

Mastergrads oppg. 2011

THIN LAYER CAPPING WITH BIOCHAR ON MARINE
SEDIMENTS CONTAMINATED WITH PAHS,
AND THE EFFECT OF DIFFERENT CAPS ON MARINE
SEDIMENTS CONTAMINATED WITH DIOXINS

AINA WINTHER

Wint



NORWEGIAN UNIVERSITY OF LIFE SCIENCES
DEPARTMENT OF PLANT AND ENVIRONMENTAL SCIENCES
MASTER THESIS 60 CREDITS 2011



Acknowledgements

The master thesis is conducted at the Department of Plant- and Environmental Sciences, the Norwegian University of Life Sciences (UMB), Ås, and the Norwegian Geotechnical Institute (NGI), Oslo. The thesis constitutes 60 study points and was conducted during spring and autumn 2011, which is within the set time frame.

My supervisors have, with their great enthusiasm and engagement, impacted me in more ways than just increasing a scientific interest and the enjoyment of working with this experiment, but also I have evolved and learned much more at both scientific and personal level during this year than any other. It has been quite the ride.

I'd like to give a special thanks to Sarah Hale, my supervisor at the NGI, for always encouraging me and taking the time. She has been invaluable. Thanks to Gerard Cornelissen, supervisor at the NGI, for providing me with this opportunity, for good advice and a fun and educational time in field in the Grenland fjords, and for inspiring me to think differently about what one person can do for the environment just by considering life style. Thanks to Jan Mulder, supervisor at the UMB, for good advice and encouragement. Thanks to Espen Eek, the NGI, for help with the modelling and positivity in field in the Grenland fjords. The people I have been in contact with at the NGI have all been helpful and engaging, helping me with my thesis, in lab, with my terrible computer and otherwise being pleasant, and among these I would mention Arne Pettersen, Geir Wold Åsli and Jessica Hansson, and the IT department.

Ås - UMB 12. December 2011

Aina Winther

ABSTRACT

Capping contaminated sediment with clean materials is a remediation method that has proved efficient. Passive capping materials physically isolate the contaminated sediment from the receiving environment and active materials sorb the contaminants, thereby making them inaccessible. Activated carbon is one active capping material that is effective in reducing the diffusion of contamination from the sediment. The objective of this thesis was to investigate if biochar could be applied as an active capping material in remediating contaminated sediment.

The efficiency of different biochars in reducing PAH diffusion from contaminated sediment to the overlying water was examined by a diffusion experiment. Biochars produced at different temperatures and from different organic materials were used as caps to test which was the most effective. These were corn stover biochar produced at 600°C, and biochar produced from oak at 250°C, 400°C, and 650°C. Diffusion jars with PAH contaminated sediment were set up for 1) uncapped sediment, 2) sediment capped with biochar and clay, and 3) sediment capped with clay, using heptane as an infinite sink for diffusing PAHs. The experiment lasted for 101 days and during this time five measurements were carried out, providing a temporal scale.

The results showed that the efficiency of the cap (oak 650 biochar) in reducing the diffusion of the PAHs fluorene, phenanthrene, and acenaphthene ranged from 77.2% to 88.1% compared to the uncapped sediment. The results showed very little difference among the biochar caps in the efficiency of retaining diffusing PAHs from the contaminated sediment. Diffusion of small PAHs exceeded the diffusion of larger PAHs, where most were not detectable. The ones that were detected measured very low concentrations, and diffusion of benzo(b)fluoranthene represented the general trend for the detectable, large PAHs.

Steady state diffusive flux of phenanthrene was reduced with 77 % for capped sediment (oak 650 cap) compared to uncapped sediment.

Sorption isotherms for the biochars were determined in order to check the strength of biochar sorption of PAHs. The isotherms were measured over four different concentrations of phenanthrene and pyrene and the biochar – water partitioning coefficient was calculated. The isotherms were presented as Freundlich isotherms. According to the results, the corn stover

biochar had the most reliable data and therefore the most reliable isotherms for both phenanthrene and pyrene (K_{biochar} for sorption of phenanthrene and pyrene to corn stover was 5.05 ml/g). Sorption of phenanthrene and pyrene to corn stover also had the highest n values, though these were highly below 1 ($n = 0.38$ for sorption of phenanthrene, $n = 0.43$ for sorption of pyrene). The biochar with the highest K_{Fr} value for sorption of phenanthrene was the oak 400 biochar ($K_{\text{Fr}} = 7.05 \text{ (ng/kg)(ng/l)}^n$), and oak 250 had the highest K_{Fr} value for pyrene sorption ($K_{\text{Fr}} = 6.61 \text{ (ng/kg)(ng/l)}^n$). K_{Fr} was not found for phenanthrene sorption to the oak 250 and oak 650 biochars, or for pyrene sorption to the oak 650 biochar. There was not enough reliable data for the oak 650 biochar to construct an isotherm.

Another part of the thesis was to investigate thin layer capping with three different materials on dioxin contaminated sediment in the Grenland fjords, as a part of the Opticap project. Field work was conducted in the Ormerfjord and the Eidangerfjord in the Grenland fjords. The aim was to test the efficiency of the capping materials 1) activated carbon and clay, 2) crushed limestone, and 3) clay in order to reduce dioxin diffusion. According to the results, all caps were efficient in reducing the dioxin flux from the sediment, and the flux was the lowest in the crushed limestone field, though there are variations between the measurements. Dioxins in free aqueous phase were also reduced in the capped fields, but there were no clear trends in which cap was the most efficient, due to currents and exchange of sea water. The dioxin flux from the sediment was measured with semi-permeable membrane device (SPMD) and the dioxins in free aqueous phase were measured with polyoxymethylene (POM). The measurements were done by employing a flux chamber which was put on the sea floor and collected at different time points.

SAMMENDRAG

Tildekking med rent materiale av forurensede sedimenter er et miljøtiltak som har vist seg å være effektivt. Passive tildekkingsmaterialer fungerer fysisk ved å isolere forurensningen fra omgivelsene, mens aktive tildekkingsmaterialer binder forurensningene og dermed utilgjengeliggjør den. Aktivt karbon er et aktivt tildekkingsmateriale som effektivt reduserer diffusjonen av forurensning fra sedimentet. Målet i denne oppgaven var å undersøke om biokull kan bli benyttet som et aktivt tildekkingsmateriale som et miljøforbedrende tiltak av forurensede sedimenter.

Effektiviteten ulike biokull hadde i forhold til å redusere diffusjon av PAHer fra forurenset sediment til vannfasen over ble undersøkt ved et diffusjonseksperiment. Biokull produsert ved ulike temperaturer og med ulikt opphavsmateriale ble benyttet som tildekkingsmateriale for å teste hvilket biokull som ville være mest effektivt. Disse var biokull av mais produsert ved 600°C og biokull av eik produsert ved 250°C, 400°C og 650°C. Diffusjonsprøver ble satt opp for 1) utildekket sediment, 2) sediment tildekket med biokull- og leirblanding og 3) sediment tildekket med leire. Heptan ble brukt som en endelig oppsamling for diffunderende PAHer. Forsøket varte i 101 dager og i løpet av denne tiden ble det tatt fem målinger, hvilket gav en konsentrasjonsgradient.

Resultatene viste at effektiviteten tildekking (eik 650 biokull) hadde i å redusere diffusjon av PAHene fluoren, fenantren og acenaften varierte mellom 77.2 % og 88.1 % sammenliknet med utildekket sediment. Det var ingen markant forskjell i effektiviteten til de ulike tildekkingsmaterialene. Diffusjon av små PAHer overgikk diffusjon av de store PAHene, der de fleste ikke hadde diffundert. The store PAHene som hadde diffundert målte veldig lave konsentrasjoner, og diffusjon av benzo(b)flouranten representerte den generelle trenden for disse.

Steady state diffusiv fluks av fenantren ble redusert med 77 % for tildekket sediment (eik 650 tildekking) sammenliknet med utildekket sediment.

Sorpsjonsisotermene for biokullene ble bestemt for å sjekke hvor sterkt biokullet kunne binde PAHer. Isotermene ble målt over fire forskjellige konsentrasjoner av fenantren og pyren, og

fordelingskoeffisienten mellom biokull og vann ble beregnet. Isotermene ble presentert som Freundlich isotemer. I følge resultatene hadde mais biokullet de mest troverdige dataene og presenterte dermed de mest pålitelige isotermene for både fenantren og pyren (K_{biokull} for sorpsjon av fenantren og pyren til mais biokull var 5.05 ml/g). Sorpsjon av fenantren og pyren til mais biokullet hadde også de høyeste n verdiene, selv om disse var langt under 1 ($n = 0.38$ for sorpsjon av fenantren, $n = 0.43$ for sorpsjon av pyren). Det biokullet som hadde høyest K_{Fr} verdi for sorpsjon av fenantren var biokullet eik 400 ($K_{\text{Fr}} = 7.05 \text{ (ng/kg)(ng/l)^n}$), mens biokullet eik 250 hadde høyest K_{Fr} verdi for sorpsjon av pyren ($K_{\text{Fr}} = 6.61 \text{ (ng/kg)(ng/l)^n}$). Det ble ikke funnet K_{Fr} verdier for sorpsjon av fenantren til biokullene eik 250 eller eik 650, eller for sorpsjon av pyren til biokullet eik 650. Det var ikke tilstrekkelig nok data til å lage isoterm for biokullet eik 650.

En annen del i oppgaven var å undersøke tynn tildekking med ulike tildekkingsmaterialer av dioksinforurensede sedimenter i Grenlandsfjordene, som en del av prosjektet Opticap. Det ble utført feltarbeid i Ormerfjorden og Eidangerfjorden i Grenlandsfjordene. Målet var å teste effektiviteten tildekkingsmaterialene 1) aktivt karbon og leire, 2) knust kalkstein og 3) leire hadde på reduksjonen av diffusjon av dioksiner. I følge resultatene var alle tildekkingsmaterialene effektive i å redusere diffusjon av dioksiner. Det feltet med lavest diffusjon var i feltet med knust kalkstein, skjønt det var variasjoner mellom målingene. Dioksiner i fri vannfase ble også redusert i feltene med tildekking, men det var ingen klare trender for hvilket tildekkingsmateriale som var mest effektivt. Dette skyldes strømminger og utskifting av sjøvann. Fluksen av dioksiner fra sedimentet ble målt med semi-permeable membran redskap (SPMD) og dioksiner i fri vannfase ble målt med polyoksymetylen (POM). Målingene ble gjort med et flukskammer, utstyrt med SPMD og POM, som stod på havbunnen inntil det ble hentet opp for målinger.

Table of contents

| | |
|--|----|
| Acknowledgements | I |
| ABSTRACT | II |
| SAMMENDRAG | IV |
| Glossary of abbreviations | 1 |
| 1.0 Introduction | 2 |
| 1.1 Thesis aims, objectives and hypotheses | 4 |
| 2.0 Background | 5 |
| 2.1 Persistent organic pollutants (POPs) | 5 |
| 2.1.1 Polycyclic aromatic hydrocarbons (PAHs) | 5 |
| 2.1.2 Dioxins | 7 |
| 2.2 National environmental goals and the situation of today | 9 |
| 2.3 Remediation of contaminated sediments | 10 |
| 2.3.1 Passive material capping | 12 |
| 2.3.2 Active material capping | 12 |
| 2.3.3 Biochar | 13 |
| 2.3.4 Opticap | 14 |
| 2.4 Factors influencing contaminant release through a cap | 15 |
| 2.4.1 Bioturbation | 15 |
| 2.4.2 Molecular diffusion | 16 |
| 2.4.3 Advection | 17 |
| 2.5 Sorption of contaminants | 18 |
| 2.5.1 Carbonaceous geosorbents | 18 |
| 2.5.2 Sorption isotherms | 19 |
| 3.0 Methodology: PAH contaminated sediment and thin layer capping with biochar | 21 |
| 3.1 Method development of the diffusion experiment | 21 |
| 3.2 Material description | 23 |
| 3.3 Diffusion experiment set up | 26 |
| 3.3.1 Comparison between heptane and tenax as infinite sinks for PAHs | 28 |
| 3.3.2 Quantification of evaporation of heptane and hexane | 30 |
| 3.3.4 Recovery of the spiked standard | 30 |
| 3.4 Soxhlet extraction of Bergen sediment and clay | 32 |
| 3.4.1 Silica gel clean up | 32 |

| | |
|---|----|
| 3.4.2 GCMS analysis..... | 33 |
| 3.5 Freely dissolved PAH concentrations | 34 |
| 3.5.1 POM extraction | 35 |
| 3.6 Sorption of PAHs to biochar | 35 |
| 3.6.1 Determination of sorption isotherms | 35 |
| 3.6.2 Calculating the biochar – water partitioning coefficient (K_{biochar}) | 36 |
| 3.7 Quality assurance | 37 |
| 4.0 Field work with dioxin contaminated sediment in the Opticap project..... | 38 |
| 5.0 Results PAH contaminated sediment and thin layer capping with biochar..... | 40 |
| 5.1 Total PAHs and freely dissolved PAHs in Bergen sediment, clay, sea water and biochar | 40 |
| 5.2 Diffusion of PAHs through biochar cap and steady state diffusive flux of phenanthrene | 42 |
| 5.2.1 Steady state diffusive flux | 44 |
| 5.3 K_{biochar} and sorption isotherms | 45 |
| 6.0 Results dioxin contaminated sediments in the Grenland fjords | 48 |
| 7.0 Discussion | 50 |
| 7.1 Total PAHs and freely dissolved PAHs in Bergen sediment, clay, sea water and biochar | 50 |
| 7.2 Diffusion of PAHs through biochar cap..... | 52 |
| 7.2.1 The efficiency of capping with biochar..... | 52 |
| 7.2.2 Steady state diffusive flux | 53 |
| 7.2.3 Differences in sorption efficiency between the different caps | 53 |
| 7.2.4 Diffusion of small and large PAHs | 54 |
| 7.2.5 Formation of biofilm..... | 55 |
| 7.3 K_{biochar} and sorption isotherms..... | 55 |
| 7.4 Dioxin contaminated sediments in the Grenland fjords | 57 |
| 8 Conclusion and further research | 58 |
| 9 References..... | 60 |
| 10. Appendixes..... | 65 |

Glossary of abbreviations

AC: activated carbon

AFG: acidic functional groups

AOM: amorphous organic material

BC: black carbon

CG: carbonaceous geosorbents

DBL: diffusive boundary layer

DMF: dimethylformamide

GC-MS: gas chromatography mass spectrometry

HOC: hydrophobic organic compounds

Klif: Norwegian Climate and Pollution Agency

NGI: Norwegian Geotechnical Institute

NIVA: Norwegian Institute for water research

NOM: natural organic matter

PAH: polycyclic aromatic hydrocarbons

PCB: polychlorinated biphenyls

POM: polyoxymethylene

POPs: persistent organic pollutants

SC1: sediment capped with corn stover

SC2: sediment capped with oak 250

SC3: sediment capped with oak 400

SC4: sediment capped with oak 650

SCC: sediment capped with clay

SNC: sediment no cap

SPMD: semi permeable membrane device

TCDD: 2,3,7,8 – Tetrachlorodibenzodioxin

TEQ: toxic equivalents

TOC: total organic carbon

UMB: University of Life Sciences (universitetet for miljø- og biovitenskap)

1.0 Introduction

The Norwegian coastline is greatly influenced by human activity, and has received contaminants from industrial areas, cities and other sources over several decades. This has led to contamination of the coastline by organic pollutants and metals in various concentrations. The sediment becomes a sink for pollution, as hydrophobic organic contaminants (HOC) are sequestered on the sea floor and bio accumulate (Kraaij et al., 2003, Pierzynski et al., 2005, Eek, 2008). Contaminants bind strongly to the sediment, thus the sediment can become a source of contaminants to the seawater and cause problems for benthic fauna, fish and humans feeding on fish and shellfish (Miljøstatus, 2011, Eek, 2008). In heavily polluted areas, marine life is clearly affected and reduced and human intake of seafood from such areas may cause health problems. With no treatment of the contamination, it may spread to new areas with sea currents. In Norway, 80 % of the population lives near the coast and the fishery industry is an important source of income (Miljøstatus, 2011).

The degree of seriousness of HOCs in the environment has not always been as obvious as today, as the picture in figure 1 shows, though today the consequences are more evident and there is an increased



Figure 1: Spraying with DDT on the beach, New York 1945
Stortingsmelding 14 (2006-2007)

understanding of the importance of a healthy environment. Today there are restrictions on discharges and treatment of harmful products implemented in national and international laws, and measures against pollution and remediation of old contamination is high on the political agenda (Miljøstatus, 2011). One strategy to improve the environment is to control the discharges, which has led to a gradual improvement of the marine environment (Eek, 2008), another is to apply remediation measures to the existing contamination. For HOC contaminated marine sediments, measures include dredging, capping, bioremediation and natural attenuation. Dredging is removing the contaminated sediments, capping is applying a layer of clean material on top of the sediments, bioremediation is microbial degradation, and natural attenuation is monitored natural sedimentation of clean material. When capping sediments, the contaminants in the sediment are made inaccessible to the water above by applying a clean layer of either active

or passive material. An active material, such as activated carbon or biochar, strongly sorbs the contaminants and is effective in a thin layer, while a passive material, such as sand, is less effective in sorbing contaminants and the main function is to physically retain the contaminants by applying a thicker layer. Passive material caps are most common on smaller areas, and active materials are more suitable for larger areas.

Capping with active materials on HOC contaminated sediment has been carried out at several sites with great success; in the Opticap project two dioxin contaminated fields were capped with activated carbon mixed with clay and the dioxin diffusion from the contaminated sediment was greatly reduced (NGI, 2009). Capping with biochar, which is also an active capping material, has not been tested before. It is expected that biochar will be an effective measure, though not as effective as activated carbon because of its structure and lack of activation process. Previous work shows that biochar sorbs HOCs well (Cao et al., 2009, Sun and Zhou, 2008), and it is already being used as a remediation method in contaminated soils (Chen and Yuan, 2011). Biochar is produced via the pyrolysis of organic materials, such as dairy manure, food waste and vegetation. The advantages of biochar are that it can be produced from waste material, thereby making use of this in the remediation of contamination and it is relatively cheap and easy to produce. In addition it stores carbon in a more stable form and thus removes carbon from the atmosphere (Roberts et al., 2010).

Capping is an important measure to improve the quality of the marine life and the water column. The improved quality may classify the sea water and sediment as much better according to Klif's classification guidelines (see appendix 1) and remove existing dietary advice.

1.1 Thesis aims, objectives and hypotheses

The main purpose of this thesis is to examine the effectiveness of biochar as a thin layer cap on a marine sediment contaminated with PAHs. The biochars were corn stover produced at 600°C, and oak produced at 250°C, 400°C, and 650°C. By using different types of biochar the importance of the source of biochar material and the production temperature is tested. PAH contaminated sediment from Bergen port represents the pollutant source. To examine the effect of capping with biochar and its ability to retain PAHs diffusing from the sediment and through the cap, diffusion experiments will be used.

The hypotheses with the biochar capping experiment are as follows:

- The biochar will bind the PAHs diffusing from the sediment, thereby reducing the flux of PAHs to the water phase above the cap
- Thin layer capping with biochar will likely be less effective compared to thin layer capping with activated carbon
- The biochar produced at the highest combustion temperature is expected to be the most efficient, as aliphatic groups are removed and the number of sorption sites increases
- The biochar caps is expected to be more effective than a pure clay cap

Also as part of the Opticap project, the effect of thin layer capping of sediments contaminated with dioxins is investigated through the field campaign in the Grenland fjords and subsequent analysis of some samples. In the Opticap project, different capping materials have been applied in order to test which is the most effective in preventing dioxins to diffuse through the cap.

2.0 Background

2.1 Persistent organic pollutants (POPs)

POPs are described as compounds that are resistant to degradation or degrade very slowly and biomagnify; meaning they concentrate upwards in the food chain and bioaccumulate in fatty tissue. Many are toxic to organisms, giving carcinogenic effects, breakdown of the immune defence and damaging fertility and DNA (Miljøstatus, 2011, Miljøverndepartementet, 2006-2007).

2.1.1 Polycyclic aromatic hydrocarbons (PAHs)

PAHs consist of two to several fused benzene rings, which are six carbon atoms linked in an aromatic circle. Three C=C double bonds exist within a benzene ring, forming a very stable chemical structure (Pierzynski et al., 2005). They form linearly, angularly or in clusters (Neff, 1979). PAHs are nonpolar and lipophilic; they prefer an organic phase over water. Chemical analyses and assessment of PAHs in the environment is usually carried out by assessing 16 of the most common and harmful PAHs based on the U.S. Environmental Protection Agency guidelines. Their chemical structures are demonstrated in figure 2, and the physicochemical properties are presented in table 1 (Fetter, 1992).

Table 1: Physicochemical properties of some PAHs (Fetter, 1992)

K_d is the solid-water distribution ratio

| PAH | Molecular weight | Solubility in water | K_d |
|----------------------|------------------|---------------------|-----------|
| | g/mol | mg/L | |
| Naphthalene | 128.16 | 31.7 | 1.300E+03 |
| Acenaphthene | 154.21 | 7.4 | 2.580E+03 |
| Acenaphthylene | 152.20 | 3.93 | 3.814E+03 |
| Fluorene | 166.20 | 1.98 | 5.835E+03 |
| Fluoranthene | 202.00 | 0.28 | 1.900E+04 |
| Phenanthrene | 178.23 | 1.29 | 2.300E+04 |
| Anthracene | 178.23 | 0.07 | 2.600E+04 |
| Pyrene | 202.26 | 0.14 | 6.300E+04 |
| Benzo(a)anthracene | 228.00 | 0.01 | 1.257E+05 |
| Benzo(a)pyrene | 252.30 | 0.004 | 2.822E+05 |
| Chrysene | 228.20 | 0.006 | 4.201E+05 |
| Benzo(b)fluoranthene | 252.00 | 0.0012 | 1.148E+06 |
| Benzo(ghi)perylene | 276.00 | 0.0003 | 1.488E+06 |
| Benzo(k)fluoranthene | 252.00 | 0.0006 | 2.021E+06 |
| Dibenz(ah)anthracene | 278.35 | 0.0025 | 1.668E+05 |

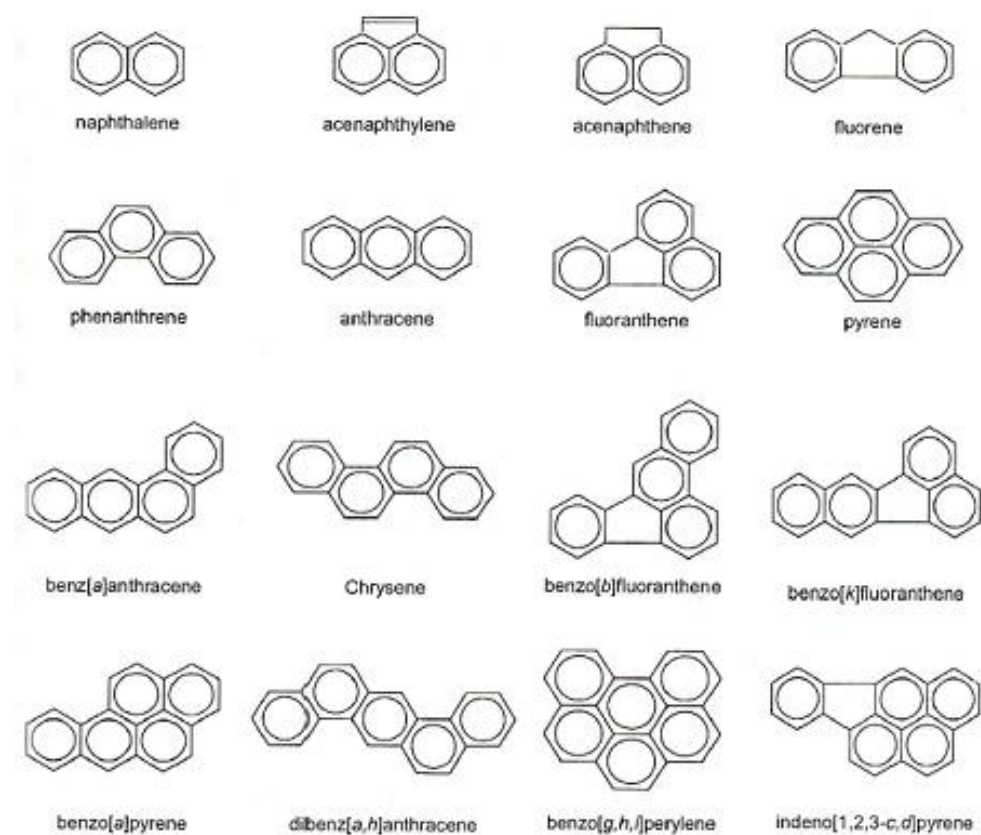


Figure 2: 16 - EPA PAHs

The molecular weight of a PAH determines its resistance to oxidation and reduction, so the largest compounds, 4-6 ring aromatics are more resistant to degradation, are more hydrophobic and are less volatile than the smaller ones. PAHs are sensitive to photo-degradation and will be more persistent in the deeper layers of a water column, as the light decreases with increasing depth. The hydrophobic characteristics of PAHs are such that they exist mostly in soil, sediment and organic matter. It is believed that the concentration of PAHs in sediments is a thousand times larger than the PAH concentration in solution (Neff, 1979), which may be explained by the large K_d values; the solid – water distribution ratio, of PAHs (Fetter, 1992).

PAHs are formed from anthropogenic and natural processes by for example incomplete combustion, where the main source is the aluminium industry and via burning of wood (Pierzynski et al., 2005, Miljøstatus, 2011). Settlement of airborne particles from industrial activity may also carry PAHs long distances, as the PAHs are contained in the particles. The emissions of PAHs were reduced by 50 % from 2005 to 2007, mainly because of modernisation of the industry (Miljøstatus, 2011).

2.1.2 Dioxins

Dioxins are benzene rings with different numbers of chlorine atoms attached, and it is the chlorine atoms that decide the different dioxin compounds and the toxicity. Dioxins are made in combustion of organic matter, with limited access to oxygen and the presence of chlorine. The temperature interval is between 300 and 500°C, at higher temperatures the compounds are destructed (NGU, 2008). In the environment 210 different dioxin compounds exist, though only 17 of these are harmful. Dioxins are measured by their toxicity factor, and their toxicity is compared to the most harmful dioxin, TCDD, which stands for 2,3,7,8 – tetrachlorodibenzodioxin (see figure 3). The sum of dioxins in a sample is expressed as toxic equivalents (TEQ) (Folkehelseinstituttet, 2008), and is calculated by multiplying the concentration of the dioxin compound by its TEQ factor, as shown in table 2.

Table 2: Dioxin compounds and toxic equivalent factor (TEQ)

| TEQ factor | Dioxin |
|------------|---------------------|
| 1 | 2,3,7,8-TCDD |
| 0,5 | 1,2,3,7,8-PeCDD |
| 0,1 | 1,2,3,4,7,8-HxCDD |
| 0,1 | 1,2,3,6,7,8-HxCDD |
| 0,1 | 1,2,3,7,8,9-HxCDD |
| 0,01 | 1,2,3,4,6,7,8-HpCDD |
| 0,001 | OCDD |
| 0,1 | 2,3,7,8-TCDF |
| 0,05 | 1,2,3,7,8-PeCDF |
| 0,5 | 2,3,4,7,8-PeCDF |
| 0,1 | 1,2,3,4,7,8-HxCDF |
| 0,1 | 1,2,3,6,7,8-HxCDF |
| 0,1 | 1,2,3,7,8,9-HxCDF |
| 0,1 | 2,3,4,6,7,8-HxCDF |
| 0,01 | 1,2,3,4,6,7,8-HpCDF |
| 0,01 | 1,2,3,4,7,8,9-HpCDF |
| 0,001 | OCDF |

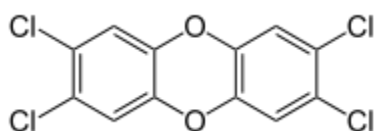


Figure 3: Structure of tetrachlorodibenzodioxin

From 1995 to 2008, dioxin emissions from all sources were reduced by 68 %, due to closing in a lot of industrial companies (Miljøstatus, 2011). In 2005, the largest dioxin source was the industry, and during the past years the most important sources have been wood burning in private homes and the boat and shipping traffic.

2.2 National environmental goals and the situation of today

Emissions over a long period of time have resulted in high concentrations of contaminants in several Norwegian fjords. Between 1993 and 1996 an investigation on environmental contaminants in sediments in Norwegian fjords revealed that around 90 locations of 120 were strongly contaminated with one or several contaminants (Miljøstatus, 2011). 17 locations have been prioritised by the Norwegian Climate and Pollution Agency, Klif, (see figure 4 for which locations) and will undergo further investigation and remediation. The Norwegian government's national environmental goal is to stop or significantly reduce prioritised pollutants. On the list of prioritised pollutants are amongst others PAHs and dioxins, which have both been reduced significantly from 1995 to 2008. Emissions and use of chemicals that are dangerous to health and the environment should be continuously reduced until prohibited in 2020. The goal for sediment in Norwegian fjords is that sediment polluted with contaminants that pose a danger to human health or the environment should not pose a risk for serious contamination. By 2015 remediation of the prioritised 17 locations should be carried out where possible, and the sources of contamination be under control (Miljøstatus, 2011).



Figure 4: The prioritised Norwegian fjord locations

Contamination in Norwegian fjords poses a larger risk than elsewhere in the world, as Norwegian fjords are generally characterized by being deep with a sill in the fjord opening, making the fjords more resistant to water exchange. This way, contaminants from industry and harbours may settle on the sea bed with little transport with the currents (Miljøstatus, 2011).

The use and emission of HOCs have been reduced significantly over the past decades, as a result of new guidelines on treatment of environmentally dangerous compounds, restrictions on emissions from industry, certain components have been banned from use and taken off the market, modernization of industrial processes and improved waste treatment.

2.3 Remediation of contaminated sediments

There are many measures to improve the aquatic state in the marine environment, but the most effective ones are thick layer capping, thin layer capping and dredging. Natural attenuation, sedimentation of natural organic matter (NOM), takes a long time in the seas, as a lot of the NOM is degraded before it reaches the sea floor. The sedimentation rate in many areas receiving contaminants has been estimated at a few mm per year; with the consequence that the concentration of contaminant's peaks lies within the upper 5-20 cm (Eek, 2008).

Dredging contaminated sediments means removing the material that is contaminated until clean sediment remains. The sediment removed needs to be stored in a landfill or isolated on the sea floor in a disposal site (Myrvoll et al., 2002), such a remediation method has been successfully carried out at Malmøykalven in the project "Clean Oslo fjord". The project was commenced in 2006 and contaminated sediments in Bjørvika and Pipervika, inner Oslo fjord, were first dredged and 95-99% of the contaminated sediment was removed, before a layer of clean sand was laid on top of the dredged sediment. In the remediated area, renewed marine life has appeared and the sea bed is the cleanest in a hundred years. The dredged material was isolated at 66 m depth at Malmøykalven, by a 40 cm thick layer of crushed gneiss (Oslo kommune., 2011). The dredging activity may cause sediment particles to spread over a wider area (Myrvoll et al., 2002), though applying a cap and combining dredging with capping will prevent the spread of contaminants (Oslo kommune., 2011). Dredging can also be negative because it can destroy natural habitats of the organisms in the area, and it can be very expensive.

Capping contaminated sediments involves isolating the sediments with a layer of clean material in order to reduce contaminant flux and release to the water column (Jacobs and Förstner, 1999, Palermo et al., 1998). Capping is an effective measure that lasts for a long time, but the sources of contamination need to be under control or cease to exist before capping is considered (Myrvoll et al., 2002). A cap protects against erosion and isolates the benthic organisms living in the sediments from the contaminated sediments. This is one of the most important physical functions of a cap (Eek et al., 2008, Palermo et al., 1998), while the most important physicochemical function of a cap is the reduction of the flux of contaminants from the sediment. The contaminants move from the sediment particles into the sediment pore water, then into the cap where they sorb to the cap material. When the contaminants in the pore water in the cap and the contaminants bound to the cap are in equilibrium, the cap is in a steady state (Eek et al., 2008), until further diffusion of contaminants from the sediment takes place. The sorption capacity of the capping material dictates the retention time of contaminants in the cap.

Capping increases the diffusion distance of the contaminants (as demonstrated in figure 7, section 2.4.2), which means that the contaminants have to travel further to get to the aqueous phase, they use longer time to diffuse, and depending on the material, they may sorb to the cap. The concerns with thin layer capping are bioturbation through the cap, which might cause the contaminated sediment to mix with the cap, or water transport in parts of the cap due to bioturbation, and uneven distribution of the cap, giving a smaller total thickness and reducing the effect in those areas (Eek et al., 2011).

The thickness of the cap is determined by factors such as benthic activity at the site, currents and wave activity, potential for consolidation, and the physicochemical properties of the sediment, cap and contaminants. The location is also important when determining the thickness of the cap; boat activity and anchoring, and the sea floor's structure (uneven sea floor may cause an uneven layer when capping in thin layers) can affect this decision (Palermo et al., 1998, Myrvoll et al., 2002). A reasonable capping thickness was estimated to 15-20 cm by Palermo et al. (1998), while Myrvoll et al. (2002) claim 30 cm is a good thickness for keeping the contaminant flux within acceptable limits and preventing benthic organisms interfering with the contaminated sediment. With an active cap, the thickness may be reduced, as the active material increases the efficiency of the cap by sorbing the contaminants.

Remediating contaminated sediments has mainly been concentrated to city and industry ports. One of the most extensive capping projects in Norway was the capping of 90 000 m² heavily metal contaminated sediment in Eitrheimsvågen, Odda, 1992. The sediments were capped with geotextile and 30 cm of sand. Another experience with capping in Norway is the capping in the bay of Hannevika, Kristiansand, 1998. This was mostly industrial waste contamination and the purpose of the project was to test the ability to cap soft sediment with a layer of sand. Internationally capping of contaminated sediments has been done in several ports, and one of the most extensive projects was in the Eagle Harbour, USA, 1993. An area of 216 500 m² sediment was capped with a 100 cm thick sandy material (Myrvoll et al., 2002).

2.3.1 Passive material capping

Passive materials used in capping include amongst others crushed limestone, crushed gneiss, sand, and silt. These materials are easily available and often relatively cheap (Eek et al., 2008), and work by retaining contaminants physically by isolating the sediments from the overlying water. Often such caps are several centimetres thick.

Capping sediments with a mineral cap has shown positive results. Eek et al (2008) tested a 1 cm cap of crushed gneiss and crushed limestone on PAH and PCB contaminated sediments from Oslo harbour, respectively. The aim was to compare diffusion of 15 PAHs and 7 PCBs from capped and uncapped sediments. Compared to the sediments not capped, the flux from the capped sediments was 3.5 – 7.3% of the flux from the uncapped sediments over a period of 410 days. The flux of PAHs from uncapped sediment was 3.8µg/m/d, while the flux of PCBs from uncapped sediment was 0.010µg/m/d. The time to breakthrough of pyrene through the gneiss and the limestone cap was 22 days and 110 days respectively.

2.3.2 Active material capping

Active materials are materials that sorb the contaminants, thereby making the contaminants unavailable. Active materials include activated carbon and zeolite minerals (Jacobs and Förstner, 1999).

A study by Zimmerman et al. (2004) showed that sediment treated with 3.4 wt % activated carbon reduced aqueous equilibrium PCB and PAH concentrations by 92 % and 84 %, and

SPMD concentrations of PCB and PAH by 77% and 83%. The authors conclude that adding activated carbon to HOC contaminated sediment could be an effective in-situ, non-removal method.

2.3.3 Biochar

Biochar is produced by incomplete combustion of carbon-rich biomass (Cao et al., 2009). Combustion temperature has a significant impact on the physicochemical properties of the biochar. Higher combustion temperatures provide larger surface areas; a study with different production temperatures of pine needle produced biochars showed at temperatures of 400°C the surface area was 112.4m²/g, and as temperature increased, aliphatic alkyl, esters and other similar groups were removed (Chen et al., 2008). This is supported by other studies; Chun et al. (2004) found that wheat residue biochar produced at 500-700°C had a surface area > 300m²/g and that biochars produced at low temperatures (300-400°C) were not fully carbonized, and had a surface area <200m²/g, 40-50% organic carbon, and >20% oxygen. Compared to activated carbon surface areas and total pore volumes, biochars are lower, which is explained by the activating process of the activated carbon, creating a more porous material (Chen et al., 2008, Yang and Sheng, 2003, Chun et al., 2004). According to Chun et al. (2004) surface areas and porosity of activated carbon is 15-56 times that of biochar.

Increasing combustion temperature reduces volatile matter and increases the inorganic content (ash, black carbon (BC)) (Mukherjee et al., 2011). Biochar produced at low temperatures (250°C and 400°C) had limited surface nanopores and mostly micropores, while in biochar produced at a higher temperature, up to 44% of the biochar's surface was dominated by nanopores. The surface of biochar is contained within acidic functional groups (AFG), which are amongst other carboxylic acids and phenolic acids. Increasing temperature reduced AFG, but there were no differences of relevance of AFG between the different types of biochar, and thus temperature seems to have a big impact on the characteristics of biochar.

One concern with biochar is that it might break down in the environment over a short period of time. Activated carbon has proved to be very resistant to microbial degradation, and one prominent reason is the well-structured carbon matrix. Biochar is quite similar to activated carbon, and is anticipated to attain good resistance to microbial degradation as well (Yang and Sheng, 2003). During a year study of CO₂ release from different produced biochars, Zimmerman

(2010) found that degradation of biochar is related to combustion temperature, grain size and the conditions; biochar produced at low temperature (250°C) and fine grain size was the most labile, while biochar produced at high temperature (650°C) and coarse grain size was the most resistant to degradation. Under abiotic conditions the carbon release from the biochar constituted 50-90% that of biochar under microbial conditions.

2.3.4 Opticap

In 2009 the project Opticap was commenced as a co-operation between the Norwegian Geotechnical Institute (NGI), the Norwegian Institute for water research (NIVA) and the companies Secora, Agder Marine, NOAH and Hustadmarmor, with the agenda to increase knowledge about materials and methods for thin layer capping to reduce the spread of contamination from contaminated sediments. The secondary goals were 1) gaining more knowledge on the physical properties of the capping materials that are of importance for the result when applying to the sea bed from boat, 2) the effect of thin layer capping on the environmental status of the sediment and the water phase above the sediment, and 3) secondary negative effects of thin layer capping on benthic fauna and the ecosystem within the affected area (Eek et al., 2011, NGI, 2009).

The project was conducted in the Grenlandfjords; Ormerfjorden and Eidangerfjorden, near Porsgrunn (see figure 5). These fjords are contaminated with dioxins and the areas contaminated are quite vast in area (70 000 m²), therefore it was decided to use thin layer capping as a more cost-effective measure than thick layer. In the project there were four fields in the Ormerfjord, each with different capping material, in the Eidangerfjord there were two fields, and with one reference field for each fjord. The field in the Eidangerfjord was the largest, with 40 000 m² at 100 metres depth, and was capped with an approximately 5 cm thick layer of pure marine clay mixed with activated carbon. The fields in the Ormerfjord, at 10 000 m² each and at 30 metres depth, were capped with an approximately 5 cm thick layer of respectively pure clay mixed with activated carbon, pure clay, and crushed limestone. The fields are shown in appendix 2.



Figure 5: The Grenland fjords. The shaded areas are areas with dietary restrictions



Figure 6: Securing the flux chambers with rope before placement on the sea bed

2.4 Factors influencing contaminant release through a cap

When the traditional sources of contamination are gone, the places that accumulated the pollution, such as the sediment, may become a source of contamination to the water phase, depending on the conditions and type of contamination (Miljøstatus, 2011). Factors that influence contaminant release from the sediment are mainly bioturbation, molecular diffusion, advection and sorption (Palermo et al., 1998), but physical disturbances such as waves, currents and boats also contribute (Miljøstatus, 2011). These factors are important to consider when deciding thickness and material of a capping layer.

2.4.1 Bioturbation

Bioturbation is considered the largest contributor of chemical release from the sediments and the pore water to the water column (Thibodeaux and Bierman, 2003). Benthic organisms inhabit the upper layer of the sediments, down to 60 cm depth, and mix the sediment so that old contaminated sediment is mixed with freshly settled particles, thereby keeping the old

contaminants in circulation and available to both the benthic organisms and fish feeding on the sediment, as well as to the overlying water (Palermo et al., 1998, Eek, 2008). As bioturbation occurs in the top cm of the surface, which is also where the cap would be, this influences a cap's efficiency. Even though the contaminated area might not be heavily contaminated, the concern is that the contaminants biomagnificate from the benthic organisms to the fish at the top of the food chain, causing health concerns for humans by intake of such sea food.

2.4.2 Molecular diffusion

Molecular diffusion also contributes to release of contaminants to the pore water. Diffusion occurs in areas with a concentration gradient, meaning from high concentration zones to lower concentration zones; in a case where a cap is applied to a contaminated sediment from the sediment pore water to the sea water.

The diffusion can be estimated by Fick's first law (Schwarzenbach et al., 2003):

$$F = -D \frac{\partial C}{\partial x} \quad (1)$$

Where F is the diffusion flux per unit area and time ($\text{ng}/\text{cm}^2\text{s}^{-1}$), D is the molecular diffusion coefficient (cm^2/s), and $\frac{\partial C}{\partial x}$ is the concentration gradient (ng/cm^3).

Between the sediment and the water phase there is a thin film of stagnant water; the diffusive boundary layer (DBL). Depending on the flow velocity of the water and the surface of the sediment the thickness of the DBL varies from 0,2mm to > 1mm (Jorgensen and Revsbech, 1985), and limits diffusion to an extent (Eek, 2008).

Figure 7 describes the HOC concentration profile in capped and non capped sediment when assuming steady state molecular diffusion (Eek et al., 2008). The DBL exists between the sediment or cap and the water phase, and between the water phase and here, the cyclohexane phase. The cyclohexane is the organic phase that acts as a sink for contaminants diffusing from the sediment, in the same way that heptane, hexane and tenax could. The DBL delays diffusion from the sediment and can be correlated to Fick's law.

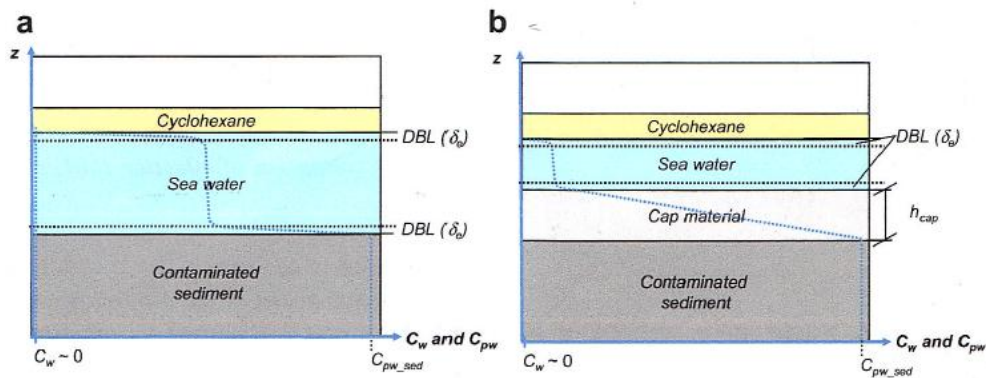


Figure 7: HOC concentration profile assuming steady state molecular diffusion in a system with a) uncapped sediment and b) capped sediment. The sink for diffusive PAHs is the cyclohexane phase. (Eek et al., 2008)

2.4.3 Advection

Advection refers to upwards transport of pore water within a medium (sediment or cap). It is enhanced by several factors. Consolidation occurs when sediments are capped, causing pressure to the sediment as a consequence of the weight of the above lying material, and vertical stress (Eek et al., 2007). Consolidation can also happen to the cap, which is important to take into consideration when deciding thickness (Palermo et al., 1998). Submarine ground water discharge is another mechanism that causes advection; ground water sieving through the sediment will affect the cap and the release of contaminants (Eek et al., 2007). Gases such as methane and carbon dioxide produced by microbial degradation in the sediment, may dissolve in the pore water and with oversaturation be discharged as gas bubbles through the sediment (Kesteren and Kessel, 2002). The formation of gas bubble nucleation occurs when the gas is not transported by convective or diffusive transport, and with increasing formation it may cause cracks to the sediment and allow the pore water and gas bubbles to be released. This may affect a cap in terms of physical disturbance and allow release of contaminated pore water through the cracks in the sediment and cap to the water column.

Advection may transport contaminants from the sediment, though this is dependent on the solubility of the contaminants in the pore water, sorption to the sediment or within the cap, and the order of magnitude of advection (Eek et al., 2007).

2.5 Sorption of contaminants

Hydrophobic and nonpolar compounds preferentially associate with nonpolar environments, such as organic matter, soils, and sediments. The strong sorption between the compounds and these phases is termed hydrophobic sorption (Pierzynski et al., 2005, Stumm and Morgan, 1996).

Sorption can be in the form of adsorption, absorption, and partitioning and describes a material's ability to retain certain compounds (Pierzynski et al., 2005). Sorption of nonpolar organic compounds to colloidal organic material (humic colloids) and amorphous organic matter (AOM) occurs as absorption (Cornelissen et al., 2005, Stumm and Morgan, 1996). To AOM and clay minerals it may also occur as ligand exchange (chemisorption), water bridging, hydrogen bonding, partitioning or ion exchange. Ion exchange is when a sorbate (the contaminant) has a different charge than the sorbent (the organic material). This binding is pH dependent, as the charge of the metal oxides and organic material will differ from positive at low pH to neutral or positive at high pH (Pierzynski et al., 2005), the charge of the clay minerals is permanent. Sorption to carbonaceous geosorbents (CG) is characterized by adsorption.

Sediments contain organic matter, carbonaceous material, and clay, making the sediment a sorption site for contaminants, both inorganic and organic (Pierzynski et al., 2005).

2.5.1 Carbonaceous geosorbents

Carbonaceous geosorbents are also referred to as black carbons (BC), and include soot, kerogen, coal, and ash (Johnson et al., 2001, Cornelissen et al., 2004). BC constitutes around 9% of the total organic carbon fraction in sediments (Cornelissen et al., 2005, Jonker and Koelmans, 2002b). Sorption of organic compounds to CG occurs as nonlinear adsorption and compared to absorption to AOM is 10-1000 times stronger. CG is porous, with several internal and external surface sites, occlusion sites and nanopores. This is where the adsorption occurs, and is demonstrated in figure 8. The figure demonstrates the processes involved with the sorption to BC and AOM. For planar PAHs, their shape allows them to fit into narrow pores or interlayer spacings in soot and soot-like materials (Jonker and Koelmans, 2002b, Cornelissen et al., 2004). The nonplanar compounds might, due to their size, not be able to fit into the smaller nanopores. These compounds can bind to surface sites, though as this increases the distance between the compound and the sorbent the dispersive electronic interactions are weakened. Cornelissen et al.

(2004) discovered the nanoporosity of environmental black carbon varied in size from <4 to 10 Å. The same study also revealed nanopore surface area was near 58m²/g for sediment black carbon.

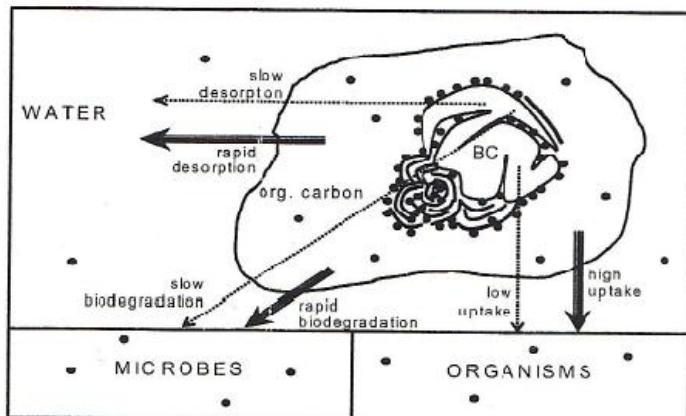


Figure 8: Sorption of HOC to AOM and BC

Also, other contaminants or organic matter may compete for the sorption sites, thereby reducing sorption capacity of target compounds (Cornelissen et al., 2004, Chen et al., 2008, Hale et al., 2009). NOM may cause pore blockage of the char in the short term, though over time the target compound will diffuse through the organic material and reach the sorption sites (Hale et al., 2009).

2.5.2 Sorption isotherms

Adsorption of a compound can be described with a sorption isotherm, which represents the amount of material bound at the surface as a function of the material present in the aqueous phase at equilibrium of a constant temperature (Stumm and Morgan, 1996). The two simplest isotherms are the Langmuir and the Freundlich isotherms.

Langmuir often refers to chemisorption; a molecule is bound to a surface by covalent or short-range electrostatic bonds, and is based on the principle that the adsorption sites on the surface of a solid become saturated by adsorbate from the solution (Pierzynski et al., 2005, McBride, 1994).

The equation can be describes as follows (equation 2):

$$\Gamma = \Gamma_{\max} (K_{\text{ads}} [A] / 1 + K_{\text{ads}} [A]) \quad (2)$$

Where Γ is the relationship between the adsorbate on the surface sites and the mass adsorbent, Γ_{\max} is adsorption capacity, K_{ads} is the equilibrium constant, and A is the adsorbate in solution (McBride, 1994).

The Freundlich isotherm applies to nonlinear sorption of solids with heterogenous surface properties. The equation can be described as follows (3):

$$C_s = K_f * C_w^n \quad (3)$$

Where C_s is the quantity of sorbate associated with the sorbent ($\text{mol} \cdot \text{kg}^{-1}$), C_w is the total concentration of the sorbate in solution ($\text{mol} \cdot \text{L}^{-1}$), K_f is the Freundlich constant, and n is the measure of the nonlinearity involved (Stumm and Morgan, 1996, Schwarzenbach et al., 1993).

There are different Freundlich isotherms, depending on the n value, see figure 9.

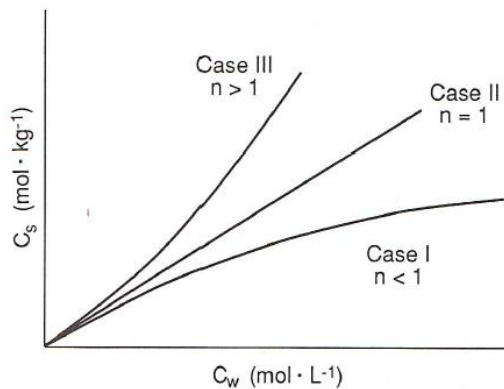


Figure 9: Freundlich sorption isotherms

If $n < 1$, the sorbent (here biochar) becomes saturated with sorbate (here PAHs) as the concentrations of sorbate increases. Further sorption may for instance be difficult as the specific binding sites become occupied. A situation where sorbed molecules change the sorbent surface into increasing further sorption is a situation where $n > 1$. When $n = 1$ the isotherm is linear and the sorption process is not dependent on the quantity of the sorbate (Schwarzenbach et al., 1993).

3.0 Methodology: PAH contaminated sediment and thin layer capping with biochar

The main experiment seeks to test the effectiveness of thin layer capping with biochar on sediment contaminated with PAHs. The laboratory diffusion experiment is set up according to previous capping experiments (Eek, 2008, Nag, 2008), and the experiments are set up in order to answer the hypotheses in section 1.1.

3.1 Method development of the diffusion experiment

Prior to the final experimental set up different methods were tested in order to find the most optimal diffusion experiment set up.

The consistency of the clay needed to be smooth enough to apply to an even layer on top of the sediment, or it would lump and be difficult to work with, as shown in figure 10. In order to allow an even clay layer to be applied, sea water was added to the clay and diluting it in the ratio clay : sea water 2:1.



Figure 10: Too thick clay caused lumps and unevenness

The sediment was applied with a syringe, which worked well, but the same method with the clay caused spilling on the inside glass wall of the jar. It was easier to add the clay and even it out with a spoon. Adding the cap using a syringe and applying the cap in the water phase above the sediment, with the intention of allowing the cap to settle naturally was tested. This method could

not be applied because the settling of the particles took several days and the biochar was separated from the clay to lie on top of the water surface. Also the cap did not distribute very evenly. Adding the capping material with a syringe caused parts of the cap to stick inside the syringe and at many occasions splash out of the syringe, leaving the glass wall inside the jar contaminated, and for this reason was not used as an application method.

The capping material was added to the jars with a spoon and evened out. The height of the cap was set at 1 cm, though it was expected that it would sink due to consolidation. When applying the cap, some material was lost as it would stick to the equipment. This might have reduced the mass to some extent and the capping height was in some cases not completely 1 cm.

The difficulties with the biochar were making it sink and remain settled on top of the sediment when the sea water was applied. Because of the low density and high porosity it needed to be made heavier, which may be done by adding salt. Mixing the biochar in a thick mixture of water and salt was considered, but that would make it difficult to mix it with the clay into the correct proportions and also add another factor to the advection of contaminated pore water. The method used was to mix the biochar with the diluted clay and let it stand overnight.

3.2 Material description

In the diffusion experiment, sediment collected from Bergen (142.8 g) was used within all the different jars. The sediment was collected from Vågen, which is a part of “Byfjorden” in the centre of Bergen (BT, 2011). Decades with large amounts of industrial activity related to the harbour and the city, as well as airborne contribution, have resulted in sediments classified as heavily polluted with POPs. It is presumed that the polluted sediments have contributed to the restrictions on consuming fish and seafood from many of the fjords around Bergen (Kryvi et al., 2011).

The sediment used in the experiments was from one 10 litre batch collected from a 100 litre container full of sediment. The sediment was six years old and has been stored in a cooling room (4°C) at the NGI since it was first collected. It has been used by others in previous experiments and may have undergone some degradation due to the exposure to air and the time it has been stored for.

The four different caps consisted marine clay (51.6 g) mixed with 5 % (2.58 g) of respectively corn stover biochar and oak biochar produced at 250°C, 400°C and 650°C, the biochars will be referred to as corn stover, oak 250, oak 400, and oak 650.

The corn stover biochar was produced by BEST Energies, USA, under slow pyrolysis with an N₂ atmosphere at 600°C, with no further treatment. The material was predried and charred for between 80 and 90 minutes, and the final temperature was held for 20 minutes. The oak biochars were produced by Andy Zimmerman at the University of Florida, according to the method described in Zimmerman (2010). The biochars were produced from Laurel oak (*Quercus laurifolia*). The oak 250 biochar was produced under full atmosphere, while the oak 400 and 650 biochars were pyrolysed under N₂.

The clay was collected from the tunnel underneath the Oslo fjord and was free of contamination, due to the unexposed position. Since collected it has been stored in a 100 litre container in the cooling room at the NGI. It has been used by others in experiments and thereby in short periods been exposed to air.

In all the diffusion jars sea water from NIVAs research station at Solbergstrand, from 90 metres depth, was used.

Heptane (C₇H₁₆, Merck, purity GC > 99.3%) was used as a sink for the PAHs diffusing from the sediment and through the cap. The PAHs are hydrophobic and will therefore enter the organic phase, the heptane, meaning the water phase contains a negligible amount of PAHs. For the first time point tenax was used as a sink for diffusing PAHs in the diffusion jars with sediment and no cap, to compare the effectiveness as a sink. Tenax is a porous polymer with a very strong sorption capacity for organic compounds. It is 2,6-diphenyl-*p*-phenylene oxide and when added to water floats (Cornelissen et al., 1997).

The physical/ chemical properties of the materials employed in the diffusion set up are described in table 3 and 4. These properties were used to calculate thickness of a 1 cm cap, the 5% biochar mass and to check advection.

Table 3: Properties of materials in the diffusion experiment.

| | Density (g/cm ³) | Water content (%) | Conductivity (mS/cm) |
|------------------|------------------------------|-------------------|----------------------|
| Sediment | 1.18 | 69 | 45.2 |
| Clay | 1.34 | 30 | 51.8 |
| Sea water | 0.94 | - | 51.9 |

Table 4 describes the physic-chemical properties of the biochars employed in the diffusion experiment. The sum of the percentage of carbon, oxygen, hydrogen, and nitrogen should constitute 100 %. Therefore the percentage of carbon, nitrogen and hydrogen were measured for the oak biochars, and the percentage of oxygen calculated as the difference. For the corn stover biochar, all parameters were measured, and it is clear a 100 % mass balance it not reached. This may be due to a high percent of ash.

Table 4: Physico-chemical properties of the biochars

| Material | C % | O % | H % | N % | pH | Micropore surface area $\text{m}^2 \text{g}^{-1}$ |
|-----------------------|------|------|------|-----|-----|---|
| Cornstover biochar | 41.6 | 8.1 | 1.5 | 0.4 | 9.9 | 178 (measured with N_2) |
| Oak 250 | 62.6 | 34.1 | 0.19 | 3.1 | 3.5 | 1 (measured with N_2) and 331 (measured with CO_2) |
| Oak 400 | 67.9 | 27.5 | 0.37 | 4.2 | 6.7 | 2 (measured with N_2) and 252 (measured with CO_2) |
| Oak 650 | 75.4 | 21.3 | 0.46 | 2.8 | 9.1 | 225 (measured with N_2) and 528 (measured with CO_2) |

The density of the oak 250 biochar was 1.34 g/cm^3 and 1.50 g/cm^3 for the oak 650 biochar (personal communication Andy Zimmerman). Some of the particles would float and some particles would sink, which made it difficult to measure the density.

Polyoxymethylene (POM) with $55 \mu\text{m}$ thickness (see figure 11), was used as a passive sink for PAHs in equilibrium. The POM arrives as a thick rod from CS Hyde Company, USA, and before use it is cut into strips using a laith and then cleaned. The cleaning process was done in several steps; first POM was shaken over night in methanol, then in heptane, and lastly in deionized water. The POM was rinsed in deionized water five times before being stored in a glass container with deionized water. Before used the POM was dried with a tissue and cut to the correct mass.



Figure 11: POM-55

3.3 Diffusion experiment set up

The diffusion experiment was carried out according to figure 12, using sediment capped with clay mixed with 5% biochar (SC1-4), sediment capped with clay (SCC) only, and sediment with no cap (SNC). The SNC and SCC were set up as reference points and to compare effectiveness between the clay cap and the clay mixed with biochar cap. The set up was done in triplicates in glass jars. Measurements of PAHs diffusing from the sediment were done at five different time points, one time point for the jars with tenax.

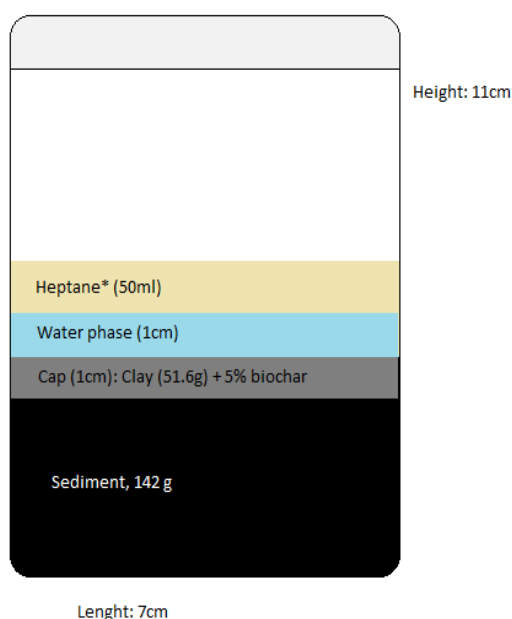


Figure 12: Diffusion set up

*At time 3 and 4 hexane (C_6H_{14}) was substituted for heptane
For diffusion jars with no cap, 1.5cm water phase was applied.

The sediment batch collected was homogenized with a drill for approximately 15 minutes, during which time hydrogen sulfide (H_2S) was released from the sediment, implying degradation processes and anoxic conditions.

In all jars, 142.8 g of sediment was carefully added with a 100 ml syringe, making sure that no sediment would spill on the walls inside the jar. If so, these jars were reset to avoid any contamination and heterogeneity between the jars. The sediment top was evened out by carefully shaking the jar by hand on the bench and remaining uneven areas were smoothed out with a plastic spoon.

Before mixing the biochar with the clay, the biochar was crushed in a mortar and sieved through a 500 μm sieve. It was not expected that crushing the biochar would change the physicochemical properties of the biochar. To create a 1 cm high cap, the mass of the cap was found based on the volume of a 1 cm high cap (equation 4) and the density of the clay (equation 5). The capping material was thereby made by mixing 5% of biochar (2.58 g) with 51.6 grams of clay.

$$V = \pi r^2 h \quad (4)$$

Where V is the volume (ml), r is the radius of the jar and h is the height (cm) of the cap. With a radius of 3.5 cm, the cap had a volume of 38.48 cm^3 .

$$m = \rho * V \quad (5)$$

where m is the mass of the diluted clay (g, without biochar) and ρ is the density (g/cm^3) of the diluted clay.

After the cap was added, sea water was added on top of the uncapped sediment and the cap with a 50ml syringe, holding the tip against the glass wall and carefully adding the water avoiding any disturbance to the cap or sediment. When adding the sea water a thin film of fine particles was made. To avoid any direct contact between these particles and the heptane layer, sea water was added until the film ran off and then the water was removed by a syringe until 1cm for the batches with a cap and 1.5 cm for the batches with just sediment remained.

Differences in pore water density in the layers may cause advection of pore water between the layers, which happens when the conductivity in the above layer is lower than the below layer (Eek, 2008). Conductivity of the sediment and the clay was measured on centrifuged mass with a 712 Conductometer Metrohm. As the differences between the layers were small and there was a higher conductivity in the above layer, no correction was made.

Finally, 50 ml of heptane was added by carefully pouring in on top of a plastic spoon held to the inside of the glass wall to minimize disturbance to the cap or sediment.

Measuring the PAHs diffusing from the sediment was done by removing the heptane after 17, 25, 35, 60, and 101 days. New heptane was added after removal and measurements continued in the same system, to exclude errors in the possible sediment heterogeneity.

The heptane samples were spiked with a recovery standard (20 µl, PAH mix: d₈-Naphthalene, d₁₀-Phenanthrene, d₁₀-Pyrene, d₁₂-Benz(a)anthracene, d₁₂-Benzo(ghi)perylene), cleaned in silica gel clean up (described in section 3.4.1) and analysed in the GC-MS (described in section 3.4.2). Then the results could be analysed.

3.3.1 Comparison between heptane and tenax as infinite sinks for PAHs

For three jars with sediment and no cap, tenax (1g, Alltech) was used as an infinite sink for PAHs diffusing from the sediment to compare with heptane, see figure 13. Prior to application the tenax was rinsed with heptane and acetone according to the method by Cornelissen et al. (1997).

At the first time measurement (at 17 days) the tenax was removed and extracted twice in a solution of acetone (20ml) and heptane (20ml) for 24 hours (figure 13). NaSO₄ was added to remove the water from the solvent, and a recovery standard (20µl, PAH mix) was added before the solvent was reduced to 1ml, cleaned up using a silica gel column and analyzed via the CG-MS.



Figure 13: Tenax extraction (left) and tenax as an infinite sink (right).

Comparison of heptane and tenax as infinite sinks for PAHs is presented in table 5. The results show that heptane was the most effective infinite sink.

Table 5: Comparison of heptane and tenax as infinite sinks for diffusing PAHs. The numbers in bold mean that the highest concentration of PAH compound was measured at the represented infinite sink. n.d: not detected; the concentration of the compound was under the detection limit. * Measured concentration for one of three replicates only

| PAH | Tenax | | Heptane | |
|----------------|---------------|--------------------|---------------|--------------------|
| | ng/g | Standard deviation | ng/g | Standard deviation |
| Naphthalene | 0.0295 | 0.0082 | 0.0819 | 0.0179 |
| Acenaphthylene | 0.0333 | * | 0.0059 | 0.0000 |
| Acenaphthene | n.d | * | 0.0590 | 0.0257 |
| Fluorene | 0.0046 | * | 0.0814 | 0.0333 |
| Phenanthrene | 0.0112 | 0.0019 | 0.2358 | 0.1130 |
| Fluorantene | 0.0078 | 0.0014 | 0.0468 | 0.0196 |
| Pyrene | 0.0749 | 0.0109 | 0.1417 | 0.0397 |
| Benzo(a)pyrene | 0.0046 | * | n.d | * |

In the diffusion jars, the tenax, which consist of small, fine beads, lie on top of each other and in contact with the water phase. The tenax that is not in contact with the water phase will most likely not contribute that much in the sorption of PAHs. Also, the air between the tenax beads makes sorption more difficult (personal communication Gerard Cornelissen). The reason for testing tenax as an infinite sink was because of the concern that heptane might solve in the water and increase the solubility of PAHs in the water phase. Eek et al. (2008) used cyclohexane in the diffusion experiments. The solubility of cyclohexane in water is 57 mg/l (0.007 %) at 25°C and the effect of cyclohexane dissolved in water on the solubility of PAHs in water occurs only when the concentration of cyclohexane > 1%. McAuliffe (1966) found the solubility of *n*-heptane in water was 2.93 ± 0.20 mg/l water, and the solubility of *n*-hexane in water was 9.5 ± 1.3 mg/l water, at 25°C. Other literature describe heptane as insoluble in water (ScienceLab.com, 2005, Gadiv Petrochemical Industries Ltd., 2011). K_{hw} (*n*-hexane – water partition constant) for *n*-hexane is 52,000 ($\text{mol} \cdot \text{L hexane}^{-1} / \text{mol} \cdot \text{L water}^{-1}$) at 25°C (Schwarzenbach et al., 2003). The small solubility of heptane and hexane is unlikely to contribute to increased solubility of the PAHs accumulated in the organic phase.

Previous studies show that the method that was used is sufficient (Cornelissen et al., 2001). The comparison was done in triplicate, but only for one time point, and may benefit from being investigated further.

3.3.2 Quantification of evaporation of heptane and hexane

The evaporation of heptane and hexane in the diffusion jars was quantified in order to check loss during each measurement. Jars with respectively 50 ml heptane and hexane were measured over a period of days and the percentage loss calculated.

The time measurements were carried out by removing the heptane and replacing it with new 50 ml at each day of measurement. During the time periods between each measurement the percentage of heptane and hexane evaporated from the jar would be according to table 6.

Table 6: Heptane and hexane evaporation in %

| Days | Heptane (%) | Hexane (%) |
|------|-------------|------------|
| 17 | 1.2 | 1.4 |
| 25 | 0.5 | 0.7 |
| 35 | 0.6 | 0.9 |
| 60 | 1.6 | 2.1 |
| 101 | 2.6 | 3.5 |

Heptane evaporation from the diffusion set was measured at approximately 0.064% per day, and hexane evaporation was measured at approximately 0.085% per day. Losses of heptane and hexane were minimal, as can be seen by the results. Hexane was expected to evaporate to a larger extent than heptane, due to the chemical structure and molecular mass (hexane's molecular mass is 86.18 g mol^{-1} , heptane's molecular mass is $100.21 \text{ g mol}^{-1}$).

3.3.4 Recovery of the spiked standard

A recovery standard was added to all samples to check the loss of sample, due to processes such as evaporation or spilling.

The diffusion time measurements, soxhlet and freely dissolved PAH concentrations in the sediment, clay and sea water, all showed quite variable recoveries of the standard, which can be seen in table 7. However, the recovery of the spiked standard in the experiment with freely dissolved PAHs in the corn stover biochar and the oak 250 and oak 650 biochars are presented in table 8. The standard deviations for these are very low.

Naphthalene evaporates very easily and was not detected for any of the recovery.

Table 7: Recovery of the standard, based on the average of the replicates

| Compound | Recovery average |
|-------------------------------------|------------------|
| d ₁₀ -Phenanthrene | 74 ± 37 |
| d ₁₀ -Pyrene | 84 ± 45 |
| d ₁₂ -Benz(a)anthracene | 92 ± 51 |
| d ₁₂ -Benzo(a)pyrene | 107 ± 72 |
| d ₁₂ -Benzo(ghi)perylene | 59 ± 30 |

Table 8: Recovery of the spiked standard for the freely dissolved PAHs in cornstover, oak250 and oak650 biochars, based on the average of the replicates

| PAH compound | Biochar | |
|-------------------------------------|------------|---------------|
| | Cornstover | Oak 250+650°C |
| d ₁₀ -Phenanthrene | 59 ± 1.4 | 60 ± 8 |
| d ₁₀ -Pyrene | 67 ± 1.3 | 69 ± 4.7 |
| d ₁₂ -Benz(a)anthracene | 74 ± 6.8 | 70 ± 8 |
| d ₁₂ -Benzo(a)pyrene | 115 ± 4.5 | 89 ± 13 |
| d ₁₂ -Benzo(ghi)perylene | 85 ± 12 | 80 ± 2.7 |

The reason for the variable recovery and high standard deviations for the samples from the time measurements, Soxhlet, and freely dissolved PAH concentrations is that the recovery standard was diluted with heptane for most of the samples. This caused a lower recovery than what would have been if the standard had been used in concentrated form. Due to the uncertainty on which samples that were and were not spiked with the diluted standard, the recovery was not corrected for any of the samples.

Previous work in the same laboratory has provided good recovery of the spiked standard, using the same recovery standard in its concentrated form. The recovery of the standard in the experiment with freely dissolved PAHs in the corn stover biochar and the oak 250 and oak 650 biochars all showed good recovery. This is also confirmed by the low standard deviation.

3.4 Soxhlet extraction of Bergen sediment and clay

A soxhlet extraction was performed on the sediment and the clay in order to analyse the content of PAHs, as demonstrated in figure 14. The soxhlet was performed according to the US EPA method 3540 C, with some modifications. The soxhlet was done in triplicate. Sediment and clay (approximately 1 g) were added to the extraction thimbles, and toluene ($C_6H_5CH_3$, Merck, purity of > 99.8%, 90ml) was used as the extraction solvent. Toluene was preferred as extraction solvent, as this was found to be most efficient compared to other solvents (Jonker and Koelmans,

2002a). A recovery standard (IS mix 1000 ng PAH/ml, 20 μ l) was added to each sample.



Figure 14: Soxhlet extraction of Bergen sediment and clay

After six hours the extraction was stopped and toluene was reduced to 1ml in centrifuge tubes. Samples were cleaned up via a dimethylformamide (DMF) as described by Mandalakis et al. (2004) and a silica gel clean up (described in section 3.4.1) before analysed on the GC-MS (described in section 3.4.2).

3.4.1 Silica gel clean up

Silica gel clean up was performed according to the US EPA method 3630 C. The columns consisted of glass wool, silica gel (3cm) and water absorbent, Na_2SO_4 . The column was rinsed with heptane (5ml) and then the sample eluted through, followed by 10 ml heptane. This was concentrated to 0.5 – 1 ml, put into GC-MS vials and PCB 77 (25 μ l) was added as an internal standard to check the performance of the GC-MS.

3.4.2 GCMS analysis

The GC-MS (gas chromatography mass spectrometry) detects compounds by their mass ion charge ratio. The model used for all samples was Agilent Technologies 5973 Network Mass Selective Detector and Agilent Technologies 6850 Network GC System. The GCMS method was described by Brandli et al. (2008).

The GC-MS takes 10 μ l of the sample and runs this through the GC column. The data from the GC-MS was analysed using computer software. Each peak in the spectrogram represented the amount of a PAH in the sample, and the area of the peaks were integrated before the data was further evaluated in excel. A calibration curve was obtained by running four calibration standards with concentrations of 1 ng/ml, 10 ng/ml, 100 ng/ml, and 1000 ng/ml.

The results were calculated on a mass basis for the sediment or POM. The calibration curve was used to determine the sample concentration from a peak height. All samples were corrected for PCB 77.

The GC-MS has a different detection limit for each PAH, as presented in table 9. The calibration curve starts with a concentration of 1 ng/ml, and because it is linear, lower sample concentrations may still be compared to the calibration standards.

Table 9: Detection limits of the PAHs in the GC-MS

| PAH | Detection limit (ng) |
|----------------------|-----------------------------|
| Naphthalene | 0.1838 |
| Acenaphthylene | 0.2222 |
| Acenaphthene | 0.4241 |
| Fluorene | 0.3611 |
| Phenanthrene | 0.2458 |
| Anthracene | 0.2505 |
| Fluoranthene | 0.1317 |
| Pyrene | 0.1266 |
| Benz(a)anthracene | 0.0209 |
| Chrysene | 0.0219 |
| Benzo(b)fluoranthene | 0.1818 |
| Benzo(k)fluoranthene | 0.1931 |
| Benzo(a)pyrene | 0.1798 |
| Indeno(123cd)pyrene | 0.4463 |
| Dibenz(ah)anthracene | 0.4196 |
| Benzo(ghi)perylene | 0.4836 |

3.5 Freely dissolved PAH concentrations

Freely dissolved PAH concentrations in the biochars, sediment, clay, and sea water were found in order to check for background concentrations in the capping materials and to check the concentrations in the sediment pore water.

PAH concentrations in the sediment, clay and sea water were determined by adding approximately 1g of respectively sediment and clay, and 50ml sea water, in 50 ml glass flasks of Milli pore water (40ml) and 1% NaN₃ (0.5ml), and POM (0.2 g). This stood shaking end over end for one month, after which the POM was removed, cleaned with Millipore water and tissue, and extracted as described in section 3.5.1 (POM extraction).

PAH concentrations were measured in biochars by adding approximately 0.2g of biochar to Millipore water (40ml) and 1% NaN₃ and POM (0.4 g). The POM was removed after two months with end over end shaking, and extracted as described in section 3.5.1 (POM extraction).

3.5.1 POM extraction

To extract the PAHs from the POM, the POM was shaken end over end in a solution (40ml) of acetone and heptane (80:20 ml) and a PAH recovery standard (20µl) for 2-3 days. This removes the PAHs from the POM into the extraction solution.

The POM was re-extracted over four days to test the efficiency of the first extraction. This showed that 3.5% of the PAHs were detected during the re-extraction, and therefore the first extraction was sufficient.

3.6 Sorption of PAHs to biochar

In order to check the strength of biochar sorption of PAHs, a sorption isotherm was determined at four different concentrations of PAHs and the biochar-water partitioning coefficient was calculated. The data was evaluated using a Freundlich isotherm.

3.6.1 Determination of sorption isotherms

POM, biochar (0.05g), water (40ml) and NaN_3 (1%; 400µl), were added to each vial, and spiked with a standard (pyrene and phenanthrene at respectively 174.0 µg/ml and 133.7µg/ml) of different concentrations of PAHs. The spiking volumes of the standard were adjusted to add 1 µg, 1.5 µg, 2 µg and 3 µg of pyrene, so 6µl, 9µl, 12µl, and 18µl were added. The resulting phenanthrene masses were 0.77 µg, 1.155µg, 1.54 µg, and 2.31 µg.

The vials were mixed end over end for one month to reach equilibrium. In a well mixed system with POM and activated carbon, one month is enough to reach equilibrium (Jonker and Koelmans, 2001). Measurements of corn stover and oak 400 biochars were done in duplicate and oak 250 and oak 650 biochars were done in singles. After shaking, the POMs were extracted, cleaned up using silica gel and analysed via GC-MS.

3.6.2 Calculating the biochar – water partitioning coefficient (K_{biochar})

To calculate K_{biochar} a mass balance (equation 6) describing the distribution of PAHs in a mixture of phases was used. The equation was solved for the concentration of PAHs in the char, C_{char} . Known values were the mass of char, POM, water and the total amount of PAHs; M_T . The concentration of PAHs in the POM, C_{POM} , was found from extracting the POM.

$$M_T = C_{\text{char}} * M_{\text{char}} + C_{\text{POM}} * M_{\text{POM}} + C_w * V_w \quad (6)$$

M_T : total amount of PAHs (μg)

C_{char} : concentration of PAHs in the char ($\mu\text{g/g}$)

M_{char} : mass of biochar (g)

C_{POM} : concentration of PAHs in the POM ($\mu\text{g/g}$)

M_{POM} : mass of POM (g)

C_w : concentration of PAHs in the water ($\mu\text{g/ml}$)

V_w : volume of water (ml)

The unknowns left were the concentration of PAHs in the water, C_w , which was solved by equation 7, where the distribution coefficient for POM, K_{POM} (ml/g), was a known value from Cornelissen et al (2008).

$$K_{\text{POM}} = C_{\text{POM}} / C_w \quad (7)$$

The biochar – water partitioning coefficient, K_{biochar} , was determined according to equation 8:

$$K_{\text{biochar}} = C_{\text{biochar}} / C_w \quad (8)$$

3.7 Quality assurance

The diffusion experiment was done in triplicate in order to assure more certain measurements and because of heterogeneity of the sediment, as the system in one jar would differ to another to some extent.

Samples that showed unusual values when quantifying from the GC-MS were rerun so to exclude errors from the GC-MS. During the laboratory experiments the GC-MS was cleaned once and the column was cut several times. The sample volume in the GC vials was reduced as far as possible in order to allow the GC-MS detect the compounds.

The height of the cap was measured over time at the first time measurement. In several jars the height had in certain areas reduced by 0.5 cm. This could be caused by compression of the clay and advection of pore water in the clay.

Adding sodium azide (NaN_3) to the diffusion jars would prevent formation of bacteria. However, sodium azide was not added, as previous experiences with this has shown negative effects, such as cracks in the sediment (Nag, 2008). It was expected that a bacteria film would form with time. This became evident at around the second time point, after 25 days, especially in the jars with biochar and clay caps and in the jars with sediment with tenax. The biofilm formed on top of the cap and sediment and in the water phase, leaving the water orange, as shown in figure 13 and 15.



Figure 15: Bacteria formation in the water phase in the diffusion set up

4.0 Field work with dioxin contaminated sediment in the Opticap project

The aim of the field work was to measure the dioxin flux from the sediment and the dioxins in free aqueous phase in the Grenland fjords, and was a part of the Opticap project. The measurements started in September 2009, and the results from the field work are from three different times.

Dioxin contaminated areas in the Eidangerfjord and Ormerfjord have been capped in order to remediate the area, and the effectiveness of the capping has been measured by placing flux chambers on top of the cap. On the inside of the chambers semi-permeable membrane devices (SPMDs) were attached. SPMDs function as infinite sinks for dioxins, as they have a high distribution coefficient for HOCs (Eek, 2008), and measures diffusive flux from the sediment to the pore water, see figure 16. Polyoxymethylene (POM) was attached on top of the chamber, see figure 17. POM passively accumulates contaminants until equilibrium is established between the POM and the surrounding water. This gives a measurement of the concentration of dioxins in the POM and from this, contaminants in free aqueous phase, C_w , can be calculated for each field.



Figure 16: Flux chamber with insertion of SPMD



Figure 17: Flux chamber with POM attached, measuring free aqueous concentration, C_w

The flux chambers were constructed at the NGI. They were lowered on to the sea bed with a crane on board the boat and ropes secured the chambers to shore. The flux chambers were left for 5-6 months on the sea bed before they were collected. Collecting the chambers from the sea bed was done by hoisting them by the rope with a crane on board the boat. On board the SPMDs

and POMs were removed from the flux chambers and put separately in labelled boxes and taken to the NGI where they were stored at -18°C.

In the lab, the POMs were cleaned with a moistened tissue, weighed and sent to Horst Rottler, Oekometric, Germany, along with the SPMDs for analysis of dioxins.

5.0 Results PAH contaminated sediment and thin layer capping with biochar

5.1 Total PAHs and freely dissolved PAHs in Bergen sediment, clay, sea water and biochar

The Bergen sediment has previously been classified as heavily contaminated with organic contaminants by Klif's classification guidance, but in order to check the sediment batch used in the diffusion experiments, a soxhlet was carried out. Table 10 shows the PAH concentrations in the sediment batch and the clay batch. The results show lower PAH concentrations that what may have been expected.

Table 10: PAH concentrations in the Bergen sediment batch and the clay batch. The standard deviation is from the average of three measurements. n.d (not detected); concentrations are below detection limit. * Measured concentration for one of three replicates only

| Freely dissolved PAH concentrations | | | | |
|-------------------------------------|-------------------------------|--------------------|-------------------------------|--------------------|
| Material | Sediment | | Clay | |
| Compound | Average concentration ng/g | Standard deviation | Average concentration ng/g | Standard deviation |
| Naphthalene | 31 | 5 | 22 | 2 |
| Acenaphthylene | n.d | n.d | n.d | * |
| Acenaphthene | n.d | n.d | n.d | * |
| Fluorene | 31 | n.d | 44 | 11 |
| Phenanthrene | 166 | 48 | 27 | 6 |
| Anthracene | 49 | 1.8 | 4 | * |
| Fluoranthene | 335 | 49 | 3.2 | 0.4 |
| Pyrene | 358 | 43 | n.d | * |
| Benz(a)anthracene | 159 | 14 | 2 | * |
| Chrysene | 189 | 7 | 0.6 | * |
| Benzo(b)fluoranthene | 252 | 59 | n.d | * |
| Benzo(k)fluoranthene | 241 | 32 | n.d | * |
| Benzo(a)pyrene | 221 | 5 | 16 | * |
| Indeno(123cd)pyrene | 300 | 45 | n.d | * |
| Dibenz(ah)anthracene | n.d | * | n.d | * |
| Benzo(ghi)perylene | 286 | 33 | n.d | * |
| Total | 2569 | 167 | 81 | 37 |

The results can be compared to Klif's classification guidance, which are shown in appendix 1. According to the classification guidance, the sediment batch used in the diffusion experiments would be classified between good and moderate.

Table 11: Freely dissolved PAH concentrations in the Bergen sediment batch, the clay batch and sea water. The standard deviation is from the average of three replicates. n.d: not detected because the concentrations are below the detection limit. Measured concentration for one of three replicates only

| | Pore water concentration, C_w | | | | | |
|----------------------|---------------------------------|--------------------|-------------------------------|--------------------|-------------------------------|--------------------|
| Material | Sediment | | Clay | | Sea water | |
| Compound | average concentration ng/L | Standard deviation | Average concentration ng/L | Standard deviation | average concentration ng/L | Standard deviation |
| Naphthalene | 77 | * | 80 | 46 | n.d | * |
| Acenaphthylene | n.d | * | n.d | * | n.d | * |
| Acenaphthene | n.d | * | n.d | * | n.d | * |
| Fluorene | n.d | * | n.d | * | n.d | * |
| Phenanthrene | 29 | 10 | n.d | * | n.d | * |
| Anthracene | 16 | 5 | n.d | * | n.d | * |
| Fluoranthene | 40 | 11 | n.d | * | n.d | * |
| Pyrene | 100 | 19 | n.d | * | n.d | * |
| Benz(a)anthracene | 13 | 3.3 | n.d | * | n.d | * |
| Chrysene | 3.8 | 0.9 | n.d | * | n.d | * |
| Benzo(b)fluoranthene | 12 | 1.6 | n.d | * | n.d | * |
| Benzo(k)fluoranthene | 8 | 7 | n.d | * | n.d | * |
| Benzo(a)pyrene | 10 | 2.6 | n.d | * | n.d | * |
| Indeno(123cd)pyrene | n.d | * | n.d | * | n.d | * |
| Dibenz(ah)anthracene | n.d | * | n.d | * | n.d | * |
| Benzo(ghi)perylene | n.d | * | n.d | * | n.d | * |
| Total | 257 | 91 | 80 | 46 | 0 | 0 |

The results in table 11 show freely dissolved PAH concentrations in the Bergen sediment batch, the clay batch and the sea water that were used in the diffusion experiment. The clay and the sea water hardly contain any freely dissolved PAHs, while the sediment contains some. In the calculation of C_w , K_{POM} values were used from Cornelissen et al. (2008).

The naphthalene measured in the clay pore water (80 ng/L) is clearly due to a background contamination and too high to be a realistic concentration in the clay, which is otherwise free of PAHs. Measurements of naphthalene will therefore be disregarded throughout the thesis.

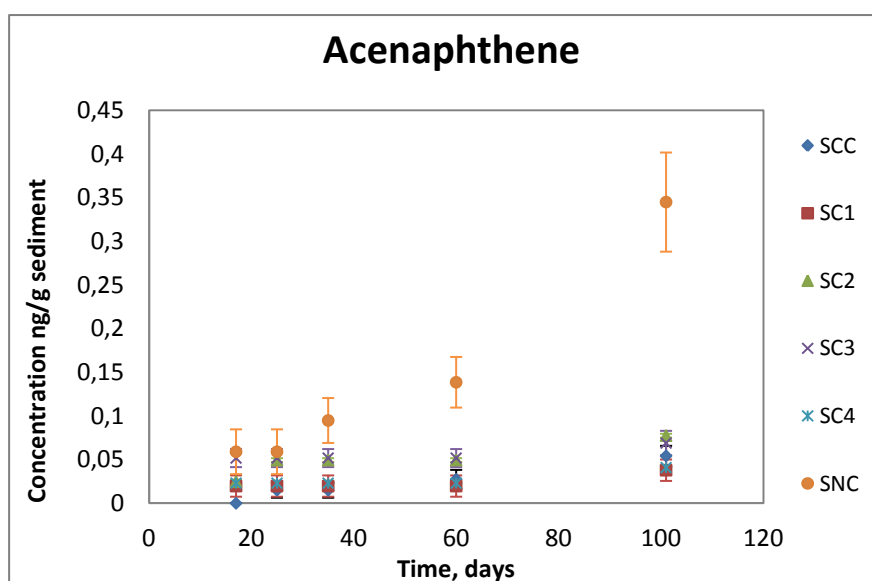
Table 12: Freely dissolved PAHs in the biochars. The standard deviation is the average of three replicates.

| Biochar | Freely dissolved concentration (ng/L) |
|------------|---------------------------------------|
| Cornstover | 1.30 ± 0.12 |
| Oak 250 | 0.31 ± 0.09 |
| Oak 400 | 0.36 ± 0.08 |
| Oak 650 | 0.28 ± 0.15 |

The freely dissolved PAH concentrations in the biochars applied in the diffusion experiment are shown in table 12. The results are unpublished data provided by Sarah Hale.

5.2 Diffusion of PAHs through biochar cap and steady state diffusive flux of phenanthrene

The diffusion of PAHs from the sediment is very limited for both capped and uncapped sediment. There does not seem to be any breakthrough of PAHs through the biochar caps, but the uncapped sediment show a clear trend of increasing PAH concentrations with time. Some concentration of the smaller PAHs was measured, though for the larger PAHs little was measured. The large PAHs desorb more slowly from the sediment than smaller PAHs.



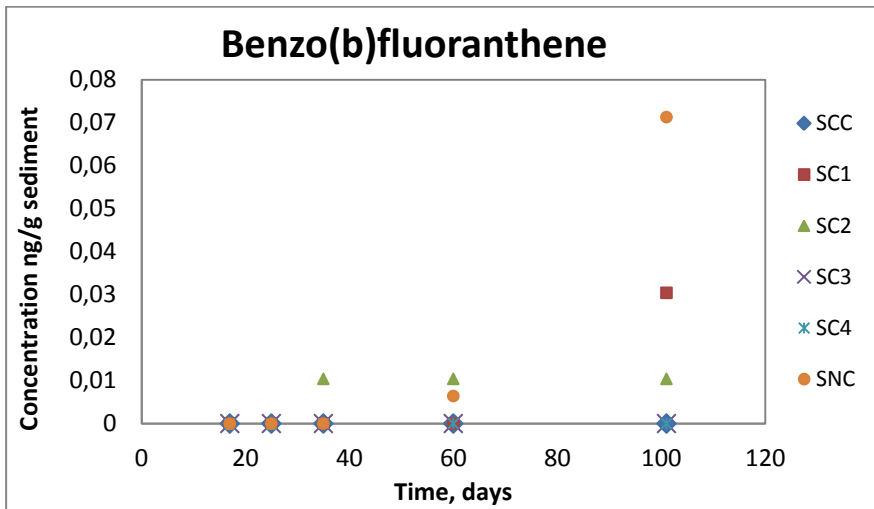
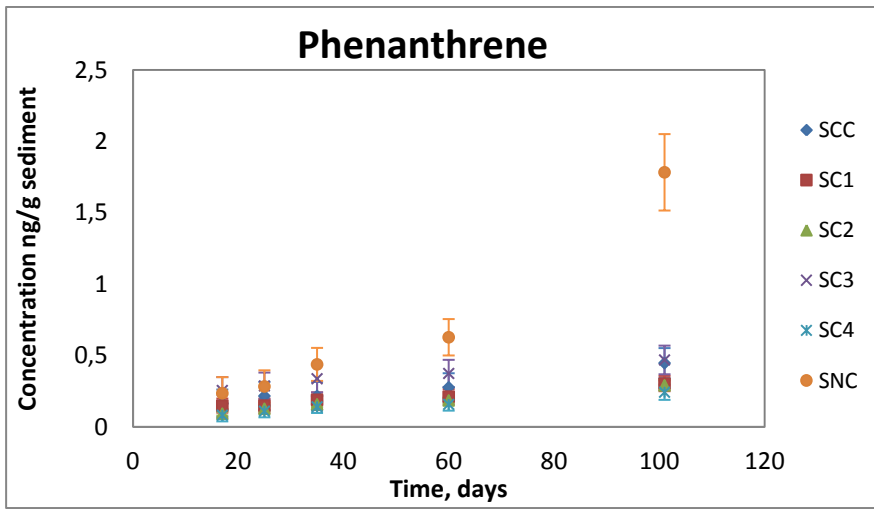
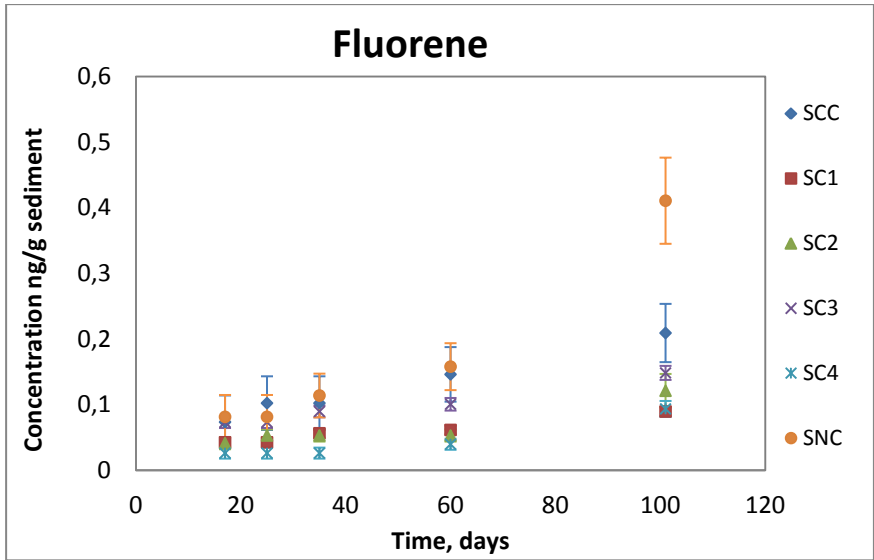


Figure 18: Diffusion of the PAHs acenaphthene, fluorene, phenanthrene, and benzo(b)fluoranthene. SCC- sediment clay cap, SC1- sediment capped with corn stover, SC2- sediment capped with oak250, SC3- sediment capped with oak400, SC4- sediment capped with oak650, SNC- sediment no cap. SC1-4 are a mix of clay and biochar. The standard deviation represents the deviation on three replicates of the measurements. The benzo(b)fluoranthene plot has no standard deviation, as only one of the replicates measured concentration.

The plots, shown in figure 18, for acenaphthene, flourene, and phenanthrene show a clear trend over time. It is evident that the uncapped sediment (SNC) has higher concentration compared to the capped sediment. There does not appear to be any significant differences between the efficiency of the caps, though for phenanthrene and fluorene the clay cap (SCC) has a higher PAH concentration compared to the other caps.

Plots for acenaphthene, flouranthene, and pyrene are presented in appendix 3. These PAHs had concentrations above the analytical detection limit at more than three time points for at least one cap, while the other PAHs did not and are therefore not presented as plots.

5.2.1 Steady state diffusive flux

Steady state diffusive flux was calculated for phenanthrene. A comparison was made for the steady state diffusive flux from uncapped sediment (J_{ised}) and sediment capped with biochar (oak 650) (J_{icap}). The results are presented in figure 19.

The calculations of the steady state diffusive flux were done according to Fick's first law:

$$J_{ised} = (D_i / \delta_{DBL}) * (C_{ipw} - C_{iw}) \quad (9)$$

$$J_{icap} = (\varepsilon * D_i / \tau * (h_{cap} \delta_{DBL})) * (C_{ipw} - C_{iw}) \quad (10)$$

D_i ($D_{iphen} = 4.57 * 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and the thickness of the DBL ($\delta_{DBL} = 0.34 \text{ cm}$) was taken from Eek et al. (2008), the porosity ($\varepsilon = 0.653$) was found on the basis of the porosity of AC and clay by Nag (2008), though the porosity of the biochar is lower. The tortuosity ($\tau = 1.15$) is equal to $\varepsilon^{1/3}$. C_{iw} is the phenanthrene accumulated in the heptane at each time point measurement (see plot for phenanthrene), C_{ipw} is the concentration of phenanthrene in the sediment pore water (see phenanthrene table 11), and the height of the cap (h_{cap}) was 0.5cm, representing the actual height in the diffusion experiment.

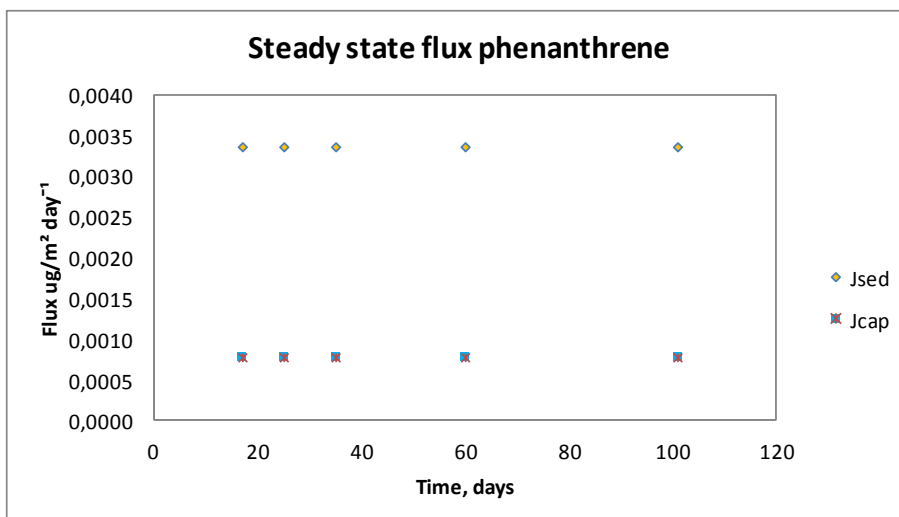


Figure 19: A comparison of steady state diffusive flux of phenanthrene through biochar cap (oak 650) and uncapped sediment

5.3 K_{biochar} and sorption isotherms

To understand more about the diffusion experiment, sorption capacities of the biochars were examined for the two PAHs phenanthrene and pyrene. The sorption isotherms are presented in figure 19 and 20. Enough reliable data were available for the cornstover and oak 250 biochars to construct sorption isotherms for phenanthrene and pyrene sorption, and also for the oak 400 biochar to construct an isotherm for pyrene sorption. For the oak 650 biochar, the large standard deviations, lack of n values and unreliable data made it difficult to produce an isotherm. According to the results, the oak 250 biochar sorbs phenanthrene and pyrene the strongest compared to the other biochars.

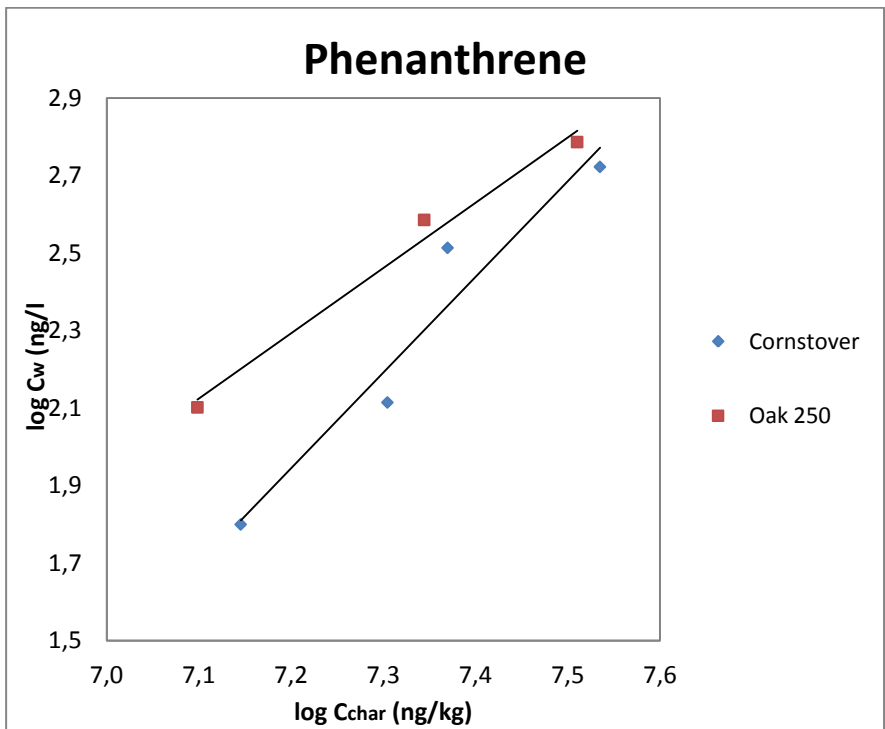


Figure 20: Sorption isotherms for phenanthrene based on duplicate measurements

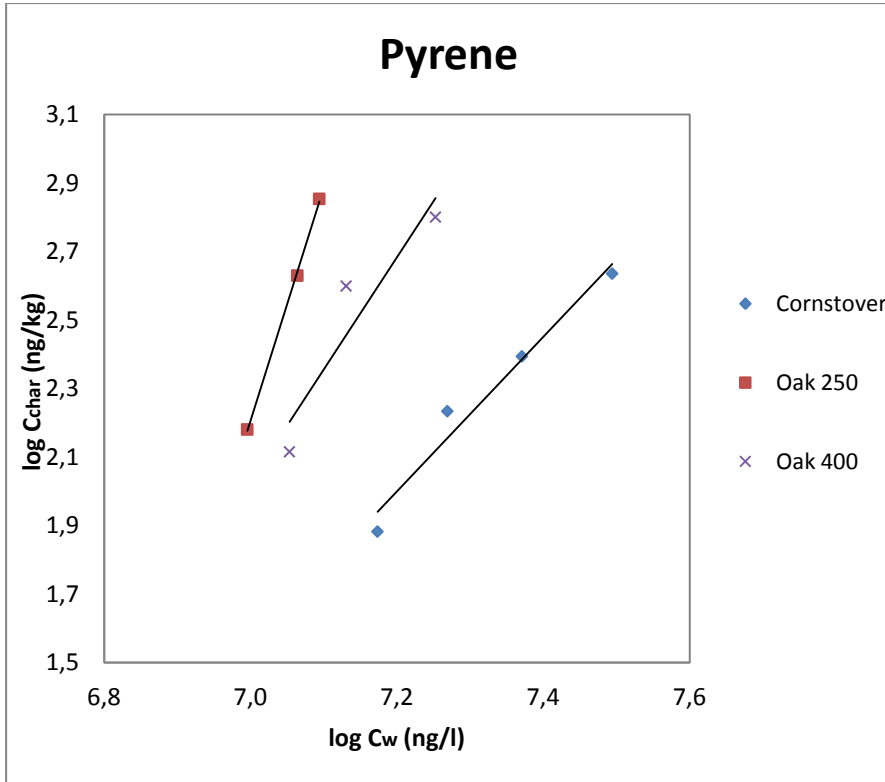


Figure 21: Sorption isotherms for pyrene based on duplicate measurements

Table 13: Freundlich coefficients and exponents and K_{biochar} . Data not available or not detected.

| | Phenanthrene | | | |
|------------|-----------------|---|-------|------------------------------------|
| | n | $K_{\text{Fr}} (\text{ng/kg})(\text{ng/l})^n$ | R^2 | $K_{\text{biochar}} (\text{ml/g})$ |
| Cornstover | 0.38 ± 0.07 | 6.47 ± 0.16 | 0.94 | 5.05 ± 0.26 |
| Oak 250 | * | * | 0.99 | 4.83 ± 0.15 |
| Oak 400 | 0.08 ± 0.04 | 7.05 ± 0.19 | * | 4.84 ± 0.34 |
| Oak 650 | * | * | * | * |
| | Pyrene | | | |
| | n | $K_{\text{Fr}} (\text{ng/kg})(\text{ng/l})^n$ | R^2 | $K_{\text{biochar}} (\text{ml/g})$ |
| Cornstover | 0.43 ± 0.06 | 6.35 ± 0.13 | 0.97 | 5.04 ± 0.18 |
| Oak 250 | 0.14 ± 0.35 | 6.61 ± 0.91 | 0.99 | 4.43 ± 0.28 |
| Oak 400 | 0.28 ± 0.16 | 6.41 ± 0.40 | 0.87 | 4.62 ± 0.22 |
| Oak 650 | * | * | * | 4.36 ± 0.42 |

According to the results presented in table 13, $n < 1$ for all the biochars. R^2 is a measure of the goodness of fit, where a value of one is a perfect fit. K_{Fr} is the Freundlich capacity coefficient. K_{biochar} is the biochar – water partitioning coefficient, and describes the sorption to the biochar. This value was obtained by taking the average of the four different concentration measurements

For all the biochars where n values could be calculated, they were far below one. The standard deviation is very high for several of the values. For oak 250 and oak 400, n is 0.14 ± 0.35 and 0.28 ± 0.16 respectively. The standard deviations for the K_{biochar} values were also high.

6.0 Results dioxin contaminated sediments in the Grenland fjords

The fields in the Ormerfjord were capped with 1) crushed limestone, 2) clay, 3) activated carbon mixed with clay, and 4) was the reference field. In the Eidangerfjord field 5) was capped with activated carbon mixed with clay, and field 6) was the reference field. The fields are presented in appendix 3.

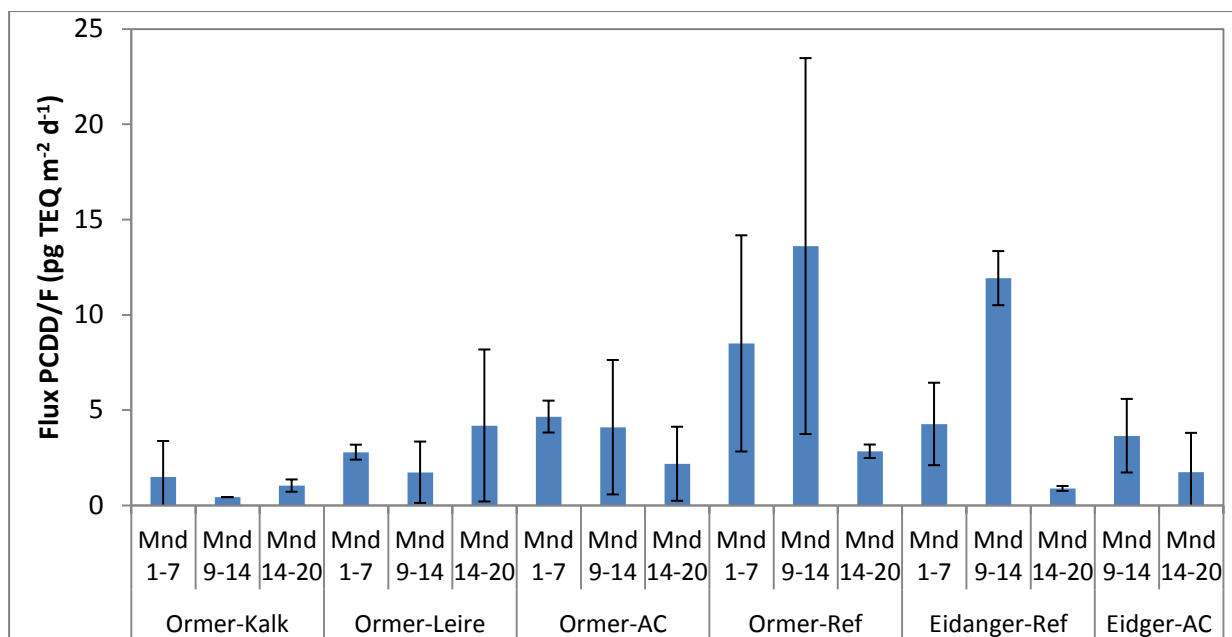


Figure 22: Flux of dioxins (pg TEQ m⁻²d⁻¹) for each field at three different time points; June 2010, November 2010 and May 2011. From left to right the fields are: the Ormerfjord – crushed limestone, clay, activated carbon, and reference field. The Eidangerfjord – reference field and activated carbon field. The data and analyses for the two first time points are collected from and performed by Gerard Cornelissen, 2011, and the third is coordinated and calculated by Aina Winther, all unpublished data.

Figure 22 shows the dioxin flux from the sediment, accumulated in the SPMD in the flux chamber at three different time points (June 2010, November 2010, and May 2011). The values of the capped fields can be compared to the reference fields in each fjord.

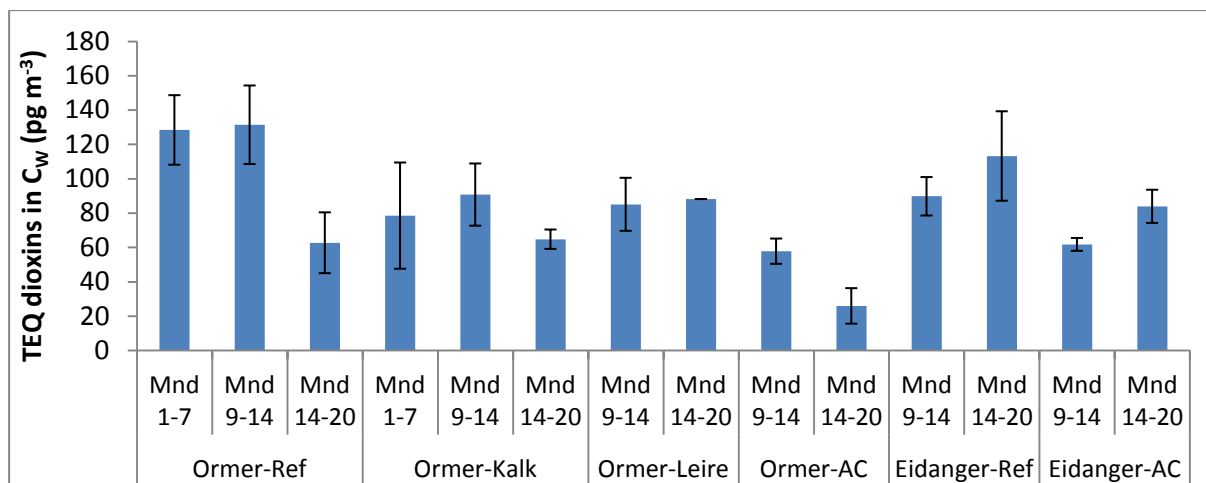


Figure 23: Dioxin water concentration (pg m^{-3}) in toxic equivalent factor (TEQ) for each field at three different time points; June 2010, November 2010 and May 2011. From left to right the fields are: the Ormerfjord – crushed limestone, clay, activated carbon, and reference field. The Eidangerfjord – reference and activated carbon field. The data and analyses for the two first time points are collected from and performed by Gerard Cornelissen, 2011, and the third is coordinated and calculated by Aina Winther, all unpublished data.

The results in figure 23 show the dioxin aqueous concentration measured using POM expressed as TEQ at three different times (June 2010, November 2010, and May 2011) for the reference field and the limestone field in the Ormerfjord, and at the two last times for the remaining fields. Because of currents and exchange of sea water, measuring dioxin water concentration is difficult. This is why there are only two measurements for some fields; the dioxin concentration accumulated in the POM was beneath the detection limits.

7.0 Discussion

7.1 Total PAHs and freely dissolved PAHs in Bergen sediment, clay, sea water and biochar

The concentration of total and freely dissolved PAHs was investigated for all the materials used in the experiment to determine native contamination in the materials.

The results from the soxhlet on the Bergen sediment batch show that the content of PAHs was not as high as previously measured. The total concentration of PAHs in the sediment batch in this experiment was 2569 $\mu\text{g}/\text{kg}$. This classifies the sediment batch between good and moderate, according to Klif's classification guidance. The concentration of sum PAHs in Nag's sediment batch was 17667 $\mu\text{g}/\text{kg}$, which classifies the sediment as bad, according to Klif's classification guidance (appendix 1). The lower PAH concentrations in the sediment used in this experiment can be explained by degradation during the time it has been stored and that the sediment batch was collected from a large container (100 L) in the cooling room and then homogenized.

The soxhlet results on the clay batch show that the clay is very clean, and the limited amount of PAHs detected are not likely to contribute any PAH contamination. Fluorene was detected at a higher concentration in the clay than in the sediment, and this may be explained by errors with the GC-MS analysis, contamination of the sample or that the clay did indeed contain more fluorene than the sediment. When comparing the total PAH concentration in the sediment to the concentration in the clay, the concentration in the clay was approximately 32 times lower.

The freely dissolved PAH concentrations in the sediment (see table 11) appear quite low; phenanthrene measured 0.029 $\mu\text{g}/\text{l}$, anthracene measured 0.016 $\mu\text{g}/\text{l}$, and pyrene measured 0.1 $\mu\text{g}/\text{l}$. These results can be compared to the measured pore water concentrations in other studies. Oen et al (2006a) used the same experimental method as here when investigating freely dissolved PAH concentrations in sediment from Oslo Harbour, and found that C_w was 0.062 $\mu\text{g}/\text{l}$ for phenanthrene, 0.066 $\mu\text{g}/\text{l}$ for anthracene, 0.49 $\mu\text{g}/\text{l}$ for pyrene, and even less for the larger PAHs. Arp et al. (2011) measured pore water concentrations of PAHs in 335 sediment samples from 19 different contaminated places. The results for urban sediment, which was defined as "no identified source area", showed that the PAH concentration in the pore water ranged from 0.10 $\mu\text{g}/\text{l}$ to 341.60 $\mu\text{g}/\text{l}$. The pore water concentration of phenanthrene ranged from not detected to 27.690 $\mu\text{g}/\text{l}$, and the concentration of anthracene ranged from not detected to 3.053 $\mu\text{g}/\text{l}$, while

the concentration of pyrene ranged from not detected to 7.899 $\mu\text{g/l}$. The larger PAHs showed lower pore water concentrations, many of which were not detected at all.

The clay and the sea water were virtually uncontaminated, but naphthalene was measured in the clay. Naphthalene is quite difficult to measure, as it often evaporates from the sample, and is present in high quantities as a background contamination. The clay and sea water are not considered to pose a contamination source within the experiments.

The freely dissolved PAH concentrations in the biochars (table 12) are below the guidelines for safe levels of total PAH concentrations in soils. The corn stover biochar, which is produced in controlled pyrolysis conditions, showed higher PAH concentrations (1.30 ± 0.12 ng/L) than the oak biochars (Hale et al., in press). The oak biochars have quite similar PAH concentrations (from 0.28 ± 0.15 ng/L to 0.36 ± 0.08 ng/L), and oak 400 has the highest concentrations. The total concentration of native PAHs in the biochars are lower than the total aqueous PAH concentrations (C_w) in the sediment (see table 11). All the capping materials all showed very low native PAH concentrations that will not contribute significantly to the PAHs measured in the heptane. Hale et al. (in press) examined the total PAH concentrations and bioavailable PAH concentrations in 50 different biochars, and found that the biochars produced at high temperatures and long pyrolysis time contained the lowest PAH concentrations. The total PAH concentrations for slow pyrolysis biochars varied from 0.07 $\mu\text{g/g}$ to 3.27 $\mu\text{g/g}$, where the highest PAH concentrations belonged to the biochars produced in uncontrolled conditions. The bioavailable PAH concentrations varied from 0.17 ng/l to 10 ng/l. Compared to these concentrations, the PAH concentrations of biochars in this study are in the low range.

When comparing the freely dissolved PAH concentrations in the sediment batch used in this experiment to the concentrations by Nag (2008), the sum of PAHs in the sediment pore water was 153 ng/L, while the sum of the PAHs in the sediment pore water in the sediment batch in this experiment was 240 ng/L (when excluding the naphthalene concentration).

When considering biochar for remediation amendment, it is important to evaluate the quality of the biochar and the material source. When producing biochar, PAHs are also formed, and by choosing a material that is free for contaminants and producing it via slow pyrolysis at high temperature is likely to result in a biochar where the PAH concentrations are below the limit for safe levels of total concentrations in the guidelines (Hale et al., in press). Depending on the area

of remediation, the mass of biochar required may be very high. Large amounts of material necessary to produce this must be available, and this raises the question of what kind of material should be used. It is not acceptable to use large fields to produce organic material that is to be used for biochar production, when the same areas can otherwise be used in agriculture. Also, deforestation in order to gain biochar material is not an environmentally sound way of producing biochar. Optimal sources for biochar production are waste materials. Using a material that is otherwise a waste contributes positively to waste management strategies and thus shows further benefit of biochar (Roberts et al., 2010). Production of biochar leads to stable carbon storage and lasting carbon sequestration, and has thereby a benefit to the environment and the climate.

7.2 Diffusion of PAHs through biochar cap

7.2.1 The efficiency of capping with biochar

The diffusion of PAHs from the Bergen sediment was investigated over time with different caps and no cap in order to find out if biochar could be used as an active material as activated carbon is currently used.

It was hypothesised that the biochar caps would retain the diffusing PAHs because of sorption to the biochar (Cornelissen et al., 2005), and that biochar would be less effective than capping with activated carbon because the activation process of activated carbon creates a more porous material with superior physicochemical properties (Chun et al., 2004, Chen et al., 2008).

When looking at the results and comparing the uncapped and capped sediment in the plots, it is clear that all the caps are effective in reducing diffusion of PAHs. The difference in PAH concentration (acenaphthene, fluorene and phenanthrene) between capped and uncapped sediment is evident already at the first measurement, after 17 days. At the fifth time point measurement, after 101 days, the difference is most evident. At the fifth measurement the percentage reduction in fluorene, phenanthrene and acenaphthene concentrations are between 77.2 % and 88.1 % with capping, when comparing the oak 650 cap (SC4) to the uncapped sediment (SNC). This shows that capping is an efficient measure against PAH contaminated sediment.

The height of the cap was supposed to be 1cm, though during the experiment it sank to 0.5cm at several places of the cap in all jars. This is due to compression of the cap, as the particles in the cap compresses with time. However, even a 0.5 cm cap proved effective in reducing the diffusion of PAHs from the sediment and shows the caps were working.

7.2.2 Steady state diffusive flux

Capping with biochar has not previously been tested, but the results can be compared to what has previously been tested with thin layer capping with activated carbon. According to the results, the calculated steady state diffusive flux of phenanthrene through the biochar cap (SC4) was approximately 77 % lower than the flux from the uncapped sediment. Nag (2008) tested thin layer capping with activated carbon on the same sediment used in in this experiment. According to her results, only a few PAHs were detected, and the steady state diffusive flux from sediment capped with 0.5 cm cap was reduced approximately 75 % for all the capping materials compared to the uncapped sediment. The results are quite similar, though it was expected that capping with biochar would be less effective than capping with activated carbon, as the sorption properties of activated carbon exceeds those of biochar (Chen et al., 2008, Yang and Sheng, 2003, Chun et al., 2004).

7.2.3 Differences in sorption efficiency between the different caps

Different types of biochars were used to check if the biochar material and production temperature would affect the ability to retain diffusing PAHs. A clay cap was used as a reference for the caps with clay mixed with biochar.

It was hypothesised that the biochar caps would be more efficient than the clay cap, and that the oak 650 biochar would be the most efficient of the different biochar caps.

The most efficient biochar cap should according to what was found in literature be the oak 650 biochar, as it has has more sorption sites and less volatile matter than the biochars produced at lower temperature (Mukherjee et al., 2011, Chen et al., 2008). The PAHs that have desorbed from the sediment sorb to the cap (Eek et al., 2008). The biochar caps should be more efficient in retaining diffusing PAHs than the clay cap, because sorption to biochar should be stronger than sorption to clay. According to the diffusion results in the plots there are no clear differences in the efficiency of the different biochar caps, nor between the clay cap and the biochar caps, at any

time point. The reason might be that the experimental period was not long enough to show any clear differences, and extending the experiment may reveal differences.

7.2.4 Diffusion of small and large PAHs

Diffusion of PAHs from the sediment varies with the size and shape of the PAHs and the sorption qualities of sediment and cap. Diffusion through the cap was investigated for all the 16 US-EPA PAHs listed in figure 2.

According to the plots, small and large PAHs have desorbed from the uncapped sediment (SNC) and accumulated in the heptane, though the diffusion of the larger PAHs were less extensive than the diffusion of the small PAHs, as measured concentrations were lower. In the systems with capped sediment there was little breakthrough of PAHs for any of the caps, and hardly any of the large PAHs could be detected in the heptane. Most of the small PAHs measured detectable concentrations through the cap. The easiest detectable PAHs were acenaphthene, fluorene and phenanthrene, which also presented the best trends in the plots. The large PAHs remain sorbed to the sediment or in the cap, as no concentrations were detected for any of the time points except for the final time point for some of them. Benzo(b)fluoranthene desorbed from the sediment and measured detectable concentrations in the final time points. Benzo(b)fluoranthene (see the plot in figure 18) presented the general trend of the large PAHs that were detectable.

Most of the large PAHs were only detected at two time points, which was at the first and the final time point measurements. Detected concentrations at the first measurement may be explained by the advection process during the application of the cap, as the cap would have compressed the sediment and some of the water from the sediment spread into the cap and along the sides of the jar. At the final measurement, some PAHs have diffused through the cap. Continuing the diffusion set up in order to gain later measurements would most likely have given more detectable concentrations.

Desorption of PAHs from sediment is controlled by the amount of total organic carbon (TOC) and BC in the sediment (Oen et al., 2006b). The trend of desorption starts with rapid desorption, then slow and very slow desorption. Oen et al. (2006b) examined desorption rates from different sediments using tenax desorption method. The desorption rate constants ($k_{d, \text{slow}}$ and $k_{d, \text{very slow}}$) for the Bergen sediment was $k_{d, \text{slow}} = 2.3 \cdot 10^{-3}/\text{h}$ and $k_{d, \text{very slow}} = 19 \cdot 10^{-5}/\text{h}$ for phenanthrene,

$k_{d,slow} = 4.3 * 10^{-3}/h$ and $k_{d,very\ slow} = 22 * 10^{-5}/h$ for pyrene, and $k_{d,slow} = 5.8 * 10^{-3}/h$ and $k_{d,very\ slow} = 14 * 10^{-5}/h$ for benzo(a)pyrene in whole sample sediment.

The smaller PAHs desorb more easily than the larger, more complex PAHs, as the small PAHs are less strongly sorbed and their shape and size allow them to diffuse from the sediment particles more easily (Neff, 1979, Fetter, 1992).

7.2.5 Formation of biofilm

A biofilm may be produced by bacteria in anoxic conditions during breakdown of organic material. Adding sodium azide prevents such formation, but since this was not added, a biofilm was expected to form.

During the diffusion experiment a biofilm was produced by the bacteria. All of the diffusion jars contained a biofilm to a certain degree, but this varied with material. For the jars with uncapped sediment and tenax, the biofilm was an orange layer that covered the entire sediment surface and made the water cloudy (see figure 13). The jars with uncapped sediment with heptane had only a clear biofilm on top of the water phase, and the jars with biochar capped sediment had a biofilm on top of the cap and the water phase was cloudy (see figure 15). Sodium azide was not added, because previous studies have shown that a biofilm might reduce the PAH diffusion, and that adding sodium azide caused the sediment to crack, thereby increasing the flux of PAHs from the sediment (Nag, 2008). Leaving the system without sodium azide would also make the experiment more equal to a natural system, as bacteria exist where there is organic material. But in natural systems there is also a microbial society that feeds on bacteria, which do not exist in the laboratorial experiment. However, overall it was anticipated that the biofilm would not affect the experiment to a large extent, and any small effect it might have would be to slow down the diffusion of PAHs from the sediment.

7.3 $K_{biochar}$ and sorption isotherms

The sorption capacity of the biochars was tested to investigate how efficient the biochars were for capping the contaminated sediment and retaining PAHs that diffuse into the cap. Sorption isotherms and $K_{biochar}$ values describe how well the biochar sorbs PAHs.

It was expected that the biochar produced at the highest temperature, oak 650, would sorb the PAHs phenanthrene and pyrene the strongest, as this biochar has the most sorption sites and less

AOM disturbing the sorption sites (Chen et al., 2008, Mukherjee et al., 2011). However, according to the sorption isotherms, the corn stover biochar has the most shows the best isotherm for both phenanthrene and pyrene. There was not enough reliable data for the oak 650 biochar to construct an isotherm. When looking at the K_{biochar} , the corn stover biochar has the highest sorption for both phenanthrene and pyrene compared to the other biochars. K_{biochar} for sorption of phenanthrene to the corn stover biochar was 5.05 ml/g, while sorption to the oak 250, and 400, biochars was 4.83 ml/g and 4.84 ml/g respectively. K_{biochar} for sorption of pyrene to corn stover was 5.04 ml/g, while sorption to the oak 250, 400, and 650 biochars was 4.43 ml/g, 4.62 ml/g, and 4.36 ml/g, respectively. The biochar with the highest K_{Fr} value for sorption of phenanthrene was the oak 400 biochar, and the oak 250 biochar had the highest K_{Fr} for sorption of pyrene. K_{Fr} was not found for phenanthrene sorption to the oak 250 and oak 650 biochars, or for pyrene sorption to the oak 650 biochar.

Other studies with biochar show very variable K_{biochar} values, that are dependent on the biochar itself and the production method. Wang and Xing (2007) found that K_{biochar} for sorption of phenanthrene to biopolymer-derived biochar varied from 1.8 ml/g to 7.6 ml/g, which is the most comparable to the results in this study. The biochars were produced from cellulose and chitin at 250°C, 320°C, and 400°C. The isotherms were based on ten solute concentration levels, whereas in this experiment there were used four solute concentration levels.

The biochars are very heterogeneous and may therefore present very different results. Sorption of PAHs at the low concentrations applied in the experiments to biochar would be expected to follow a Freundlich sorption isotherm, based on previous work for activated carbon and biochar. However, according to the results, $n < 1$ for all the biochars, which would describe a situation where the biochar is saturated with PAHs as the concentration of PAHs increase. The sorption might have been better described by another sorption isotherm. Heterogeneity of the biochar, and perhaps human error in the method, may explain the nature of the results. Also, more solute concentrations might have improved the data, and given more reliable isotherms.

Other studies with sorption to biochar the data have been presented as Freundlich isotherms. Chen and Chen (2009) presented Freundlich isotherms with regression coefficients (R^2) close to one and n values varying from 0.151 to 1.098 for naphthalene sorption to biochar. The n values increased as the combustion temperature of the biochar decreased. This is comparable to the results by Chen and Yuan (2011), who presented sorption of phenanthrene to biochar produced

at different temperatures as Freundlich isotherms. Both studies showed that overall the biochar produced at the highest temperature had the highest sorption of PAHs, even though some PAHs were better sorbed to biochars produced at lower temperatures.

Biochars, as activated carbon, have several sorption sites and a very high sorption capacity, though sorption sites may become occupied by other molecules than PAHs, such as OM and non-target compounds, thereby decreasing the sorption ability of the biochar (Cornelissen and Gustafsson, 2004).

The variability in the results and some experimental difficulties make it difficult to conclusively decide which biochar is best.

7.4 Dioxin contaminated sediments in the Grenland fjords

Capping with different materials on dioxin contaminated sediment in the Grenlandfjords was tested in order to investigate capping method and technology, and to investigate the efficiency of the capping materials.

When comparing the flux from the capped fields to the reference field in each fjord, the dioxin flux from the sediment has been significantly reduced. The flux from the sediment measured in the SPMDs of the three time points varies, but the flux from the activated carbon fields in both fjords show a decreasing trend with each time point measurement. The variations can be explained by the fact that the flux chambers are put on different places on the sea bed in the field, and the sediment and the rate of dioxin contamination in the sediment is not homogenous for the whole field. However, the results show that capping with activated materials is efficient. The capping in the Eidangerfjord was done at 100 m depth, which is the deepest there has been conducted capping, and this was successful (NGI, 2009).

The dioxins in the aqueous phase, C_w , were measured with POM, and are difficult to measure accurately because of currents and exchange of sea water. However, comparing the dioxin aqueous concentrations in the capped fields to the concentrations in the reference fields in each of the fjords show that the dioxin concentrations have been reduced. Capping the contaminated sediment reduces the flux of dioxins to the water phase, therefore improving water quality.

Using activated carbon for capping large fields require large amounts of material. Capping 40 000 m², which is one field in the Eidangerfjord, required 58.8 tons of AC. This amount was mixed with clay. In total, 80 tons of AC was distributed in the Ormerfjord (2 kg/m²) and the Eidangerfjord (1.5 kg/m²) (Eek et al., 2011).

Removing contaminated sediment via dredging when the masses are very large is unrealistic to accomplish; the cost of removing large masses is immense and the sediment needs to be stored at an environmentally safe place without having to be transported over large distances (NGI, 2009). Capping means isolating the contamination, and it is important to choose materials that pose the least harm to the marine fauna in the area. Thin layer capping with active materials binds the contaminants and makes them unavailable to organisms living in the sediment without changing the substrate to the same extent as capping with different material in a thicker layer.

8 Conclusion and further research

The diffusion experiment showed that thin layer capping with biochar was effective in reducing diffusing PAHs from the contaminated sediment. Compared to the uncapped sediment, the effect of capping with a biochar and clay mixture caused a reduction of 77.2% to 88.1% for the PAHs fluorene, phenanthrene, and acenaphthene. The small PAHs diffused more than the large PAHs from the sediment. The easiest detectable small PAHs were acenaphthene, fluorene and phenanthrene. Most of the large PAHs were not detected, and the ones that were detected measured very low concentrations. Diffusion of benzo(b)fluoranthene represented the general trend for the detectable, large PAHs.

Steady state diffusive flux of phenanthrene was reduced with 77 % for capped sediment (oak 650 cap) compared to uncapped sediment.

It was hypothesised that the biochar produced at the highest temperature would be the most efficient in sorbing PAHs, but the results show very little difference among the biochar caps in the efficiency of retaining diffusing PAHs from the contaminated sediment. However, the K_{biochar} and the Freundlich sorption isotherms showed that the corn stover biochar was the strongest sorbent of PAHs (K_{biochar} for sorption of phenanthrene and pyrene to corn stover was 5.05 ml/g).

Thin layer capping with activated carbon, clay and crushed limestone in the Opticap project showed that the capping was effective in reducing the flux of dioxins from the sediment when comparing to the reference field. It was difficult to conclude which capping material was the most effective; however the crushed limestone resulted in the lowest concentrations of measured dioxin flux from the sediment.

Using active materials in capping means that less material is needed compared to passive materials, because of the thin layer and the high sorption capacity. Activated carbon has already been successfully used in remediation of contaminated sediment, but the use of biochar as thin layer capping needs to be further investigated. The method of capping with biochar needs to be further tested and developed. Testing biochar capping in field must also be done to see the efficiency in a realistic perspective, as done with different materials in the Opticap project. Biochar has not previously been used in sediment remediation, and the advantages of working with biochar need to be considered by the regulators before biochar can be used in sediment remediation. Biochar effectively sorbs pollutants, however the type of biochar to be used must be considered with respect to the production method, the material, and therefore its efficiency in reducing the contamination. The material which biochar is produced from must be environmentally safe; using waste materials in remediation means that no areas that could otherwise be used for food production are occupied. In addition, the carbon in the biochar is stable, and so the production of biochar removes carbon from the carbon cycle.

9 References

- ARP, H. P. H., AZZOLINA, N. A., CORNELISSEN, G. & HAWTHORNE, S. B. 2011. Predicting Pore Water EPA-34 PAH Concentrations and Toxicity in Pyrogenic Impacted Sediments Using Pyrene Content. *Environmental Science & Technology*, 45, 5139-5146.
- BRANDLI, R. C., HARTNIK, T., HENRIKSEN, T. & CORNELISSEN, G. 2008. Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. *Chemosphere*, 73, 1805-1810.
- BT. 2011. *Vågen* [Online]. Bergen: Bergens Tidende. Available: <http://www.bt.no/kamera/article196250.ece> [Accessed 27.07. 2011].
- CAO, X. D., MA, L. N., GAO, B. & HARRIS, W. 2009. Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine. *Environmental Science & Technology*, 43, 3285-3291.
- CHEN, B. L. & CHEN, Z. M. 2009. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, 76, 127-133.
- CHEN, B. L. & YUAN, M. X. 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *Journal of Soils and Sediments*, 11, 62-71.
- CHEN, B. L., ZHOU, D. D. & ZHU, L. Z. 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science & Technology*, 42, 5137-5143.
- CHUN, Y., SHENG, G. Y., CHIOU, C. T. & XING, B. S. 2004. Compositions and sorptive properties of crop residue-derived chars. *Environmental Science & Technology*, 38, 4649-4655.
- CORNELISSEN, G., ELMQUIST, M., GROTH, I. & GUSTAFSSON, O. 2004. Effect of sorbate planarity on environmental black carbon sorption. *Environmental Science & Technology*, 38, 3574-3580.
- CORNELISSEN, G. & GUSTAFSSON, O. 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environmental Science & Technology*, 38, 148-155.
- CORNELISSEN, G., GUSTAFSSON, O., BUCHELI, T. D., JONKER, M. T. O., KOELMANS, A. A. & VAN NOORT, P. C. M. 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental Science & Technology*, 39, 6881-6895.
- CORNELISSEN, G., PFTTERSEN, A., BROMAN, D., MAYER, P. & BREEDVELD, G. D. 2008. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environmental Toxicology and Chemistry*, 27, 499-508.

- CORNELISSEN, G., RIGTERINK, H., TEN HULSCHER, D. E. M., VRIND, B. A. & VAN NOORT, P. C. M. 2001. A simple Tenax (R) extraction method to determine the availability of sediment-sorbed organic compounds. *Environmental Toxicology and Chemistry*, 20, 706-711.
- CORNELISSEN, G., VANNOORT, P. C. M. & GOVERS, H. A. J. 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax(R) and effects of contact time and solute hydrophobicity. *Environmental Toxicology and Chemistry*, 16, 1351-1357.
- EEK, E. 2008. *Mechanisms of contaminant transport and the effect of containment of contaminated sediments*. PhD, University of Oslo.
- 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, 1629-1638.
- EEK, E., CORNELISSEN, G., SCHAANING, M., BEYLICH, B. A., EVENSTAD, T. A., HAUG, I., KIRKHAUG, G. & STORHOLT, P. 2011. Nye materialer og nye metoder for utlegging av tynn tildekking på forurenset sjøbunn. Oslo: NGI.
- EEK, E., GODOY, A., AAGAARD, P. & BREEDVELD, G. D. 2007. Experimental determination of efficiency of capping materials during consolidation of metal-contaminated dredged material. *Chemosphere*, 69, 719-728.
- FETTER, C. W. 1992. *Contaminant Hydrogeology*, New York, Mcmillan Publishing Company.
- FOLKEHELSEINSTITUTTET. 2008. *Dioksiner og dl-PCB - faktaark* [Online]. Oslo: Folkehelseinstituttet. Available:
http://www.fhi.no/eway/default.aspx?pid=233&trg=MainLeft_5648&MainArea_5661=5648:0:15,2917:1:0:0:::0:0&MainLeft_5648=5544:67050::1:5647:18:::0:0 [Accessed 01.10. 2011].
- GADIV PETROCHEMICAL INDUSTRIES LTD. 2011. *Safety Data Sheet Heptane* [Online]. Gadiv Petrochemical Industries Ltd. Available:
<http://www.gadiv.com/Uploads/dbsAttachedFiles/Heptane2011.pdf> [Accessed 07.2011 2011].
- HALE, S. E., LEHMANN, J., RUTHERFORD, D., ZIMMERMAN, A. R., BACHMANN, R. T., SHITUMBANAMA, V., O'TOOLE, A., SUNDQUIST, K. L., ARP, H. P. H. & CORNELISSEN, G. in press. Quantifying the total and bioavailable PAHs and dioxins/furans in biochars. *Submitted to Environmental Science and Technology*.
- HALE, S. E., TOMASZEWSKI, J. E., LUTHY, R. G. & WERNER, D. 2009. Sorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites by activated carbon in clean water and sediment slurries. *Water Research*, 43, 4336-4346.
- JACOBS, P. H. & FÖRSTNER, U. 1999. Concept of subaqueous capping of contaminated sediments with active barrier systems (ABS) using natural and modified zeolites. *Water Research*, 33, 2083-2087.
- JOHNSON, M. D., HUANG, W. & WEBER, W. J. 2001. A Distributed Reactivity Model for Sorption by Soils and Sediments. 13. Simulated Diagenesis of Natural Sediment Organic Matter and Its Impact on Sorption/Desorption Equilibria. *Environmental Science & Technology*, 35, 1680-1687.

- JONKER, M. T. O. & KOELMANS, A. A. 2001. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environmental Science & Technology*, 35, 3742-3748.
- JONKER, M. T. O. & KOELMANS, A. A. 2002a. Extraction of polycyclic aromatic hydrocarbons from soot and sediment: Solvent evaluation and implications for sorption mechanism. *Environmental Science & Technology*, 36, 4107-4113.
- JONKER, M. T. O. & KOELMANS, A. A. 2002b. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations. *Environmental Science & Technology*, 36, 3725-3734.
- JORGENSEN, B. B. & REVSBECH, N. P. 1985. Diffusive Boundary Layers and the Oxygen Uptake of Sediments and Detritus. *Limnology and Oceanography*, 30, 111-122.
- KESTEREN, W. V. & KESSEL, T. V. 2002. Gas bubble nucleation and growth in cohesive sediments. In: JOHAN, C. W. & CEES, K. (eds.) *Proceedings in Marine Science*. Elsevier.
- KRAAIJ, R., MAYER, P., BUSSE, F. J. M., BOLSCHER, M. V., SEINEN, W. & TOLLS, J. 2003. Measured pore-water concentrations make equilibrium partitioning work - A data analysis. *Environmental Science & Technology*, 37, 268-274.
- KRYVI, H., NØTTVEIT, O. M., GJESDAL, A. M. & SOLDAL, O. 2011. *Temamøte FoU-nytt om sedimenter. Sanering av forurensede sedimenter i Bergen havn- status på prosjekter i Vågen og tiltaksforsøk i Kirkebukten*. [Online]. Oslo: Miljøringen. Available: <http://www.miljoringen.no/filopplast/filer/2011-03-21%20Kryvi.pdf> [Accessed 27.07. 2011].
- MANDALAKIS, M., ZEBUHR, Y. & GUSTAFSSON, O. 2004. Efficient isolation of polyaromatic fraction from aliphatic compounds in complex extracts using dimethylformamide-pentane partitionings. *Journal of Chromatography A*, 1041, 111-117.
- MCAULIFFE, C. 1966. Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cycloolefin, and Aromatic Hydrocarbons. *Journal of Physical Chemistry*, 70 (4), pp 1267-1275.
- MCBRIDE, M. B. 1994. *Environmental chemistry of soils*, New York, Oxford University Press.
- MILJØSTATUS. 2011. *Tema: Hav og ferskvann. Farlige kjemikalier. Nasjonale miljømål* [Online]. Klima- og forurensningsdirektoratet. Available: <http://www.miljostatus.no/> [Accessed 01.10. 2011].
- MILJØVERNDEPARTEMENTET 2006-2007. Stortingsmelding nr. 14. Sammen for et giftfritt miljø - forutsetninger for en tryggere fremtid. In: MILJØVERNDEPARTEMENTET (ed.). Oslo: Miljøverndepartementet.
- MUKHERJEE, A., ZIMMERMAN, A. R. & HARRIS, W. 2011. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, 163, 247-255.
- MYRVOLL, F., EEK, E., LØVHOLT, F., GAUER, P., SKEI, J. & SOLHAUG, K. P. 2002. Tildekking av forurensede sjøsedimenter. Oslo.
- NAG, S. 2008. *Tynn tildekking av forurensede sedimenter - Småskala diffusjonsforsøk og modellering av diffusjon gjennom ulike dekklagsmaterialer*. Mastergrad, Norges teknisk-vitenskapelige universitet.

- NEFF, J. M. 1979. *Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates and biological effects*, London, Applied Science Publ.
- NGI. 2009. *Opticap* [Online]. Oslo: Norges Geotekniske Institutt. Available: www.ngi.no [Accessed 05.12 2011].
- NGU. 2008. *Organiske miljøgifter* [Online]. Trondheim: Norges geologiske undersøkelse. Available: <http://www.ngu.no/no/hm/Klima-og-miljo/Forurensning/Organiske-miljogifter/> [Accessed 02.10. 2011].
- OEN, A. M. P., SCHAANNING, M., RUUS, A., CORNELISSEN, G., KALLQVIST, T. & BREEDVELD, G. D. 2006a. Predicting low biota to sediment accumulation factors of PAHs by using infinite-sink and equilibrium extraction methods as well as BC-inclusive modeling. *Chemosphere*, 64, 1412-1420.
- OEN, A. M. R., BREEDVELD, G. D., KALAITZIDIS, S., CHRISTANIS, K. & CORNELISSEN, G. 2006b. How quality and quantity of organic matter affect polycyclic aromatic hydrocarbon desorption from Norwegian harbor sediments. *Environmental Toxicology and Chemistry*, 25, 1258-1267.
- OSLO KOMMUNE. 2011. *Ren Oslofjord* [Online]. Oslo: Oslo Kommune. Available: <http://www.renoslofjord.no/forsiden/> [Accessed 01.10. 2011].
- PALERMO, M. R., CLAUSNER, J. E., ROLLINGS, M. P., WILLIAMS, G. L., MYERS, T. E., FREDETTE, T. J. & RANDALL, R. E. 1998. *Guidance for Subaqueous Dredged Material Capping*. Washington, USA: US Army Corps of Engineers.
- PIERZYNSKI, G. M., SIMS, J. T. & VANCE, G. F. 2005. *Soils and Environmental Quality*, Taylor & Francis Group, LLC.
- ROBERTS, K. G., GLOY, B. A., JOSEPH, S., SCOTT, N. R. & LEHMANN, J. 2010. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. *Environmental Science & Technology*, 44, 827-833.
- SCHWARZENBACH, R. P., CSCHWEND, P. M. & IMBODEN, D. M. 1993. *Environmental Organic Chemistry*, John Wiley & Sons, Inc.
- SCHWARZENBACH, R. P., M., G. P. & M, I. D. 2003. *Environmental Organic Chemistry*, New York, Wiley-Interscience.
- SCIENCELAB.COM. 2005. *Material Safety Data Sheet n-heptane MSDS* [Online]. ScienceLab.com. Available: <http://www.sciencelab.com/msds.php?msdsId=9924237> [Accessed 07.12 2011].
- STUMM, W. & MORGAN, J. J. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*, New York, Wiley.
- SUN, H. W. & ZHOU, Z. L. 2008. Impacts of charcoal characteristics on sorption of polycyclic aromatic hydrocarbons. *Chemosphere*, 71, 2113-2120.
- THIBODEAUX, L. J. & BIERMAN, V. J. 2003. The bioturbation-driven chemical release process. *Environmental Science & Technology*, 37, 252A-258A.
- WANG, X. L. & XING, B. S. 2007. Sorption of organic contaminants by biopolymer-derived chars. *Environmental Science & Technology*, 41, 8342-8348.

- YANG, Y. & SHENG, G. 2003. Pesticide Adsorptivity of Aged Particulate Matter Arising from Crop Residue Burns. *Journal of Agricultural and Food Chemistry*, 51, 5047-5051.
- ZIMMERMAN, A. R. 2010. Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar). *Environmental Science & Technology*, 44, 1295-1301.

10. Appendixes

Appendix 1: Klif's classification guidances

Appendix 2: Plots for diffusion of acenaphthylene, fluoranthene, and pyrene

Appendix 3: Map over the fields for capping dioxin contaminated sediment in the Grenlandfjords

APPENDIX 1

Table 14: Classification of state of metals and organic compounds in sediment. Klif's classification guidance. I: background related to pre-industrial time, II: good, III: moderate, IV: bad, V: very bad

| | I | II | III | IV | V |
|------------------------------------|----------|-------------|-------------|--------------|--------------|
| | Bakgrunn | God | Moderat | Dårlig | Svært dårlig |
| Metaller | | | | | |
| Arsen (mg As/kg) | <20 | 20 - 52 | 52 - 76 | 76 - 580 | >580 |
| Bly (mg Pb/kg) | <30 | 30 - 83 | 83 - 100 | 100 - 720 | >720 |
| Kadmium (mg Cd/kg) | <0.25 | 0.25 - 2.6 | 2.6 - 15 | 15 - 140 | >140 |
| Kobber (mg Cu/kg) | <35 | 35 - 51 | 51 - 55 | 55 - 220 | >220 |
| Krom (mg Cr/kg) | <70 | 70 - 560 | 560 - 5900 | 5900 - 59000 | >59000 |
| Kvikksølv (mg Hg/kg) | <0.15 | 0.15 - 0.63 | 0.63 - 0.86 | 0.86 - 1,6 | >1.6 |
| Nikkel (mg Ni/kg) | <30 | 30 - 46 | 46 - 120 | 120 - 840 | >840 |
| Sink (mg Zn/kg) | <150 | 150 - 360 | 360 - 590 | 590 - 4500 | >4500 |
| PAH | | | | | |
| Naftalen (µg/kg) | <2 | 2 - 290 | 290 - 1000 | 1000 - 2000 | >2000 |
| Acenaftalen (µg/kg) | <1.6 | 1.6 - 33 | 33 - 85 | 85 - 850 | >850 |
| Acenaften (µg/kg) | <4.8 | 2.4 - 160 | 160 - 360 | 360 - 3600 | >3600 |
| Fluoren (µg/kg) | <6.8 | 6.8 - 260 | 260 - 510 | 510 - 5100 | >5100 |
| Fenantren (µg/kg) | <6.8 | 6.8 - 500 | 500 - 1200 | 1200 - 2300 | >2300 |
| Antracen (µg/kg) | <1.2 | 1.2 - 31 | 31 - 100 | 100 - 1000 | >1000 |
| Fluoranthen (µg/kg) | <8 | 8 - 170 | 170 - 1300 | 1300 - 2600 | >2600 |
| Pyren (µg/kg) | <5.2 | 5.2 - 280 | 280 - 2800 | 2800 - 5600 | >5600 |
| Benzo[a]antracen (µg/kg) | <3.6 | 3.6 - 60 | 60 - 90 | 90 - 900 | >900 |
| Chrysen (µg/kg) | <4.4 | 4.4 - 280 | 280 - 280 | 280 - 560 | >560 |
| Benzo[b]fluoranten (µg/kg) | <46 | 46 - 240 | 240 - 490 | 490 - 4900 | >4900 |
| Benzo[k]fluoranten (µg/kg) | | <210 | 210 - 480 | 480 - 4800 | >4800 |
| Benzo(a)pyren (µg/kg) | <6 | 6 - 420 | 420 - 830 | 830 - 4200 | >4200 |
| Indeno[123cd]pyren (µg/kg) | <20 | 20 - 47 | 47 - 70 | 70 - 700 | >700 |
| Dibenzo[ah]antracen (µg/kg) | <12 | 12 - 590 | 590 - 1200 | 1200 - 12000 | >12000 |
| Benzo[ghi]perylene (µg/kg) | <18 | 18 - 21 | 21 - 31 | 31 - 310 | >310 |
| PAH16 ¹⁾ (µg/kg) | <300 | 300 - 2000 | 2000 - 6000 | 6000 - 20000 | > 20000 |
| Andre organiske | | | | | |
| PCB7 ²⁾ (µg/kg) | <5 | 5 - 17 | 17 - 190 | 190 - 1900 | >1900 |
| PCDD/F ³⁾ (TEQ) (µg/kg) | <0.01 | 0.01 - 0.03 | 0.03 - 0.10 | 0.10 - 0.50 | >0.50 |
| ΣDDT ⁴⁾ (µg/kg) | <0.5 | 0.5 - 20 | 20 - 490 | 490 - 4900 | >4900 |

| | | | | | |
|-------------------------------|-------|------------|--------------|---------------|--------|
| Lindan (µg/kg) | | <1.1 | 1.1 - 2.2 | 2.2 - 11 | >11 |
| Heksaklorbenzen (HCB) (µg/kg) | 0.5 | 0.5 - 17 | 17 - 61 | 61 - 610 | >610 |
| Pentaklorbenzen (µg/kg) | | <400 | 400 - 800 | 800 - 4000 | >4000 |
| Triklorbenzen (µg/kg) | | <56 | 56 - 700 | 700 - 1400 | >1400 |
| Hexaklorbutadien (µg/kg) | | <49 | 49 - 66 | 66 - 660 | >660 |
| SCCP ⁶⁾ (µg/kg) | | <1000 | 1000 - 2800 | 2800 - 5600 | >5600 |
| MCCP ⁷⁾ (µg/kg) | | <4600 | 4600 - 27000 | 27000 - 54000 | >54000 |
| Pentaklorfenol (µg/kg) | | <12 | 12 - 34 | 34 - 68 | >68 |
| Oktylfenol (µg/kg) | | <3.3 | 3.3 - 7.3 | 7.3 - 36 | >36 |
| Nonylfenol (µg/kg) | | <18 | 18 - 110 | 110 - 220 | >220 |
| Bisfenol A (µg/kg) | | <11 | 11 - 79 | 79 - 790 | >790 |
| TBBPA ⁸⁾ (µg/kg) | | <63 | 63 - 1100 | 1100 - 11000 | >11000 |
| PBDE ⁹⁾ (µg/kg) | | <62 | 62 - 7800 | 7800 - 16000 | >16000 |
| HBCDD ¹⁰⁾ (µg/kg) | <0.3 | 0.3 - 86 | 86 - 310 | 310 - 610 | >610 |
| PFOS ¹¹⁾ (µg/kg) | <0.17 | 0.17 - 220 | 220 - 630 | 630 - 3100 | >3100 |
| Diuron (µg/kg) | | <0.71 | 0.71 - 6.4 | 6.4 - 13 | >13 |
| Irgarol (µg/kg) | | <0.08 | 0.08 - 0.50 | 0.5 - 2.5 | >2.5 |

| Grenseverdier for TBT | | | | | |
|---|----|--------|-------------|-------------|--------|
| TBT ¹²⁾ (µg/kg) - effektbasert | <1 | <0.002 | 0.002-0.016 | 0.016-0.032 | >0.032 |
| TBT ¹²⁾ (µg/kg) - forvaltningsmessig | <1 | 1-5 | 5 - 20 | 20 - 100 | >100 |

Table 15: Classification of state of metals and organic compounds in water. Klif's classification guidance. I: background, referring to pre-industrial time state, II: good, III: moderate, IV: bad, V: very bad

| | I | II | III | IV | V |
|---|-----------|------------------|---------------|---------------|--------------|
| | Bakgrunn | God | Moderat | Dårlig | Svært dårlig |
| Metaller | | | | | |
| Arsen ($\mu\text{g As/L}$) | <2 | 2 - 4.8 | 4.8 - 8.5 | 8.5 - 85 | >85 |
| Bly ($\mu\text{g Pb/L}$) | <0.05 | 0.05 - 2.2 | 2.2 - 2.9 | 2.9 - 28 | >28 |
| Kadmium ($\mu\text{g Cd/L}$) | <0.03 | 0.03 - 0.24 | 0.24 - 1.5 | 1.5 - 15 | >15 |
| Kobber ($\mu\text{g Cu/L}$) | <0.3 | 0.3 - 0.64 | 0.64 - 0.8 | 0.8 - 7.7 | >7.7 |
| Krom ($\mu\text{g Cr/L}$) | <0.2 | 0.2 - 3.4 | 3.4 - 36 | 36 - 360 | >360 |
| Kvikksølv ($\mu\text{g Hg/L}$) | <0.001 | 0.001 - 0.048 | 0.048 - 0.071 | 0.071 - 0.14 | >0.14 |
| Nikkel ($\mu\text{g Ni/L}$) | <0.5 | 0.5 - 2.2 | 2.2 - 12 | 12 - 120 | >120 |
| Sink ($\mu\text{g Zn/L}$) | <1.5 | 1.5 - 2.9 | 2.9 - 6 | 6 - 60 | >60 |
| PAH | | | | | |
| Naftalen ($\mu\text{g/L}$) | <0.00066 | 0.00066 - 2.4 | 2.4 - 80 | 80 - 160 | >160 |
| Acenaftylene ($\mu\text{g/L}$) | <0.00001 | 0.00001 - 1.3 | 1.3 - 3.3 | 3.3 - 33 | >33 |
| Acenaften ($\mu\text{g/L}$) | <0.000034 | 0.000034 - 3.8 | 3.8 - 5.8 | 5.8 - 58 | >58 |
| Fluoren ($\mu\text{g/L}$) | <0.00019 | 0.0019 - 2.5 | 2.5 - 5 | 5 - 50 | >50 |
| Fenantren ($\mu\text{g/L}$) | <0.00025 | 0.00025 - 1.3 | 1.3 - 5.1 | 5.1 - 10 | >10 |
| Antracen ($\mu\text{g/L}$) | | <0.11 | 0.11 - 0.36 | 0.36 - 3.6 | >3.6 |
| Fluoranthen ($\mu\text{g/L}$) | <0.00029 | 0.00029 - 0.12 | 0.12 - 0.9 | 0.9 - 1.8 | >1.8 |
| Pyren ($\mu\text{g/L}$) | 0.000053 | 0.000053 - 0.023 | 0.023 - 0.023 | 0.023 - 0.046 | >0.046 |
| Benzo[a]antracen ($\mu\text{g/L}$) | <0.000006 | 0.000006 - 0.012 | 0.012 - 0.018 | 0.018 - 0.18 | >0.18 |
| Chrysen ($\mu\text{g/L}$) | | <0.07 | 0.07 - 0.07 | 0.07 - 0.14 | >0.14 |
| Benzo[b]fluoranten ($\mu\text{g/L}$) | <0.000017 | 0.000017 - 0.03 | 0.03 - 0.06 | 0.06 - 0.6 | >0.6 |
| Benzo[k]fluoranten ($\mu\text{g/L}$) | | <0.027 | <0.027 - 0.06 | 0.06 - 0.6 | >0.6 |
| Benzo(a)pyren ($\mu\text{g/L}$) | <0.000005 | 0.000005 - 0.05 | 0.05 - 0.1 | 0.1 - 0.5 | >0.5 |
| Indeno[123cd]pyren ($\mu\text{g/L}$) | <0.000017 | 0.000017 - 0.002 | 0.002 - 0.003 | 0.003 - 0.03 | >0.03 |
| Dibenzo[ah]antracen ($\mu\text{g/L}$) | | <0.03 | 0.03 - 0.06 | 0.06 - 0.6 | >0.6 |
| Benzo[ghi]perylene ($\mu\text{g/L}$) | <0.00001 | 0.00001 - 0.002 | 0.002 - 0.003 | 0.003 - 0.03 | >0.03 |
| Andre organiske | | | | | |
| $\Sigma\text{DDT}^{1)}$ ($\mu\text{g/L}$) | | <0.001 | 0.001 - 0.025 | 0.025 - 0.25 | >0.25 |
| Lindan ($\mu\text{g/L}$) | | <0.02 | 0.02 - 0.04 | 0.04 - 0.2 | >0.2 |
| HCB ²⁾ ($\mu\text{g/L}$) | | <0.013 | 0.013 - 0.05 | 0.05 - 0.47 | >0.47 |
| Pentaklorbenzen ($\mu\text{g/L}$) | | <1 | 1 - 2 | 2 - 10 | >10 |
| Triklorbenzen ($\mu\text{g/L}$) | | <4 | 4 - 50 | 50 - 100 | >100 |
| Hexaklorbutadien ($\mu\text{g/L}$) | | <0.44 | 0.44 - 0.59 | 0.59 - 5.9 | >5.9 |
| SCCP ³⁾ ($\mu\text{g/L}$) | | <0.5 | 0.5 - 1.4 | 1.4 - 2.8 | >2.8 |
| MCCP ⁴⁾ ($\mu\text{g/L}$) | | <0.10 | 0.10 - 0.59 | 0.59 - 1.2 | >1.2 |
| Pentaklorfenol ($\mu\text{g/L}$) | | <0.35 | 0.35 - 1 | 1 - 2 | >2 |
| Oktylfenol ($\mu\text{g/L}$) | | <0.12 | 0.12 - 0.27 | 0.27 - 1.3 | >1.3 |
| Nonylfenol ($\mu\text{g/L}$) | | <0.33 | 0.33 - 2.1 | 2.1 - 4.1 | >4.1 |
| Bisfenol A ($\mu\text{g/L}$) | | <1.6 | 1.6 - 11 | 11 - 110 | >110 |
| TBBPA ⁵⁾ ($\mu\text{g/L}$) | | <0.052 | 0.052 - 0.9 | 0.9 - 9 | >9 |
| PBDE ⁶⁾ ($\mu\text{g/L}$) | | <0.53 | 0.53 - 1.4 | 1.4 - 2.8 | >2.8 |
| HBCDD ⁷⁾ ($\mu\text{g/L}$) | | <0.31 | 0.31 - 1.1 | 1.1 - 2.2 | >2.2 |
| PFOS ⁸⁾ ($\mu\text{g/L}$) | | <25 | 25 - 72 | 72 - 360 | >360 |

APPENDIX 2

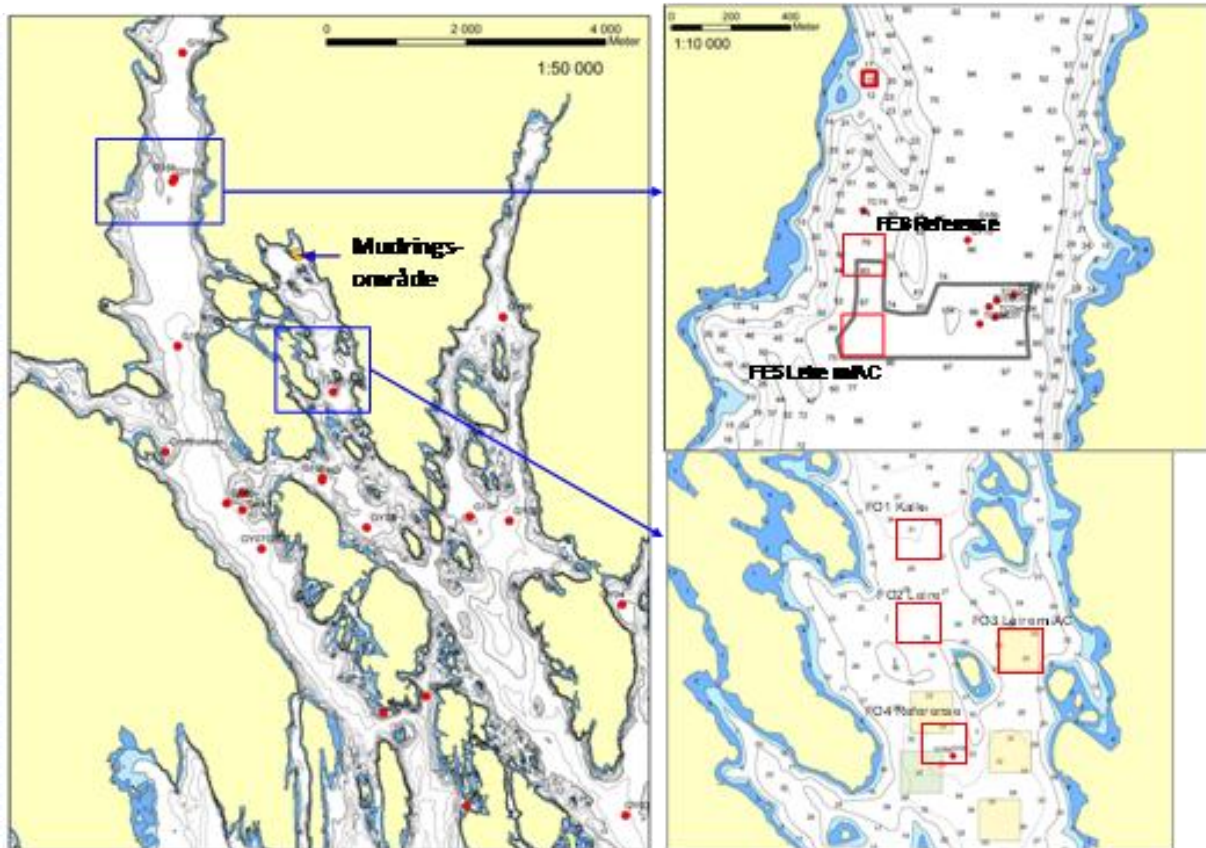


Figure 24: Map over the fields for capping dioxin contaminated sediment in the Eidangerfjord (to the left) and Ormerfjord (in the middle), the Grenlandfjords. In the Eidangerfjord the fields were the reference field and the activated carbon (AC) field. In the Ormerfjord the fields were the reference field, the AC field, crushed gneiss field, and the limestone field.

APPENDIX 3

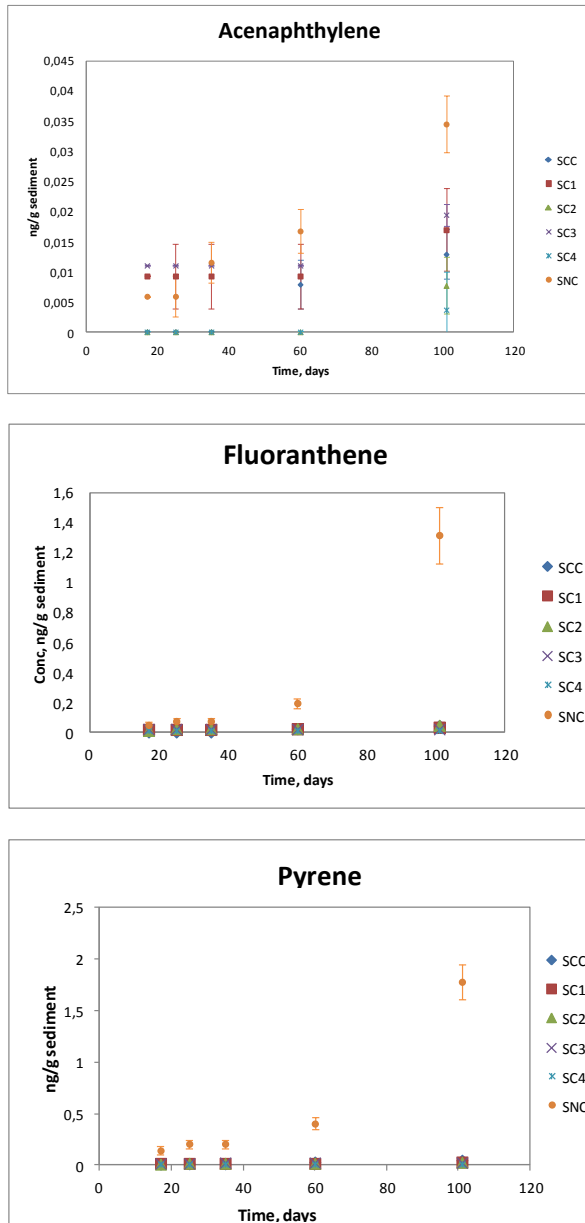


Figure 25: Diffusion of acenaphthylene, fluoranthene, and pyrene. SCC- sediment clay cap, SC1- sediment capped with corn stover, SC2- sediment capped with oak250, SC3- sediment capped with oak400, SC4- sediment capped with oak650, SNC- sediment no cap. SC1-4 are a mix of clay and biochar. The standard deviation represents the deviation on three replicates of the measurements.