swelling of bentonite (see Figure 13 and Figure 14) and limited the turbidity in the samples.

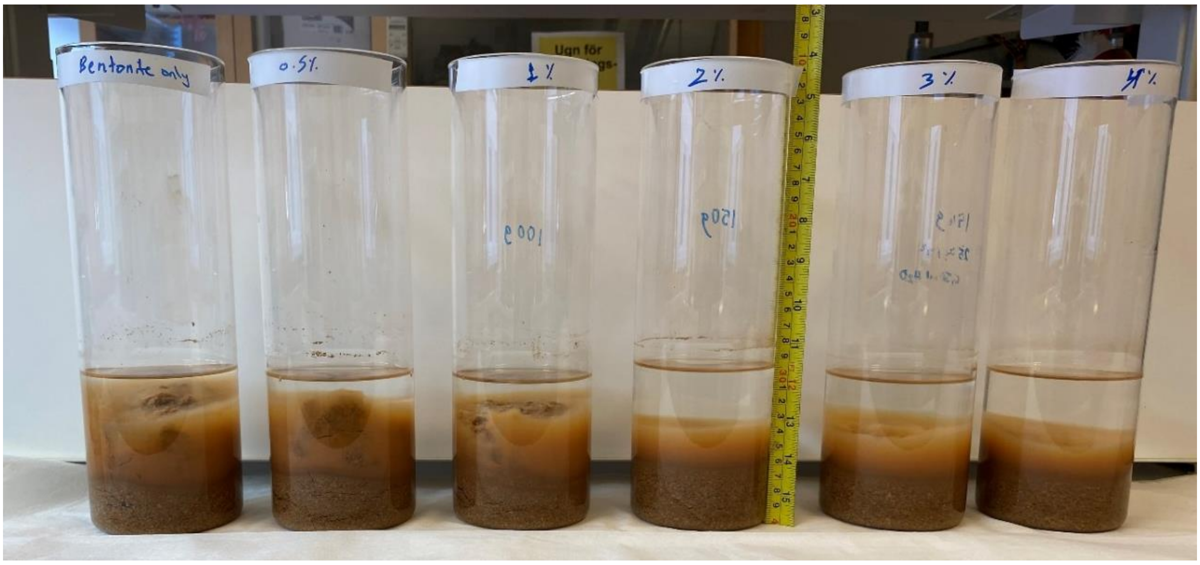


Figure 13 Effect of increasing salinity on the swelling of bentonite, after168 hour from starting the test (Al Jabban, 2021).

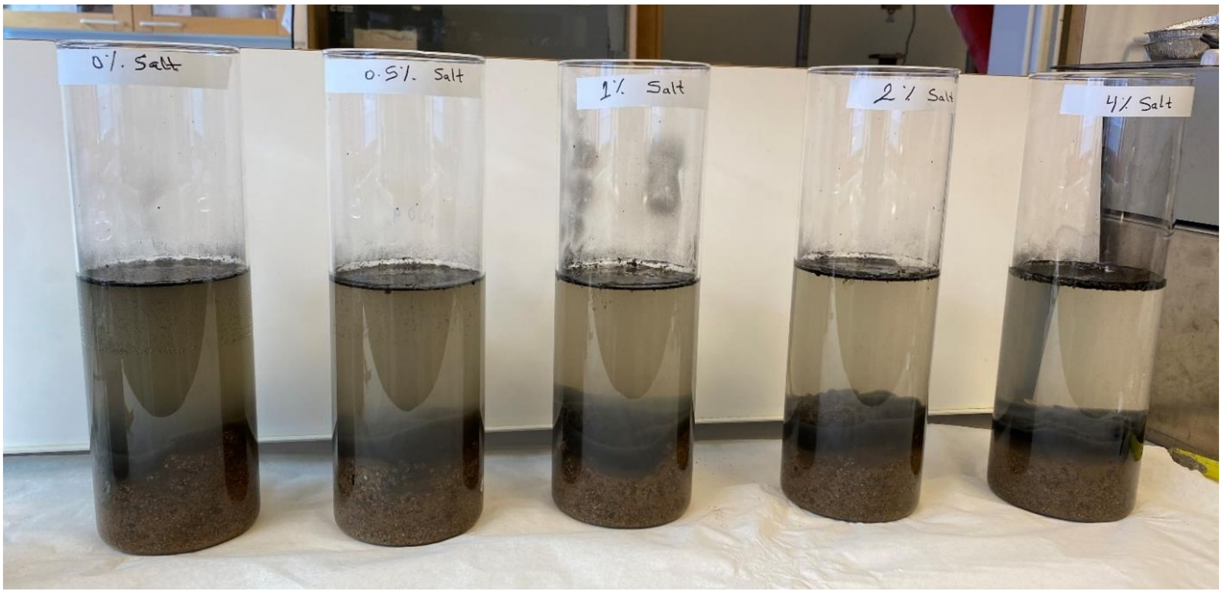


Figure 14 Effect of salt addition to the biochar/bentonite mixture, on the turbidity in the water phase after 24 hours from starting the test (Al Jabban, 2021).

The consistency of the blend and its behaviour in water were studied in aquariums. The blend was added to water though a funnel and fell freely in the water to the bottom that was cover with a layer of sand (Figure 15). The experimental set was used to determine an appropriate consistency and monitored the sedimentation velocity and the turbidity.

The result of a capping test is presented in Figure 16. the capping (black layer) has sediment above the sand layer. A close view of the layer shows lumps of bentonite (light brown) that were not properly mixed with biochar (Figure 16).

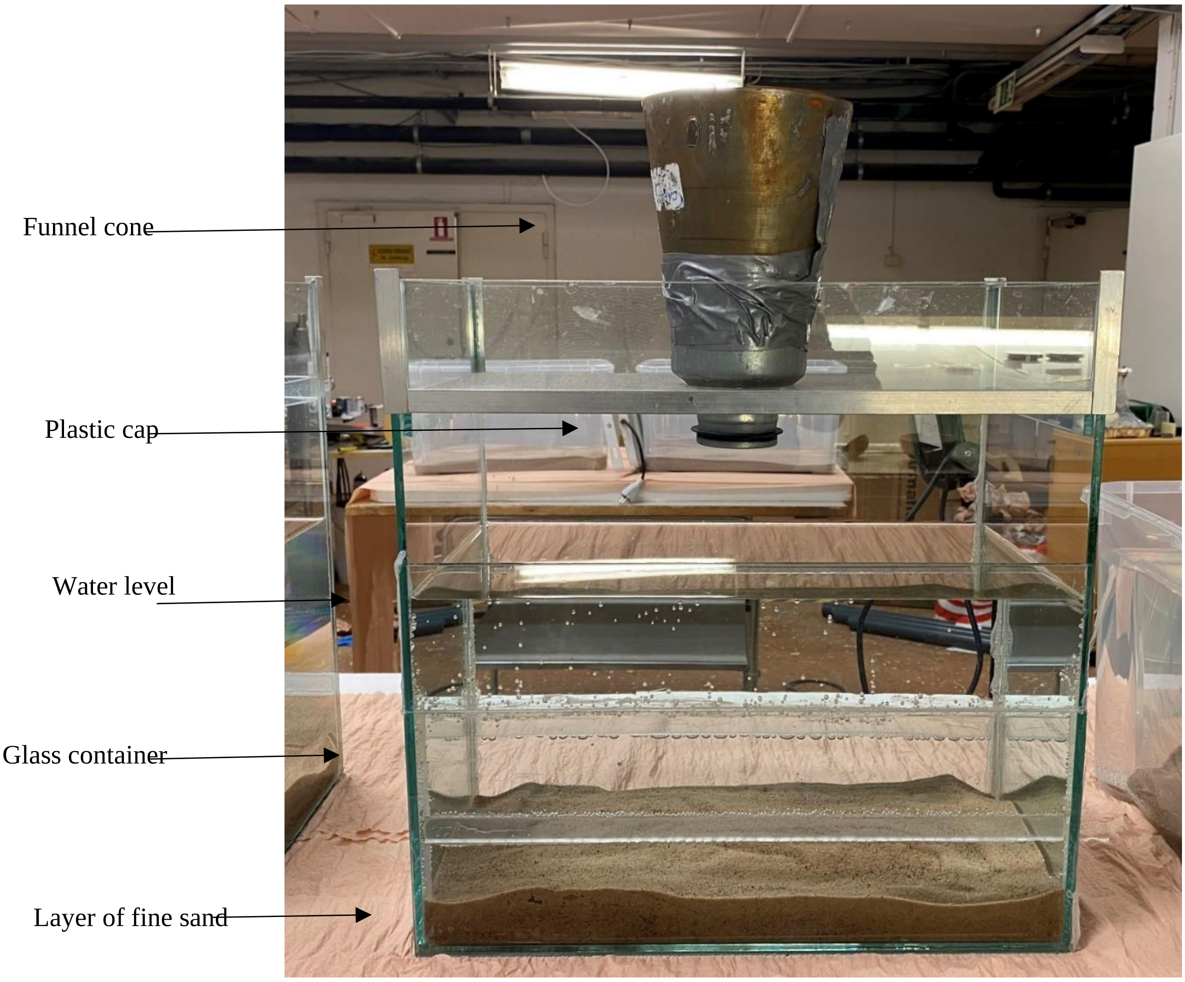


Figure 15 Aquarium experiment used for the sedimentation tests (Al Jabban, 2020).

Figure 16 *Capping after 24 hours from pouring in the aquarium. On the left, picture of bentonite lumps that were not mixed with biochar (Maurice 2021).*

The results of the laboratory investigations is presented in Table 2. The recipe was optimised in order to get a slurry with a consistency that enable pumping with as low water addition as possible i.e. as thick as possible.

Table 2 *Target recipe for the blend elaborated and acceptable span for water addition*

	Recipe kg	Blend %	Field batch kg
Bentonite	100	11,5	6 000
Biochar	22,9	2,6	1371
Salt	1	0,1	60
Water	750	85,8	44 834
Acceptable span for water addition	720-825	85,4-86,9	43 300-49 500

3.3 LTU – Alternative structure material

Parallel to the project where the selected capping material was a biochar/bentonite blend, a master thesis was done at LTU, to assess the possibility to use other structure material as an alternative to bentonite. The master thesis was written by Nathalie Pantzare and is published on LTU website (Pantzare, N. 2021).

The experiments were conducted in 30-cm jars with sediment and capping at the bottom and the water profile was sampled at three occasions (Figure 17). The water was sampled with a syringe in the middle of the column and filtrated immediately, prior to analysis. The water was not exchanged during the experiment. As the volume of water sampled small (50 ml) compared to the column (3 000 ml), no fresh water was added.

The main objective of the experiment was to assess the effect of different capping materials on the element fluxes. The leaching from the capping itself was investigated in separate experiments. As the water was not changed, the capping affected the water chemistry in the column and in turn the element mobility in a way that would not happen in the sea.

The experimental plan included three structure materials beside bentonite:

- Bentonite – 7 kg/m^2
- Rock dust, 0-2 mm– 20 kg/m^2
- Asphalt filler, a coarse fraction of rock dust, 0-5 mm – 20 kg/m^2
- Cement sludge – 20 kg/m^2

The bentonite layer was approximately 4 cm while the other materials, that do not swell, formed a 2 cm layer.

Figure 17 Experimental setup for testing of different capping materials, at LTU (Photo Natalie Pantzare).

Average concentrations of Cu and Zn after 19, 33 and 60 days in the water column above the different capping layers are compiled in Figure 18. The black bars represent Cu concentrations, and the orange bars show Zn levels. The level of dissolved Cu follows the same trend over time for all columns i.e. the Cu levels generally increase between 19 and 33 days, and then decrease at 60 days. Only the biochar+concrete layer shows continuously decreasing Cu levels over time. The highest displayed levels for all sampling occasions are in the water column above the uncapped sediment with Cu levels that ranges from 2.4 to 2.9 µg·L-1. The levels in the biochar capping were lower e.g. bentonite (0.3 ± 0.04 µg·L-1), coarser rock dust (0.3 ± 0.1 µg·L-1) and the concrete slurry (0.2 ± 0.1 µg·L-1).

Zn exhibits trends similar to Cu, with concentrations remaining approximately constant up to day 33, and then decreasing after 60 days for all capping layers except biochar+concrete material which increases with time (Figure 12). An explanation for the increase of Zn concentration above the biochar+concrete material is likely the high levels of Zn in the concrete slurry material (7 µg·L-1 released from control sample). The uncapped columns and columns with biochar mixed into the sediment displays a significant decrease (about 57-60%) in Zn levels after 60 days. This is a general trend but is more visible for the columns with a more elevated initial level.

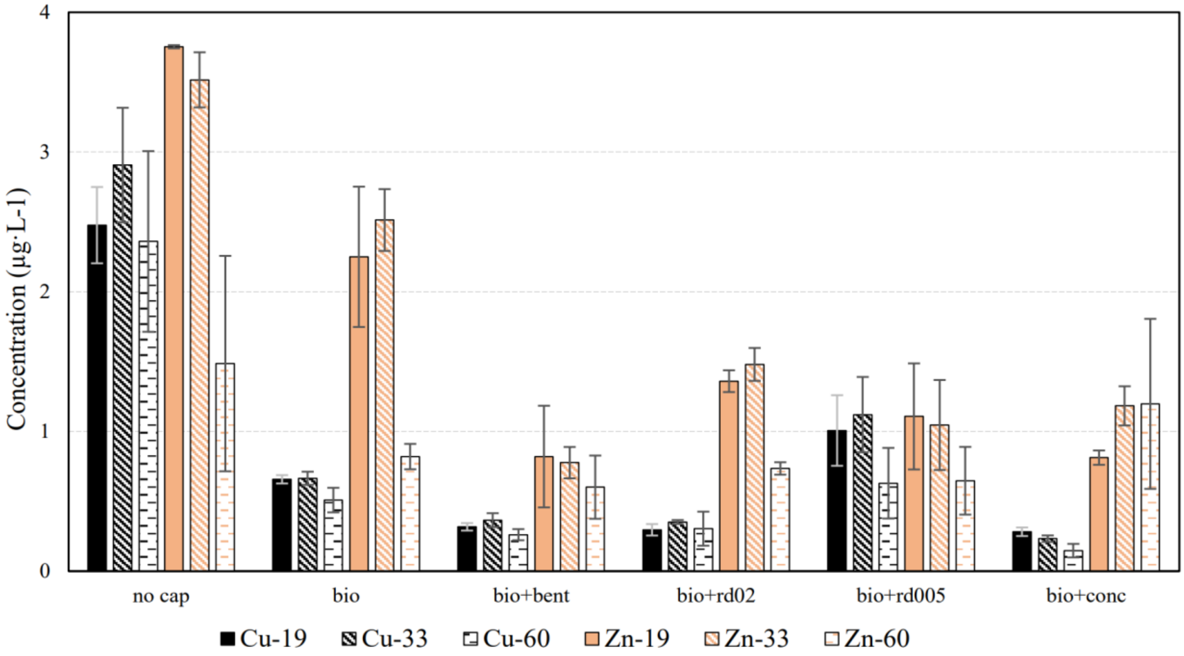


Figure 18 Average concentrations (µg·L-1) for Cu and Zn over time in the water column above the uncapped and capped sediment in the column experiment. The samples were collected after 19, 33 and 60 days. Error bars show calculated SD.

Figure 19 displays the average concentrations of Cd and Pb after 19, 33 and 60 days in the experimental columns. The black bars show the Cd levels and the green displays Pb levels. Levels of Cd and Pb released into the water column are reduced for all capping materials. The most significant reduction of Cd is seen for the biochar+concrete layer which exhibits levels below the detection limit at all sampling occasions. Furthermore, the Pb levels are increasing with time in the coarser rock dust. All capping materials, however, suggest efficient immobilization of Pb and Cd compared to levels in the uncapped columns.

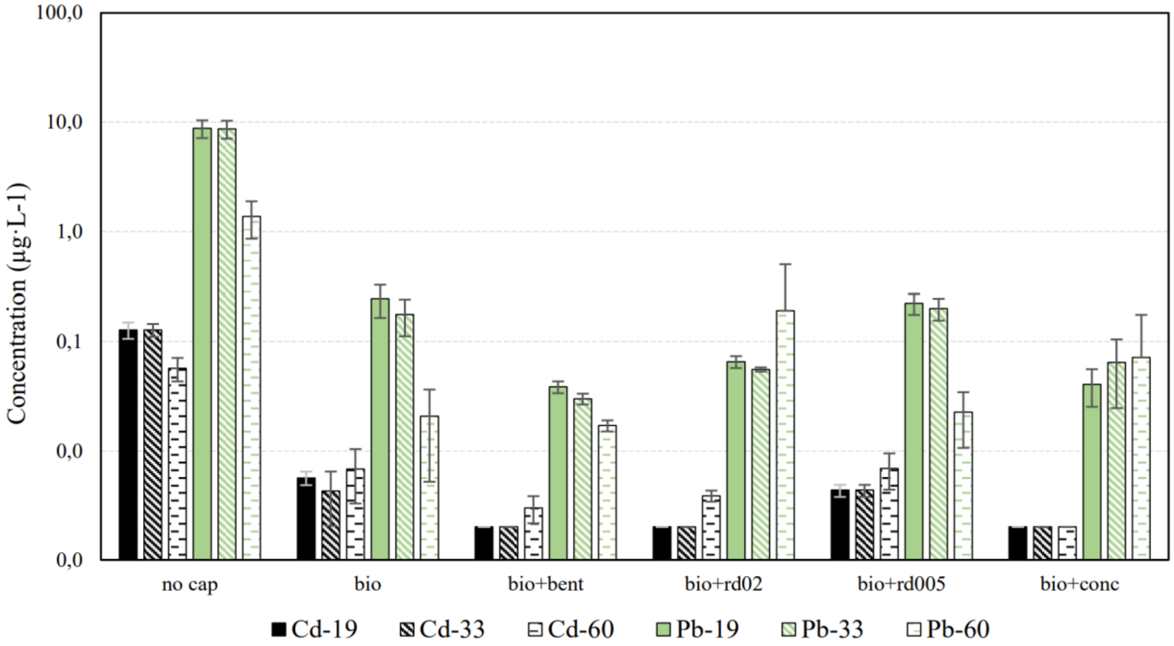


Figure 19 *Average concentrations (µg·L-1) for Cd and Pb over time in the water column above the uncapped and capped sediment in the column experiment. The samples were collected after 19, 33 and 60 days. Error bars show calculated SD.*

Average concentrations and calculated standard deviations (SD) for As and P (tot-P) levels over time are presented in Figure 20. The two elements are plotted together as they both are anions and were observed to follow the same trend for release through the capping materials. Release of As from sediment to the water column is delayed when applying a capping layer on top of the sediment. However, As levels in uncapped columns (133 ± 30 µg·L-1) and bentonite columns (41 ± 18 µg·L-1) are high which indicate the development of anaerobic conditions.

The biochar+bentonite capping layer immobilized As at early stages of the experiment, followed by increased As concentration with time. The levels of As above the capping layer was believed to be controlled by the redox conditions in the columns and adsorption onto Fe-Mn oxides formed in the more oxidized surface layer. However, the overall increasing As (and P) levels with time (Figure 20) suggest that the sediment and overlying water is getting more anoxic as oxygen is depleted in the column.

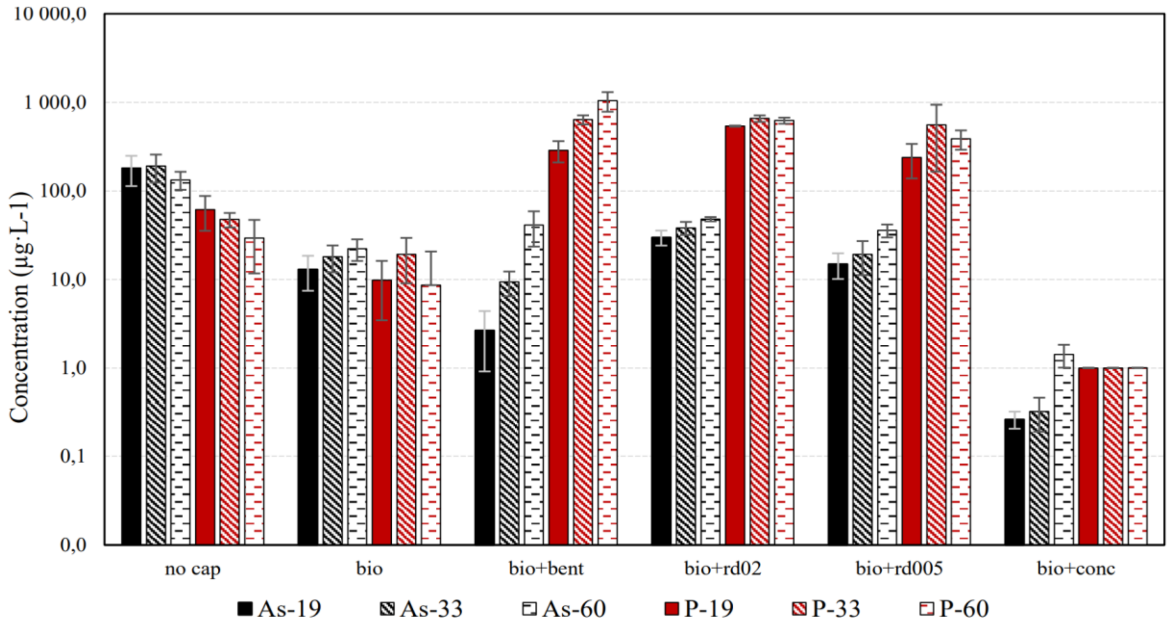
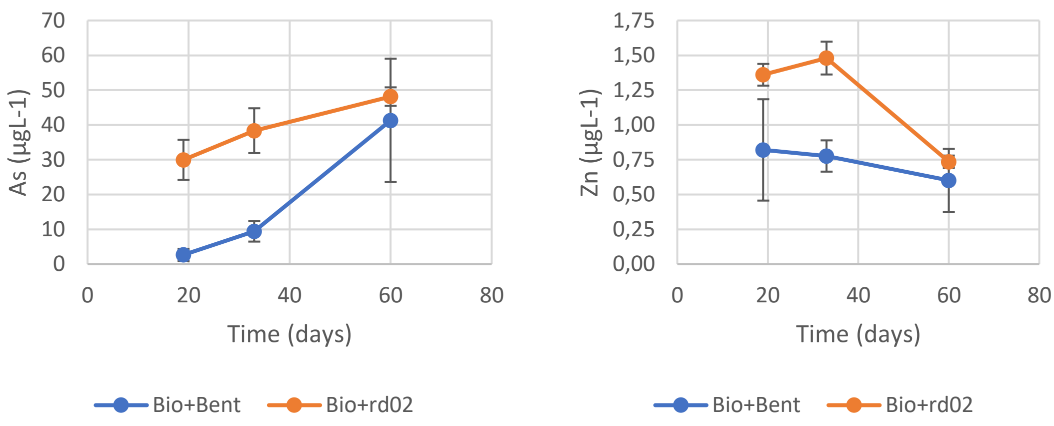
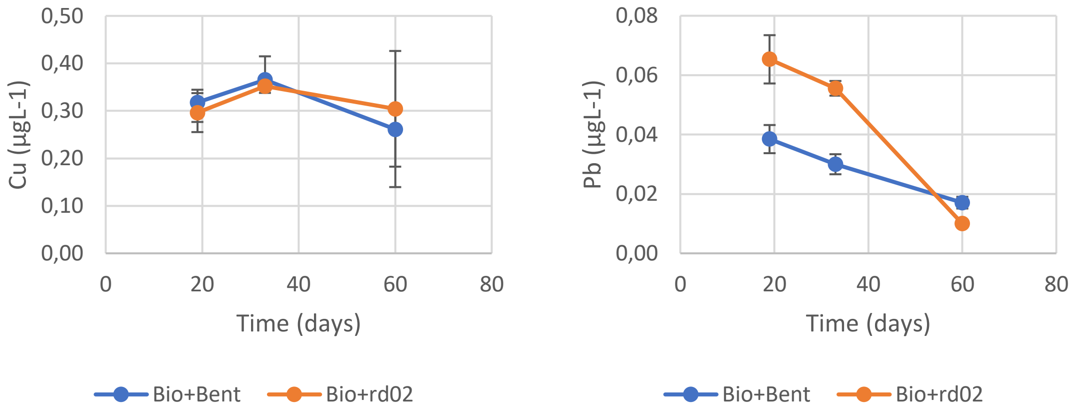


Figure 20 *Average concentrations (µg·L-1) for As and P over time in the water column above the uncapped and capped sediment in the experimental columns. The samples were collected after 19, 33 and 60 days. Error bars show calculated SD.*

A comparison between the effect of the covers with coarse rock dust and bentonite is presented in Figure 21. The biochar/bentonite cover exhibit lower concentrations at the beginning of the experiment, which is interpreted as the barrier effect of the clay minerals. Mixing biochar to sediment or rock dust gave initially higher levels in the water. After 60 days of experiment, the difference is however eliminated, i.e. both structure materials work equivalently. The initial concentrations are a combination of the initial physical barrier effect of the bentonite and possibly release of trace element from the rock dust.


a) Concentration of As with time

b) Concentration of Zn with time


c) Concentration of Zn with time

b) Concentration of Pb with time

Figure 21 *Comparison between the bentonite/biochar and the rock dust/biochar covers. Evolution of the concentration of As, Zn Cu, and Pb with time.*

4. Field experiment

The capping mixture was dosed and mixed at the Swerock concrete station outside of Skellefteå, directly in concrete truck and transported by truck to the test site (Figure 22). The mixture was pumped with a concrete pump i.e. a truck with a long arm and a pipe (Figure 23Figure 22). The pump was then connected to a floating pipe to reach the test area (Figure 24). See Appendix 5 for further details.

Figure 22 Preparation of the pumping activities with the pump to the right and the concrete truck transporting the capping mixture (Maurice 2021).

Figure 23 Concrete pump extended above the bay (Maurice 2021).

Figure 24 Floating pipe was mounted to the crane lorry to transport the capping mixture to the test area and spreading of the capping mixture from the floating dock (Flodin, 2021).

According to the mixing ratios of biochar/bentonite/water predetermined in laboratory environment, each individual load of mixture consisted approximately of:

- 20 kg salt,
- 300 kg biochar, CP1 from Jacobi carbon
- 1,2 tons bentonite,
- 9 m^3 water.

The goal was to apply approximately 3 kg/m^2 of biochar mixture, to ensure a capping thickness of at least 1.6 kg/m^2 , which corresponds to the amount used in laboratory experiments NGI (see Appendix 3).

The field work that was executed in 3 days included:

- Day 1: Preparations and site visit, collecting of 4 diffusion chambers for sediment sampling in the test area (for evaluation of background values/contamination situation), and turbidity measurements,
- Day 2: Covering with 2 loads of biochar mixture and turbidity measurements,
- Day 3: Covering with 2 loads of biochar mixture, turbidity measurements and slam tests of the sediment.

The outer boundaries of the test area were marked with anchored floats which served as navigation marks for the test. Additional two anchored floats had been placed in the area, one at a 40-meters distance and another at 80-meters distance from the test site, as part of the control program for turbidity. Two boats rented from the Bureå harbour (Bureå båtklubb) were used for the test i.e. a floating dock and a smaller boat. The floating dock was used move the pipe above the area and distribute the biochar mixture, see Figure 25.

Figure 25 Application of the capping mixture from the floating dock (Maurice 2021).

The capping material was applied above the test area to sink through the water profile. At the application point, the mixture is visible in the water. However, the material sunk immediately and no spreading of a turbidity plume outside the test area was observed. At some stage, the mixture was applied above the surface to reach longer from the floating dock. Even in such conditions, where a larger volume of water was affected, no turbitity variation increase was measured outside the test area. After 30 minutes, the turbidity levels inside the test area were back to the background levels at 0,5 metre from the bottom and below the surface (Figure 26).

Salt addition is believed to have had the expected effect, increasing the blend density, enhancing sedimentation and limiting turbidity. The salt water/slurry has a higher density than water and salt limit the swelling of bentonite, keeping the thickness of the slurry.

Figure 26 Spreading of the capping mixture in the water. The dark "cloud" (Flodin 2021).

A total of 4 loads à 12 tons of biochar mixture was spread in the test area. The field experiment was successfully executed and lasted for about 30-45 minutes for each batch. The mixture is believed to be more or less evenly distributed in the test area even tough, the cover might be slightly thinner in the north-east part of the area, which was difficult to reach with the floating dock on days 1.

The water samples taken within and around the test area showed low turbidity values at both 0.5- and 1.5-meters depth. The turbidity values were increased in connection with the covering (FNU values between 32-53), where the mixture was pumped out, but had decreased to the background values (FNU values between 2-5) when the turbidity was measured again after 1 hour. Outside the test area, 10 meters outside and at control points, 80 meters from the area, no distinct changes in turbidity were detected. This indicates that the biochar mixture settled rapidly which was also desirable.

The conclusion from pilot experiment is that the covering was successfully performed, and the biochar mixture settled relatively rapid after it had been pumped into the water, which was established with the turbidity tests.

5. Evaluation of the capping efficiency

The efficiency of the capping was evaluated at two occasions (September 2021 and June 2022) using diffusion chambers measuring the flux of PAH through the cover to the sea water. The samplers (four on each location) were placed above the capped area and the reference area. Prior to the pilot experiment, the flux of PAH was measured once, at both locations, a baseline. The chamber lays on the surface and does not penetrate through the capping. The formation of cracks in the capping is unlikely. If such occur, it may lead to an underestimation of the efficiency of the capping.
Beside the use of diffusion chambers, sediment profiles were taken from the capped area, once, in February 2022, to assess the capping ocularly. The presence of small bentonite aggregates indicated the presence of the capping. However, it was not possible to precisely distinguish the capping from the underlying sediment, as both are black. Based on difference in consistency, the capping was estimated to ca 5-8 cm.

5.1 Method

The evaluation of the capping efficiency was done using SPMD-membranes fixed at the bottom of a diffusion chamber, a vessel that isolate a volume of water from the surrounding sea (Figure 27). The membrane is an infinite sink which adsorb all the PAH-compounds diffusing through the sea bottom (capped or not).
The chamber was placed for approximately 4 weeks and the membrane was retrieved and sent for analysis of PAH.

Knowing the surface area covered by the chamber and the period during which was placed, it is possible to transform the amount of PAH retrieved from the membrane (in µg) to a flux per square meter and time unit.

Figure 27 Preparation of the diffusion chamber. The diffusion chamber (left) in which the SPMD is placed at the bottom on a frame (middle). The membrane after being in contact by the sediment (right).

5.2 Result

May-June 2021

The flux of PAH-compounds through the bottom sediment surface was measured, before the pilot experiments, to compare the reference area and the untreated test area (Figure 28). For all compounds, the flux of PAH-compounds was higher from the test area than from the reference area.

The spatial variation between the four replicates was high, and the difference between the two areas is therefore not statistically significant.

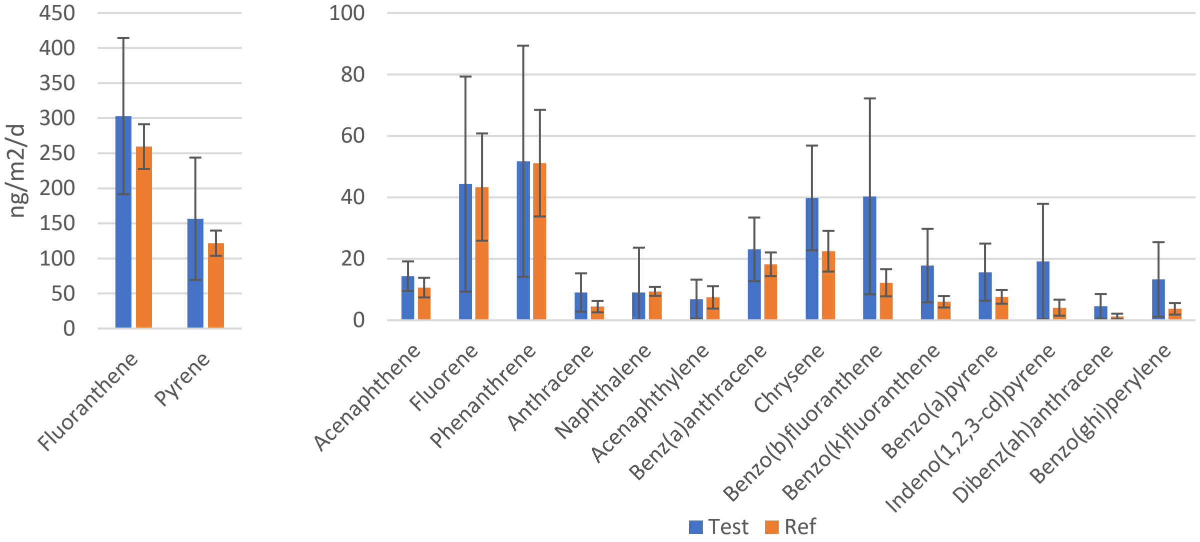


Figure 28 Comparison of PAH-flux from the reference and the test area during spring 2021, before the pilot experiment. The errors bars show the calculated standard deviation (n=4).

August-September 2021

Two months after the capping was installed, the flux of PAH-compounds was measured above the test area and the refence area (Figure 29). For all compounds, except Phenanthrene, the fluxes were significantly lower through the capping compared to the reference area. For several compounds (Naphthalene, Fluorene, and Acenaphthylene) the flux appears as negative i.e., the concentration in the SPMD membrane was lower after one month in the chamber than in the blank.

For Acenaphthene and Anthracene the concentrations were below the reporting limit from the samples above the capped area. Positive fluxes were measured for all compounds in the reference are.

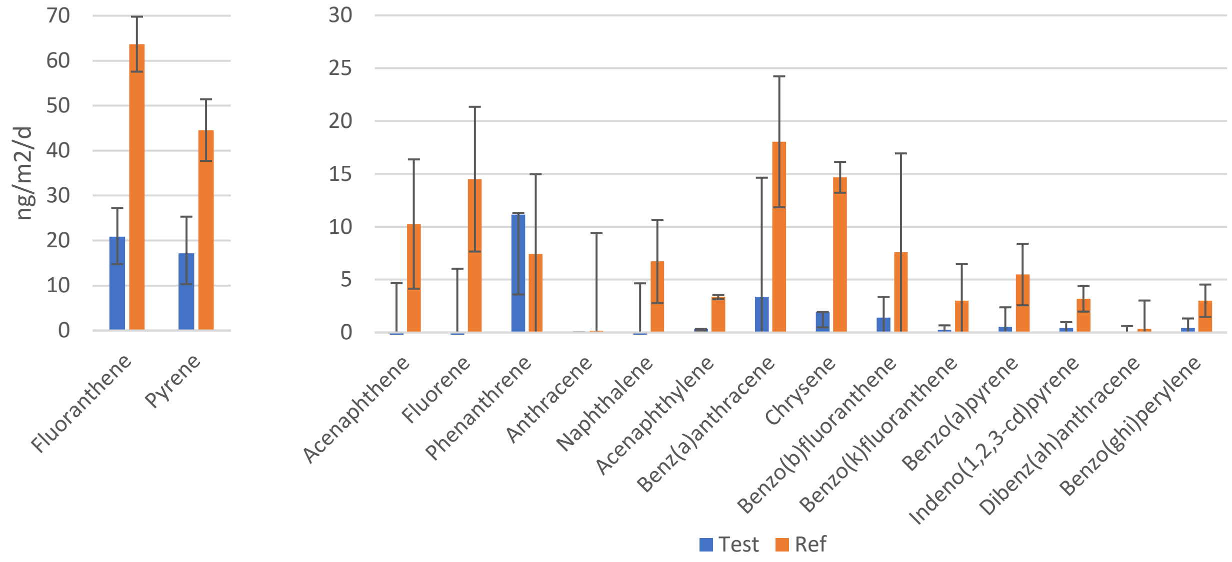


Figure 29 *Comparison of PAH-flux from the reference and the test area during autumn 2021, after the pilot experiment. The errors bars show the calculated standard deviation (n=4).*

May-June 2022

The measurement of the PAH-fluxes above the capped area, after one year, indicated fluxes close to the detection limit for most compounds except Fluoranthene and Pyrene. For those two compounds, the fluxes from the capped area are significantly lower than from the reference area. For the remaining compounds, the fluxes are significantly lower, compared to the reference area. On the overall, the capping had a clear effect on the diffusion of PAH to the sea water.

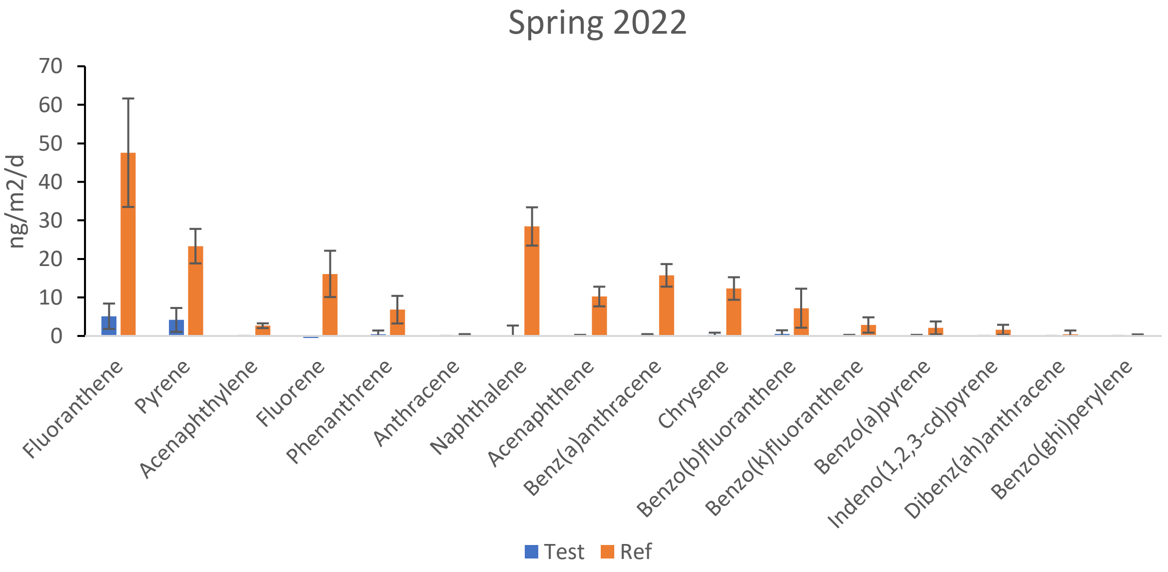


Figure 30 *Comparison of PAH-flux from the reference and the test area during spring 2022. The errors bars show the calculated standard deviation (n=4).*

Variation of the fluxes in the reference area.

For several compounds, the flux of PAH was significantly higher in June 2021 compared to September 2021 and June 2022 (Figure 31). The difference between the fluxes in June 2021 and the two other occasions is unclear. A seasonal variation is not likely as the spring measurements done at the same time of the year in the reference area showed different outcome 2021 and 2022.

A comparison between fluxes from the uncapped and capped test area, before and after capping, is not done as it would show even higher reduction of the pollutant fluxes, as fluxes were generally high during spring 2021. Therefore, comparing fluxes the uncapped and capped test area is believed to overestimate the effect of the capping.

On the opposite, as the reference area showed lower fluxes than the test area prior to capping and assuming it was valid for the rest of the period, the comparison between the capped test area and the uncapped reference area is believed to underestimate the effect of the capping.

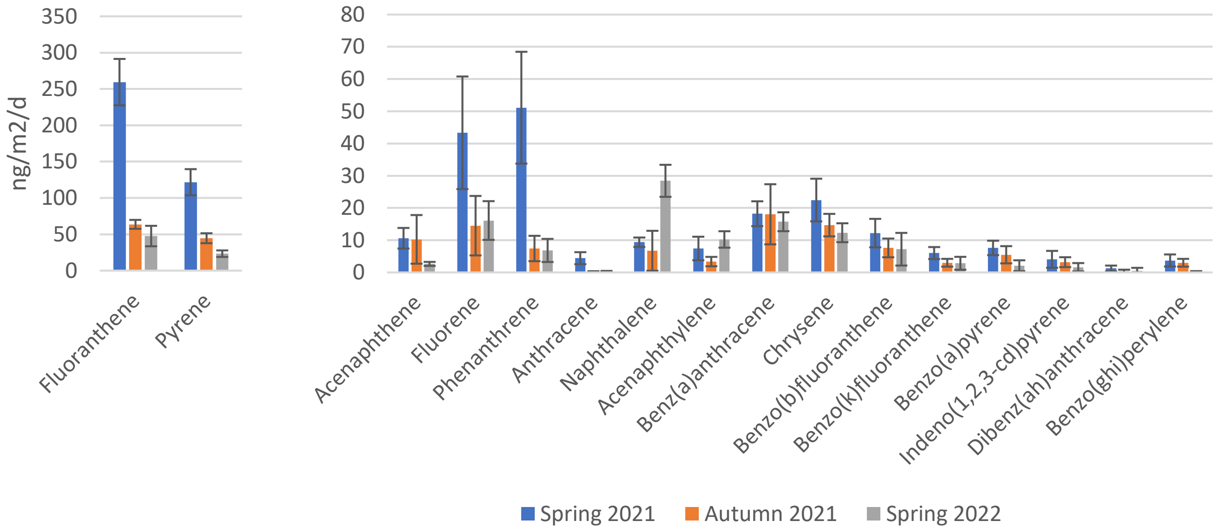


Figure 31 *Comparison of PAH-flux from the test area during before (S=Spring) and after (A=Autumn), after the pilot experiment. The errors bars show the calculated standard deviation (n=4).*

5.3 Discussion

Field test (PAH) – overall reduction of the mobility of PAH

The efficiency of the capping is calculated as the difference between the flux from the reference area and the covered area with the assumption that the diffusion is comparable, between the sites. Both field measurement campaigns show a high level of reduction of the PAH flux through the capping compared to the refence area. Fluoranthene, Pyrene, Acenaphthene, Fluorene, Benz(a)anthracene, Chrysene are the compounds occurring at the highest concentrations. The results of the field area indicate a reduction of PAH diffusion from the sediment to the water body. Fluoranthene and Pyrene are the compounds showing the lowest reduction level (60-70 and 80-90% respectively, for the autumn 2021 and the spring 2022

- For 15 of 16 PAH -compounds, a reduction was observed in September 2021, between the capped and the reference area i.e., Phenanthrene showed higher levels from the test area. The measurement during June 2022 showed a decrease for all compounds.
- For three compounds i.e., Naphthalene, Acenaphthene, Fluorene the reduction appears to be over 100% during September 2021. Reduction over 100% was observed only for Fluorene during June 2022. The flux appears as negative i.e., the concentration in the SPMD membrane was lower after one month in the chamber than in the blank, which leads to a calculated reduction above100%. The method with diffusion chambers is not designed to measure negative fluxes i.e., the migration of PAH from the water back to the capping. These negative fluxes are considered as an artefact of the method.
- One compounds for which the diffusion appears to increase (Phenanthrene). The diffusion of Phenanthrene decreased for both areas between spring and autumn 2021. The decrease was highest for the reference area and as a consequence, the diffusion through the capping seemed to increase compared to the reference.

To assess the effect of the capping, the test area is compared to the reference area. The comparison of the measurement for the reference area indicates a decreased diffusion in September compared to June 2021. The lower diffusion after capping (September 2021) is therefore assumed to be a combination of a general lower diffusion and the effect of the capping.

The difference between the reference and the test area is one source uncertainty i.e., uncertainty between the reference and the test (the representativity of the reference) and seasonal variation:

- A variability of the measured fluxes was observed between the areas, prior to the capping (see Table 3).
- The variability of the fluxes (replicates) at the different measurement occasions was high for certain compounds, on all occasion (see Table 3).
- The analyses of the total content of the sediment showed a variation in the concentration of both trace elements and PAH. Table 4 and Table 5 illustrate the variability of the bottom sediment at the local scale (10 m).

As a consequence, the variability of the results of the diffusion chambers is believed to be partially a consequence of different pollutant concentrations in the sediment and variability of the capping efficiency e.g. local variation of the thickness.

Table 3 Overview of the fluxes of the PAH-compunds from the test and reference areas during the three monitoring periods and difference between the two areas (= reduction after capping). The fluxes are in ng/m^2 and day and average of four measurments (n=4).

	Spring 2021 (prior to capping)					Autumn 2021					Spring 2022				
	Test		Ref		Difference	Test		Ref		Reduction	Test		Ref		Reduction
	Av.	Std.	Av.	Std.	%	Av.	Std.	Av.	Std.	%	Av.	Std.	Av.	Std.	%
Fluoranthene	303,0	111,3	259,4	31,9	-17	20,9	6,4	63,7	6,1	67	5,1	3,3	47,6	14,1	89
Pyrene	156,5	87,2	121,7	18,0	-29	17,2	8,2	44,6	6,8	62	4,2	3,1	23,3	4,5	82
Acenaphthene	14,3	4,8	10,6	3,2	-35	-1,7	0,2	10,3	7,5	100	n.d.		2,7	0,6	100
Fluorene	44,3	35,0	43,3	17,5	-2	-2,1	0,0	14,5	9,2	100	-0,9	0,4	16,1	6,0	100
Phenanthrene	51,7	37,6	51,1	17,3	-1	11,1	8,9	7,4	3,9	-50	0,5	0,9	6,8	3,6	93
Anthracene	9,0	6,2	4,4	1,9	-104	n.d.		0,2	0,2	100	n.d.		0,3	0,2	100
Naphthalene	9,0	14,6	9,4	1,5	4	-4,2	11,3	6,7	6,2	100	n.d.	2,7	28,4	5,0	100
Acenaphthylene	6,9	6,3	7,4	3,7	7	0,4	0,0	3,4	1,5	89	0,1	0,2	10,2	2,6	99
Benz(a)anthracene	23,1	10,3	18,2	3,9	-27	3,4	1,9	18,0	9,3	81	0,3	0,2	15,7	2,9	98
Chrysene	39,8	17,0	22,5	6,6	-77	1,9	0,4	14,7	3,5	87	0,3	0,6	12,3	2,9	98
Benzo(b)fluoranthene	40,3	31,9	12,2	4,4	-230	1,4	1,8	7,6	2,9	81	0,6	0,9	7,2	5,1	92
Benzo(k)fluoranthene	17,8	12,0	6,0	1,9	-196	0,3	0,5	3,0	1,2	91	0,1	0,2	2,8	2,0	97
Benzo(a)pyrene	15,7	9,3	7,6	2,2	-106	0,5	0,6	5,5	2,7	90	0,1	0,2	2,1	1,7	95
Indeno(1,2,3-cd)pyrene	19,1	18,8	4,1	2,6	-370	0,4	0,9	3,2	1,5	86	n.d.		1,6	1,3	100
Dibenz(ah)anthracene	4,5	4,0	1,2	0,9	-264	n.d.		0,4	0,5	100	n.d.		0,5	0,9	100
Benzo(ghi)perylene	13,3	12,1	3,7	1,9	-257	0,4	0,9	3,0	1,2	85	n.d.		0,2	0,2	100

n.d.: not detected

Table 4 Concentration of trace elements in the sediment from both the test and the reference area- Five single samples and a composite sample (SAM) for the area (n=9). The concentrations are compared with bakgounds levels fround in Sedish water (Naturvårdverket 1999[6]). The results are expressed in mg/kg.

Element	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Sample	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS	mg/kg TS
REF-7	335	2,2	21	61	234	2,32	25,1	288	366
REF-9	467	5,2	10	51	128	2,21	15,3	233	234
REF-13	333	2,5	19	59	211	2,16	22,1	260	355
REF-17	463	3,9	11	54	149	2,2	15,3	250	252
REF-19	461	4,7	11	36	139	2,34	13,9	251	251
Ref-SAM	365	3,5	13	56	171	2,16	19,1	222	277
TEST-15	161	4,1	6	32	55,1	1,28	9,7	148	129
TEST-17	258	3,9	11	59	139	2,26	16,9	241	211
TEST-10	196	3,6	7	43	74,6	1,48	11,6	162	134
TEST-3	204	3,9	7	33	98	1,84	11,3	163	167
TEST-5	178	3,1	6	30	78,8	1,12	9,8	154	143
Test-SAM	240	4,1	8	42	93,3	1,66	17,2	196	183

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[6] Naturvårdsverket. (1999). Naturvårdsverkets bedömningsgrunder för miljökvalitet – Kust och Hav, NV rapport 4914, 1999 (senare uppdaterad).

Table 5 Concentration of PAH in the sediment from both the test and the reference area- Five single samples and a composite sample (SAM) for the area (n=9). The concentrations are compared according to the Norwegian criteria for sediment classification (Miljodirektoratet 2016)[7]. In bold underlined, values above the Swedish effect based levels (Hav, 2018)[8]. The results are expressed in mg/kg.

Element	REF-7	REF-9	REF-13	REF-17	REF-19	Ref-SAM	TEST-15	TEST-17	TEST-10	TEST-3	TEST-5	Test-SAM
Naphthalene	0,97	3,1	0,84	1,3	3,3	1	2,6	3,2	0,68	0,97	0,96	0,72
Acenaphthylene	0,23	0,73	0,2	0,62	0,89	0,44	0,59	0,55	0,32	0,26	0,16	0,35
Acenaphthene	<0,1	0,49	<0,1	0,28	0,52	<0,10	0,29	0,22	0,12	0,14	<0,1	<0,10
Fluorene	<0,1	0,84	0,12	0,69	0,85	0,39	0,52	0,4	0,23	0,29	0,15	0,26
Phenanthrene	1,1	4,2	1	2,3	4,9	1,7	3,1	3,2	0,93	1,3	1,1	1,3
Anthracene	**0,34**	**1,7**	**0,3**	**1,2**	**1,9**	**0,84**	**1,3**	**1,1**	**0,55**	**0,61**	**0,44**	**0,63**
Fluoranthene	**3,4**	**13**	**3,1**	**4,3**	**16**	**2,9**	**6,8**	**9,3**	**2,3**	**3,3**	**4**	**2,72**
Pyrene	2,5	9,3	2,3	3,2	11	2,31	5	7	1,8	2,5	3	2,2
Benz(a)anthracene	0,74	3,1	0,88	1,9	5,4	1,56	2	1,7	0,99	1,1	1,1	1,19
Chrysene	0,67	2,9	0,85	1,8	5,1	1,56	1,8	1,7	0,91	0,96	1	1,05
Benzo(b)fluoranthene	1,2	3,8	1,3	2	5,9	1,79	2,4	2,4	1	1,3	1	1,33
Benzo(k)fluoranthene	0,68	1,5	0,67	0,78	2,2	0,7	1,2	0,94	0,43	0,47	0,5	0,47
Benzo(a)pyrene	0,8	2,6	0,82	1,6	4,4	1,36	1,8	1,6	0,83	0,92	0,72	1,04
Dibenz(ah)anthracene	0,16	0,36	0,14	0,27	0,64	0,2	0,31	0,19	0,13	0,14	0,1	0,14
Benzo(ghi)perylene	0,54	1,4	0,56	0,92	2,5	0,78	1,3	0,93	0,48	0,53	0,44	0,61
Indeno(1,2,3-cd)pyrene	0,46	1,3	0,52	0,98	2,2	0,83	1,2	0,95	0,5	0,59	0,39	0,63
PAH, sum 16	14	50	14	24	68	18,4	32	35	12	15	15	14,6

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[7] Miljødirektoratet. (2016). Grenseverdier for klassifisering av vann, sediment og biota – revidert 30.10.2020.

[8] Hav. (2018). Havs- och vattenmyndighetens rapport 2018:31. Metaller och miljögifter - Effektbaserade bedömningsgrunder och indikativa värden för sediment. Kunskapssammanställning baserad på ämnesrapporter framtagna inom vattendirektivsarbetet.

6. General discussion - Evaluation of the technology

6.1 Applicability

The main advantage of the technology is that it can be applied to area that cannot be dredged because of technical limitations or because the environmental and societal benefits are too small in comparison with the costs associated with dredging. The results from the laboratory and the field experiments indicate the capping efficiently reduces the pollutant migration from sediment bottom to the water body. Trace elements stable in anaerobic conditions (Cu, Zn, Pb, etc) are trapped in the sediment, below the capping while the mobility of PAH is reduced by adsorption on the biochar. Elements mobile in anaerobic conditions (As, Fe, Mn) continue to migrate and adsorb at the interface sediment/water, when the conditions get oxic.

Compared to traditional cover alternatives (> 0,5 m), thin layer capping demands less materials to achieve the same efficiency. The material demand is rapidly a limiting factor as the surface to be capped increases. Except for situations where huge amounts of dredged sediment are available for capping, capping large areas of sediment with 0,5 m extracted pristine materials is not considered as a sustainable solution and would imply huge costs associated with material extraction and transport.

The main uncertainties regarding upscaling of the results from the pilot experiment to full scale are:

- The pilot experiment was done at an intermediate scale which does not allow a simple extrapolation of the costs and the method to a full scale. The unit cost cannot be used to dimension a large-scale capping. Mixing with a concrete truck and pumping the slurry from the shore to the test area was the most efficient method, considering the limited amount to be mixed. For full-scale operation a barge would be used on which the materials are mixed and pumped directly above the site. A barge would be more flexible, reaching the different parts of the waterbody to be capped. For a site like Bureå, in Northern Sweden, another option might be explored, i.e., apply the mixture on the ice, during the spring, before snowmelt. The albedo of the mixture and its salinity are expected to enhance ice melting and would provide a smooth distribution of the capping when the water is calm.
- The capping had to be installed before the summer of 2021 to allow at least one evaluation of the function. The timetable of the experiment was therefore tight, and bentonite was selected as structure material to be able to start the laboratory experiments and the testing of the recipe. Based on experience from NGI, bentonite is appropriate for the purpose as it effectively trapped the biochar particles. Bentonite is available on the market, and it is clean, which simplified the logistic and the communication with environmental authorities. The pilot experiment was performed 7 months after project start and the final evaluation was due 10 months after start. Bentonite is an expensive product, and it has a non-negligible environmental footprint. In real scale applications other materials (rock dust, till or sediment[9]) are cheaper candidates. For future projects, a comparison of different structure materials would allow selection of a less costly structure material. An environmental assessment of those materials should be included as part of the selection process.

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[9] Nathalie Pantzare (2021). Biochar-based thin-layer capping of contaminated sediment in Burefjärden, Northern Sweden. Assessment of biochar mixed into four structural materials for preventing release of trace elements from sediment to water Natural Resources Engineering, master's. Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering.

- The monitoring of the capping was done for one year (one season with autumn storm, frozen sea surface and spring flood. One year is short compared with the expected lifetime of the capping i.e during the time for natural sedimentation to capped further the sediment.

The technology main potential is for large areas where the environmental and societal benefits of dredging cannot balance the negative effects of dredging i.e., cost limitations, environmental consequences associated with sediment management or because of technical restrictions e.g. water depth or bottom conditions (rock, timber, etc).

Thin layer capping has limitations, and its function can be altered by external factors.

- Bottom fauna can cause bioturbation. Species such as *Marenzellaria neglecta and Marenzellaria viridis* can dig as deep as 40 cm in the sediment and perforate the capping, enhancing pollutant migration in a similar way as in untreated sediment.
- The gas generation in the sediment, as the result of anaerobic degradation of organic matter, causes the formation of gas bubbles that travel through the capping and disturb it. In Bureå Bay, a major part of the polluted bottom is fibre sediment, i.e., sediment where fibres are found. The test area is not believed to be affected by large amount of gas bubbles. In other parts of the bay, and especially in the fibre bank, the gas generation was observed, which is a limitation for the method. Such capping is not applicable on fibre banks also because of the consistency and the structure of such materials. The cover material would sink through the fibre bank, between the fibre and wood particles.
- Erosion of the capping needs to be addressed, based on the local conditions such as boat traffic and sea currents. In Bureå, even though the water depth is shallow, the risk for erosion is limited thanks to local geography with a closed bay and no boat traffic. Methods already exist to model erosion and design cover to protect the capping from disturbance from e.g., boat propeller, adapted to local conditions.
- Powdered activated biochar can lead to negative effects on sediment biota (Abel et al, 2017)[10], and too coarse granulated material has limited chemical effectiveness in reducing sediment to water fluxes. Research is ongoing to find the optimal balance between a benign material for organisms (coarse particles) and sufficient chemical effectiveness (small particles). The finest fraction of the structure material (e.g. rock dust) may also affect the biota, which needs to be addressed when relevant.

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[10] Abel, S., Nybom, I., Mäenpää, K., Hale, S. E., Cornelissen, G., & Akkanen, J. (2017). Mixing and capping techniques for activated carbon based sediment remediation–efficiency and adverse effects for Lumbriculus variegatus. *Water research*, *114*, 104-112.

The main goal of the technology is to limit the effect of polluted sediment on the water quality and the spreading of pollutant to the ecosystem and the food chain. Biochar has the ability to bind trace elements (e.g., heavy metals) and organic pollutants e.g. PAH[11]. Research has shown the ability of biochar to bind other organic molecules such as PCB[12], Dioxin, and trace elements[13,14,15].

Polluted sediment often occurs over large areas, as a consequence of spreading and sedimentation of suspended material. The polluted areas are generally more or less delineated, and the surface area affected by pollutant is usually large. While dredging is cost efficient for smaller well delineated sources, capping would be a solution for a large area with more diffuse pollution.

6.2 Durability and sustainability

The main advantage of the technology with a thin capping with a reactive component (biochar) is its material efficiency, i.e. the capping requires small amounts of material to build an efficient cover, compared to a traditional technology relying only on the thickness of the capping to limit pollutant migration. A typical traditional capping without reactive component, of e.g. 0,5 m, requires one tonne per square meter of material compared to the capping which requires small amounts of biochar (just kilograms per square meter) to sustain the functionality.

Biochar has several positive properties. Biochar has a positive carbon balance thanks to its ability to sequester carbon[16] and its stability[17]. The C sequestration potential of biochar is around 2.4 tons CO_2-e per tonne of biochar (80% stability; 80% C; 3.6 tons CO_2 per C). The use of biochar is therefore accepted as a climate change mitigation measure[18].An exciting possibility is to produce biochar from lightly contaminated waste fractions such as waste timber, biogas digestate, garden waste and even sewage sludge as the pollutants in these streams are destroyed by the high pyrolysis temperatures, and part of their carbon is sequestered. Recent data have shown that sewage-sludge derived biochars are effective sorbents for PFAS contamination in water, soil and probably also sediment.

The reactive capping requires a structure material to keep the biochar in place. In the performed pilot experiment, bentonite has probably the most significant environmental footprint. Bentonite was used in the pilot experiment because of the timetable for the project. For a full-scale

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[11] Cornelissen, G., M. Kruså, G. Breedveld, E. Eek, A. Oen, H. Arp, C. Raymond, G. Samuelsson, J. Hedman, Ø. Stokland, and J. Gunnarsson. 2011. Remediation of contaminated marine sediment using thin-layer capping with activated carbon--a field experiment in Trondheim harbor, Norway. Environmental Science & Technology **45**:6110-6116.

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

[13] Beesley, L., E. Moreno-Jimenez, and J. L. Gomez-Eyles. 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution **158**:2282-2287.

[14] Cornelissen, G., K. Amstaetter, A. Hauge, M. Schaanning, B. Beylich, J. S. Gunnarsson, G. D. Breedveld, A. M. P. Oen, and E. Eek. 2012. Large-Scale Field Study on Thin-Layer Capping of Marine PCDD/F-Contaminated Sediments in Grenlandfjords, Norway: Physicochemical Effects. Environmental Science & Technology **46**:12030-12037.

[15] Ahmad, M., A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S. S. Lee, and Y. S. Ok. 2014. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere.

[16] Lehmann, J., C. Czimczik, D. Laird, and S. Sohi. 2009. Stability of biochar in soil. Biochar for environmental management: Science and technology:183-206.

[17] Kuzyakov, Y., I. Subbotina, H. Q. Chen, I. Bogomolova, and X. L. Xu. 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by C-14 labeling. Soil Biology & Biochemistry **41**:210-219.

[18] Oliveira, F. R., A. K. Patel, D. P. Jaisi, S. Adhikari, H. Lu, and S. K. Khanal. 2017. Environmental application of biochar: Current status and perspectives. Bioresource Technology **246**:110-122

application, the use of bentonite is not considered sustainable. Bentonite is an expensive product, and it has also a significant environmental footprint for production and transport. The method and the procedure of the pilot experiment ned to be scaled up to improve the economic and environmental footprint of the technology, prior to a full-scale application. Therefore, further work is needed to verify that other structure material can be used to apply biochar and limit risks for erosion and material transport. In the Grenlandsfjords clean local clay deposits were dredged and used for this purpose, and they turned out to be a good carrier material for the activated biochar and were benign to the benthic fauna.

Mixing biochar to the sediment is one alternative to capping for reducing pollutant migration into the water. This application method was tested in laboratory experiments. To mix biochar to sediment in-situ is not feasible at a large scale. Mixing biochar into dredged sediment or different fine-grained soil (sand, till, rock dust) is however possible. The results of the laboratory experiments performed at NGI and LTU showed that the thin-layer capping reduces the PAH-diffusion. Hypothetically, to improve further the carbon balance of the technology, polluted sediment could be dredged from appropriate areas and treated with biochar in the barge before being redeposited on top of untreated polluted sediment.

Beside the production of the material, transport, mixing, and pumping of the capping material are the main resource consuming steps. As capping with reactive material requires less material, the technology has the potential to be energy and resource efficient.

The application of the capping is assumed to have a limited effect on the surrounding environment. The spreading of suspended material (turbidity) was found to be limited (not measurable) during the pilot experiment and is only a border issue at the border of the area to be treated, in a real scale application. Lateral particle transport during the application, within the area to be treated, has no negative effect.

Experience from Norwegian tests using fine-grained activated carbon indicate a negative impact on bottom fauna (Appendix 1). Even though the transport of pollutant was reduced, and the amount of pollutant in the organisms was lowered, the diversity of the bottom fauna was lower after remediation. According to literature, activated carbon may have a negative impact on benthic living organisms (Abel et al 2017[19]; Samuelsson et al 2017[20]). One hypothesis is that the organisms ingest the carbon particles. The powdered carbon < 50 µm affect and clog microvilli in the gut of the organism, where uptake of nutrients takes place (Abel et al. 2017).

However, the effect of biochar on benthic organisms remains unclear. Further work is needed to optimise both activated carbon and biochar particle size and find a compromise between efficient adsorption, easy application and minimal negative effects:

- The smaller, the more efficient as a sorbent (but risk for particle loss and effect on the bottom fauna)
- The coarser, the easier to apply, less effect on the bottom fauna, but less efficient as a sorbant
- Other types of biochar, less efficient, cheaper that could be applied at higher levels.

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[19] Abel, S., Nybom, I. Mäenpää, K., Hale, S. E., Cornelissen, G., and Akkanen, K. (2017). Mixing and capping techniques for activated carbon based sediment remediation Efficiency and adverse effects for Lumbriculus variegatus. Water Research, 114, p. 104-112

[20] Samuelsson, G. S., Raymond, C., Agrenius, S., Schaanning, M., Cornelissen, G. and Gunnarsson, J.S. (2017). Response of marine benthic fauna to thin-layer capping with activated carbon in a large-scale field experiment in the Grenland fjords, Norway. Environmental Science and Pollution Research, 24(16), 14218-14233.

6.3 Knowledge gap and research needs

Thin-layer capping with activated biochar is not a method commonly used in Sweden and experience in mixing and pumping those materials was limited. The pilot project was a demonstration of the technology under local conditions, with frozen sea during winter and low oxygen concentrations in the water body. It demonstrated the feasibility of mixing and pumping of the capping material. The contractor for the project (Swerock) has also gained experience handling the materials. Parallel to the field work and investigations, the laboratory investigation demonstrated the efficiency of the biochar to reduce the fluxes of most pollutants and that other material than bentonite could be used.

The field experiment provided proof of concept for the method and provided valuable information regarding the technical aspects of mixing and pumping. The application method gave a slurry that could be pumped and caused a minimal turbidity in the surrounding water. To reduce the formation of clumps, the various ingredients (water, salt and bentonite) should be mixed prior to spreading the slurry. The pilot experiment was not designed to assess the logistic of the technology as the mixing method was not relevant for the full-scale application. A feasibility study is necessary to extrapolate the results from the pilot experiment and evaluate the method at full-scale.

The use of other structure material such as different fractions of rock dust (a fine fraction of crushed rock, e.g. 0-4 mm) and dredged sediments should be investigated further from a technical and environmental perspective. Certain rock fractions are sometimes generated at large amounts and can be available at a low cost. Further work is needed to identify which soil and rock fractions are available and could be used to replace bentonite. Different types of biochar are available, with different properties e.g., particle size, specific surface, density. For example, a product with a density higher than water exists, which would simplify the application, assuming it has a comparable efficiency to the powdered product. Further work is needed to test different types of biochar, from different sources, with different properties, to improve further the capping construction and its efficiency. Research is needed to find the optimal biochar particle size to optimize chemical effectiveness while minimizing negative secondary impacts on benthic organisms. Also, the possibilities of applying biochars from organic waste streams should be further investigated for sediments.

Capping is a long-term reclamation strategy, i.e., it is a measure to rapidly reduce the pollutant flux and, as sedimentation continues, clean sediments will naturally accumulate and further thicken the capping with time. One year monitoring does not allow to draw conclusions regarding the expected lifetime of the remediation. Lifetime is dependent on whether the emissions have been completely halted. A long-term evaluation of the technology is therefore necessary as it is supposed to last for several decades until natural sedimentation has built on the capping. The test area is available for future evaluations of its function and a monitoring of the area is recommended. Its location also makes it easily accessible in the future. The efficiency of the capping can be measure by regular measurement campaigns. Increasing the number of samples would reduce the uncertainty of the results and provide a better statistical data set. The thickness of the capping in-place has not been measured. Controlling the capping thickness and potential changes over time require coring and sediment analysis. As the capping material and the sediment have the same colour and the same consistency, a precise ocular characterisation was not possible. Coring and measurement of total organic carbon would be a way to assess cap integrity, but this was not feasible in the short time frame of the current project.

The thin layer capping project at Grenlandsfjords (dioxins) was followed up for 10 years after cap placement, and the results indicate that cap effectiveness was at its best after 4-5 years, and diminished between 5 and 10 years after placement, probably due to dilution of the active cap material over time as sedimentation takes place.

Laboratory scale experiments gave valuable information about the pollutant fluxes, allowed to vary the capping design, and test different combinations and develop recipes. However, laboratory experiments have limitations, especially when dealing with trace elements, as the water quality in the jar or columns does not fully represent the water quality in the sea. Both pH and redox conditions in the jar and columns affect trace elements mobility in a way that is not relevant to reality. Anoxic conditions are expected to develop in the capping, in the pore water only. More work is needed to develop laboratory experiments to better control pH and redox conditions and assess the conditions found in sea environment e.g., infinite buffer capacity and constant pH.

The capping technology is believed to be applicable to other pollutants. In the pilot experiment, only the flux of PAH was assessed. Literature indicates that the method could be applied to other organic pollutants with high affinity to carbon such as PAH, dioxin and PCB[21]. Similar capping technology was also shown efficient for remediating total Hg, however, effects of thin-capping on contaminants like As and methyl-Hg remain poorly studied. The laboratory work indicated that thin capping with activated biochar is very effective for PAHs but may lead to increased fluxes of especially arsenic. This phenomenon should be studied under field conditions. To measure fluxes of trace elements, however, the diffusion chambers would have to be adapted using i.e. a DGT membrane and create a water circulation to avoid the development of redox conditions different from the sea. A flow-through chamber was developed by Mustajärvi et al (2017) to measure organic contaminants[22]. A similar construction could be built and tested in ongoing projects, with a DGT membrane to assess the remediation of trace elements.

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

[22] Eek, E. Cornelissen, G., Eriksson-Wiklund, A.K., Undemand, E., Sobeka, A. (2017). In situ benthic flow-through chambers to determine sediment-to-water fluxes of legacy hydrophobic organic contaminants. Environmental Pollution. Volume 231, Part 1, December 2017, Pages 854-862.