In situ remediation of contaminated sediments
using thin-layer capping

— efficiency in contaminant retention and ecological implications

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Abstract

Hydrophobic organic contaminants (HOCs) often reside in sediments sorbed to particles, most tightly to particles with high content of organic carbon. If persistent, such pollutants can accumulate in the sediment for many years and constitute a contamination risk for sediment-living organisms and organisms at higher trophic levels, including humans.

Since traditional remediation techniques are associated with complications (e.g. release of contaminants during dredging operations, disturbance of benthic faunal communities), or constraints (handling of large amounts of contaminated sediment and water, limitations due to depth and size of the area, high costs), there is a need for new alternative methods.

In situ remediation through thin-layer capping (a few centimeter cover) with a sorbing material such as activated carbon (AC) has been proposed as an alternative remediation method. Compared to traditional remediation techniques, AC amendment in a thin layer means less material handling and lower costs and is assumed to be less disruptive to benthic communities. The objectives of this thesis were to investigate the ecological effects from thin layer capping as well as the efficiency in contaminant retention.

Thin layer capping amended with AC proved to reduce availability of HOCs to the tested organisms, the gastropod *Nassarius nitidus* (Paper II), the clam *Abra nitida* (Paper III) and to polychaete worms (Paper II and III). The remediation technique also decreased the sediment-to-water fluxes of the contaminants (Paper II and III).

However, AC amended thin-layer capping was also found to cause negative biological effects. In laboratory studies with only a few species the negative effects were minor, or difficult to discern with the endpoints used (Paper II and III). In a larger multi-species mesocosm (boxcore) study, on the other hand, the negative effects were more prominent (Paper I) and in a large scale field study the benthic community was found to be profoundly disturbed by the AC amendment, with the effects persisting or even worsening ca one year (14 months) post amendment (Paper IV).
List of Papers


My contribution to the papers:

I. Participated in the termination of the experiment. Main contribution to data handling and statistical analysis of the functional responses. Second most important contribution to the writing.

II. Involved in the planning and the performance of the boxcore experiment. Involved in data handling and statistical analysis, and large contribution in the discussion and interpretation of the results. Contributed to the writing mainly by reviewing and commenting.

III. Involved in the field sampling and the laboratory experiment. Also involved in the analytical chemistry measurements of contaminants. Main contribution in data handling and statistical analyses. Main writer of the paper.

IV. Involved in the field sampling, and parts of the taxonomic analyses. Involved in data compilation and construction of the charts. Main writer, responsible for all the statistical analyses, and a significant involvement in the interpretations of results.
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Introduction

There is a growing concern about environmental pollution and its effects on humans and on our environment. Many contaminants are either directly discharged into water or indirectly end up in aquatic ecosystems through run-off and atmospheric deposition, and subsequently most of them are deposited in sediments. Negative ecological and toxicological effects have resulted in the ban of several persistent organic pollutants (POPs) such as DDT and PCBs since the 1970s. After banning the concentrations of e.g. PCBs have decreased in biota, but have then leveled off or even increased in sediments (Jonsson 2000).

Sediments now constitute large reservoirs for contaminants and may constitute a risk to benthic organisms and to higher trophic levels, including humans. Endocrine disruption and reproductive disorders in seal and birds of prey (Olsson et al. 1992, Bignert et al. 1995), and even in humans (e.g. decreased sperm amount and motility) have been attributed to exposure to persistent organochlorines (e.g. PCB) (Richthoff et al. 2003, Hauser et al. 2003, Rignell-Hydbom et al. 2004) as well as retarded development of children (Rogan et al. 1988). Fatty fish, e.g. herring, from the Baltic Sea has been a major exposure route for chlorinated contaminants to humans (Sjödin et al. 2000, Kiviranta et al. 2001), and the concentrations of dioxins and dioxin-like PCB congeners in fatty fish from the Baltic Sea have exceeded the EU consumption limit values. An exception from the EU regulations includes restriction of Baltic fish to domestic markets, and requirements for authorities to announce guidelines for maximum recommended consumption of fish from the Baltic Sea. Similar problems can be seen in other countries, for example high sediment concentrations of dioxins in the Grenland fjord, Norway (Breedveld et al. 2010), caused by chlorination in a previous magnesium production plant. Consequently, dioxin concentrations in benthic organisms and demersal fish are high and severe restrictions in commercial fishing and in sea food consumption from the Grenland fishing have been implemented.

Besides being a source for contaminant transfer, sediment habitats and their benthic organisms can also be negatively affected by the contaminants. Soft-sediment
habitats cover most of the ocean floor, corresponding to approximately 70% of the
global surface, and harbor an immense number of species (Snelgrove 1999), involved
in the cycling and regulation of vital nutrients (Snelgrove et al. 1997). Disturbances of
these ecosystems can affect species composition and diversity and change nutrient
fluxes (Rhoads & Germano 1986, Diaz & Rosenberg 1996, Solan et al. 2004). In the
end such structural changes can affect important processes such as the generation of
food for human consumption (Snelgrove 1999).

Awareness of the problem with contaminated soils and sediments has brought many
western countries to start remediation initiatives to clean up soils and sediments, for
example in USA (USEPA 2005), Norway (Miljøverndepartementet 2006) and in
Sweden (Regeringskansliet 2006, NV 2008). In 1999, the Swedish government
launched a series of environmental goals, and among them the goal of “an
environment free from harmful contaminants” by 2020 (Regeringskansliet 2006, NV
2008), and in Norway, there is an extensive national program to address the problem
of contaminated fjords (Miljøverndepartementet 2006).

Objectives of the thesis

The aim of this thesis was to study the effects of thin layer capping with activated
carbon on: 1) reducing contaminant release and bioaccumulation; 2) the ecology of
benthic organisms.

Ecological effects of activated carbon and various other capping materials on a
benthic community were initially studied using boxcosms with intact sediment and
fauna at NIVAs marine research station Solberstrand, Norway (Paper I). In a larger
‘full-scale’ field remediation pilot study in the Grenland fjord, Norway, the impact
from an in situ thin-layer capping remediation was assessed on two benthic
communities at 30 m and 95 m depth, respectively (Paper IV).

The contaminant retention potential of thin layer capping amended with activated
carbon (AC) was tested using a boxcosm experiment at Solbergstrand, Norway
(Paper II), and also in a laboratory bioaccumulation study (Paper III) using intact
sediment cores from an in situ remediation study in the Trondheim Harbor, Norway.
Background

Bioaccumulation and trophic transfer

Due to their hydrophobicity HOCs generally have low water solubility and readily sorb to particles and especially to carbon-rich organic matter and black carbonaceous matter such as soot particles, commonly referred to as black carbon (BC). This means HOCs accumulate in compartments rich in organic matter and black carbon (Ghosh et al., 2000; Grathwohl & Kleineidam, 2000). Hence many of these contaminants are sequestered in sediment and if they are resistant to degradation (i.e. persistent) they can remain in sediments for years or decades. However, these contaminants do not always stay in the sediment. A dynamic process with a constant desorption from and resorption to organic matter will continuously make a portion of the HOCs available to other compartments, including organisms. Organisms contain organic matter with high affinity for HOCs, thus pollutants bioaccumulate into animal tissues, especially into lipids (Matthews & Dedrick, 1984). When contaminants have entered an organism they have also entered a route for trophic transfer to other organisms in the food web. Contaminants in organisms that are preyed or grazed upon can accumulate in the new organism (grazer, predator) and for contaminants like PCB, DDT and mercury also biomagnify to higher concentrations at each trophic level, and may finally reach toxic levels (Gray 2002).

The role of sediments for ecosystem function and ecosystem services

Oceans cover about 70% of the globe and constitute 2/3 of the value of global ecosystem services (Costanza et al., 1997), including food production and climate regulation. In turn, soft-sediment habitats cover most of the ocean floor, and harbor a diverse system of species (Snelgrove 1999). The benthic system supports seafood production, e.g. through demersal fish that prey on benthic invertebrates and by the recirculation of nutrients used for plankton growth, which many pelagic fish rely on.

The pelagic system and benthic system are strongly connected through benthic-pelagic coupling, the circulation of nutrients and matter from one system to the other (Elmgren 1978, Graf 1992). Primary producers in the photic zone, such as phyto-
plankton grow by energy from the sunlight and nutrients e.g. released from soft-bottom sediment. Following planktonic blooms a large portion of the plankton biomass settles to the bottom sediment in one or a few pulses per year. The benthic organism are food limited during large parts of the year and rely heavily on this input (Elmgren 1978, Graf 1992), since the major portion of the sediment areas are in the aphotic zone and basically lack primary production. The algae are consumed by the benthic organism and nutrients, such as nitrogen, phosphorous, silicon and carbon, are recirculated back to the pelagic zone. Benthic fauna significantly facilitates the breakdown and mineralization (e.g. Heip 1995, Snelgrove et al. 1997, Welsh 2003), directly through consumption but mainly indirectly through the influences benthic fauna has on microorganisms. After nutrients have been recirculated to the photic zone the primary producers can start a new production loop. Ecosystem functions like nutrient circulation are often influenced by a set of organisms with different characteristics connected to a life on or in the sediment, such as position in the sediment, activity in the sediment and feeding mode. Deposit feeders are often dominant in sediments in the aphotic zone. In shallower water also filter feeders and suspension feeders can be abundant. These filter out suspended material, including phytoplankton and bacteria and hence these can influence the water quality.

**Bioturbation**

Bioturbation, the reworking and ventilation (bioirrigation) of sediments by benthic organisms is essential for the cycling of vital nutrients and for degradation of organic material (Kristensen & Hansen 1999, Aller 2001). The amount of movement and bioturbation by an organism, and the vertical position it inhabits in the sediment, are largely determined by the feeding manner, competition, avoidance of predators and the physicochemical conditions e.g. oxygen and sulfide levels in the sediment. Sessile and tube living organisms have a smaller contribution to bioturbation while burrow diggers, and very active species like the brittle stars and sea urchins can have a large impact on total bioturbation. Generally larger, late successional and often sensitive, macrobenthic animals have a major influence on bioturbation, the benthic-pelagic coupling and nutrient generation that supports primary production (Diaz & Schaffner 1990, Diaz & Rosenberg 1996, Lohrer et al. 2004).
Bioturbation also has implications for release and sequestration of contaminants. Changes in sulfide and oxygen levels can change the bioavailability and influence the release of heavy metals (Griscom et al. 2000). Bioturbating organisms can also damage the integrity of a remedial passive cap layer and cause leakage through the cap, which is a reason why thick layer (30-50 cm) are used in conventional capping. On the other hand, bioturbation is expected to facilitate mixing of the thin layer of an active sorbent into the contaminated sediment and increase the contaminant-sorbent association.

**Biodiversity – Redundancy – Resilience**

Biodiversity in its broadest definition spans from genetic plurality, over the diversity of traits and species, to habitat and ecosystem diversity. Generally, higher number of the components (e.g. species) means higher diversity. This thesis focuses on the number of species as primary diversity measurement. Generally, larger number of species means higher redundancy of functional traits, larger resource utilization and higher biomass (Cardinale et al. 2006, Duffy 2009). More species also reduces variance in the functionality (Duffy 2009), and provides a higher resilience to cope with perturbations (Elmqvist et al. 2003). According to the redundancy concept the integrity of the ecosystem processes often relies on a surplus of organisms, which can carry out a certain process, and loss of a single species with a specific function from a diverse community, will have a minor effect on the ecosystem function as long as other species can step in for the lost one (Walker 1992). Hence, an undisturbed diverse system generally will have a higher resilience, and conversely a disturbed and less diverse system will be more vulnerable to additional perturbations and losses of species.

However, the complex nature of an ecosystem or community makes predictions difficult, and early loss of a “key” species with a disproportionally large contribution to an ecological function can result in an instant and large drop in that function. Key species, often large, late successional organisms impart temporal stability of sediment processes and benthic food production (Heip, 1995; Diaz and Rosenberg, 1996), while following disturbance, a shift to smaller shallow-burrowing
opportunistic species often will shorten the food chains and result in larger temporal variation in the flow of energy through the system, which can affect demersal and pelagic fish populations (Heip, 1995; Diaz and Rosenberg, 1996).

So far, there is limited information on ecological effects of remedial actions with capping on benthic communities, however, an analogy can be made to the effects of organic enrichment on benthic animals as described by the benthic community succession model by Pearson and Rosenberg (1978), and the extension of this model to include effects from physical disturbance (Rhoads and Germano, 1986) and pollution (Diaz and Rosenberg, 1996). In this model, succession shows both temporal and spatial patterns with a gradual response from the disturbance's source (Heip, 1995). The contaminants in polluted sediment constitute a blend of disturbances, and after a capping remediation the capping material itself may act as a source of disturbance. However, active sorbents remediation is supposed to sequester the contaminants and make them less bioavailable, and thus offer relief from the contaminant stress biota are experiencing. The question is to what extent the benthic communities are disturbed by the capping material itself, the capacity for them to recover and the length of time it will take for a benthic community to recover following a capping treatment.

**Sediment remediation**

Dredging (Figure 1b), currently the most common clean-up method (Zimmerman et al. 2004), is a complex and costly task that includes problems with 1) handling vast amounts of contaminated wet sediments and 2) requiring areas for long-term deposition on land (NRC 2001, Zimmerman et al. 2004). Dredging is restricted to shallow waters and is not always effective, since it often also causes a large redistribution of contaminants through resuspension and volatilization, and there may be significant amounts of residual contaminants left in the sediment (Zimmerman et al. 2004, Ghosh et al. 2011). In addition dredging is also highly disruptive to the benthic community (Ghosh et al. 2011).
A different approach is sediment remediation *in situ* (‘on site’), where contaminants are either biodegraded by the addition of microorganisms (bioremediation) or rendered less available by covering the polluted sediment with a cap (Zimmerman et al. 2004). A covering, or “capping”, may be deployed using a 30-50 cm cap of clean sediment, or other geo-materials, to embed the contaminants into subjacent layers in order to reduce their release to the water and uptake in pelagic organisms (Figure 1c). However, the addition of a thick cap is also likely to change the habitat and to have a negative impact on benthic organisms, and for large areas this also means adding enormous amounts of material.

Several promising experimental studies have used activated carbon (AC) as sorbent to sequester contaminants in polluted sediments (Zimmerman et al. 2004, 2005, Millward et al. 2005, McLeod et al. 2007, Cho et al. 2009, Cornelissen et al. 2011, Beckingham & Ghosh 2011, Kupryianchyk et al. 2013), which have been successful in reducing the bioaccumulation of Hg and of several organic contaminants. Sequestration of contaminants with activated carbon has also shown to increase with time (Werner et al. 2006, Cho et al. 2007, Beckingham & Ghosh 2011). In these studies, however, AC was directly mechanically mixed into the contaminated sediment and such a direct mixing of AC or other sorbents into the contaminated sediment on site is not an option at greater depths.

**Thin layer capping and amendment with activated carbon (AC)**

Large physical perturbations to benthic communities may be avoided by deployment of a thin cap layer of sediment amended with a sorbent (Figure 1e-f), e.g. AC, on to the sediment surface and allowing the macrofauna to take care of mixing it into the sediment through bioturbation (Figure 1e-f). Sediment amendment with activated carbon is getting more and more attention (Ghosh et al. 2011), and a few different active capping materials have been tested for different pollutants, e.g. aluminum oxide for mercury (Hg) pollution (WSP 2012), and activated carbon for various organic contaminants sediments (Zimmerman et al. 2004, 2005, Millward et al. 2005, Sun & Ghosh 2007, McLeod et al. 2007, Cho et al. 2009, Cornelissen et al. 2011, Beckingham & Ghosh 2011, Kupryianchyk et al. 2013).
In situ thin layer capping remediation with an active capping material has the potential to sequester the contaminants without disrupting the benthic community (Sun & Ghosh 2007). In a remediation study in Grasse River, USA (Beckingham & Ghosh 2011) activated carbon applied as a thin-layer on top of the sediment (Figure 1e) significantly reduced the bioaccumulation of PCBs in the freshwater oligochaete worm *Lumbriculus variegatus* (Beckingham & Ghosh 2011). Recent studies have mixed AC with clay on land or on ship and then applied a thin AC-enriched slurry on top of the sediment (Cornelissen et al. 2011, 2012), the ecological effects of this type of thin-layer capping method are still largely unknown and are the focus of this thesis. (Figure 1f).

**Natural attenuation – an alternative to remediation**

In some situations natural recovery may be the best “remediation option” (USEPA, 2005). At old modestly polluted sites where sedimentation already has started to cover the contaminated sediment, Monitored Natural Attenuation (MNA) or Monitored Natural Recovery (MNR) may be a good alternative, leaving benthic biota uninterrupted (USEPA, 2005). The advantages of MNR are the low cost and that it is non-invasive, but the natural burial and risk reduction are very slow and leaving the contaminants in place can be considered disadvantageous (USEPA, 2005).
Figure 1. Sediment *in situ* remediation techniques:

a. Untreated contaminated sediment, before remediation; or left for “Natural Attenuation”.


c. Conventional 30-50 cm thick cap of clean material to block contaminant routes from native sediment to overlying water (including organism burrows through the capping layer). Benthic community buried and compressed, resulting in high organism mortality.

d. Mechanical mixing of the sorbent (e.g. AC) into the native sediment in order to facilitate close contact between sorbent and contaminant. Benthic community disrupted by the mechanical mixing.

e. Thin layer capping with a single material, for example a sorbent like activated carbon, released above the sediment surface. Subsequent mixing of the cap material into native sediment can be mediated by bioturbation.

f. Thin layer capping with an active sorbent (e.g. activated carbon) mixed in a slurry with a passive carrier material (e.g. clay), released above the sediment surface. Subsequent mixing of the cap material into native sediment can be mediated by bioturbation.
General findings

Paper I:

A mesocosm study on ecological effects of materials proposed for thin layer capping of contaminated sediments.

The aim of Paper I was to investigate the effects of capping materials on benthic fauna (macrofaunal, meiofaunal and bacteria) and on functional responses (e.g. O₂ respiration and nutrient fluxes). Boxcores with intact soft clay bottom benthic communities were collected in the field and exposed in the lab to nine different capping materials, proposed for remediation through thin layer capping (Figure 1e). The boxcores were sampled from 80 meters depth in the Langangsfjord, Norway. The tested materials were: activated carbon, Kraft lignin, sand, hyperite, clay, plaster and marble (the two last being industrial waste products) (see Figure 2).

Significant deviations from the uncapped control were observed for all the tested capping materials. The materials most similar to the indigenous sediment i.e. clay and sand, and also the coarse sand "hyperite", displayed relatively minor deviations from controls. Differences from the controls for these materials were generally seen in the structural endpoints (macrofauna richness, meiofauna community and bacterial community), although reduced flux of SiO₄ was also significantly different in the suspended clay treatment.

The largest deviations from the control were observed for the plaster and the fine and coarse marble products, where many of the functional endpoints were significantly different, as well as all the structural ones, except macrofauna abundance in the coarse marble treatment. The plaster treatment was different from control for all endpoints except for sediment oxygen flux. The differences in structural endpoints were associated to massive reductions in the abundances of benthic organisms and species. The carbonaceous material, activated carbon and Kraft lignin caused intermediate perturbations. Effects caused by Kraft lignin were more severe than those from activated carbon, mainly due to increased oxygen consumption in
presence of Kraft lignin. Probably the reduced oxygenation of the sediment in lignin treatments also affected the fauna components. Negative effects from AC were, however, also observed e.g. a reduction in macrofauna species by ca 50 % and abundance by ca 40 % compared to uncapped controls (Figure 2).

**Paper II:**

*Capping Efficiency of Various Carbonaceous and Mineral Materials for In Situ Remediation of Polychlorinated Dibenzo-p-dioxin and Dibenzofuran Contaminated Marine Sediments: Sediment-to-Water Fluxes and Bioaccumulation in Boxcosm Tests.*

The main objective was to study whether thin layer capping with carbonaceous material would reduce sediment-to-water fluxes and bioaccumulation of polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene and octachlorostyrene, in a boxcore experiment. Activated carbon and Kraft-lignin were tested as active capping materials together with passive materials e.g. clay and limestone as carrier material (Figure 1f). Sediment-to-water fluxes were measured passive samplers SPMD (semi-permeable membrane device). Bioaccumulation was measured in the gastropod *Nassarius nitidus* and polychaete worms, *Nereis* spp. The sediment and caps were also bioturbated for a couple of months by the brittle star *Amphiura* spp and the clam *Abra alba*. Condition of the exposed organisms was assessed with measurements of animal survival, wet weight and lipid content.

Sediment-to-water fluxes and bioaccumulation by the two test species, the surface-dwelling *Nassarius nitidus* and the deep burrowing *Nereis* spp., decreased with increased cap thickness and with addition of active material. Activated carbon was more efficient than lignin, and a ~90% reduction of fluxes and bioaccumulation was achieved with 3 cm caps with 3.3% AC.

Lignin had a significantly negative impact on the survival of worms. The experiment revealed no significantly negative effects from the activated carbon, although only half as many worms survived in AC compared to the cap control. Clay and the passive limestone materials did not affect the biota.
Figure 2. Macrofauna communities in the treatments in Paper I. Colored bars show mean number of individuals per m$^2$. Grey bars show mean number of taxa per boxcore. Error bars denote SE. Field control (FC), Control (CT), Suspended Clay (CS), Cut Clay (CC), Sand (SA), Hyperite (HY), Activated Carbon (AC), Kraft Lignin (LG), Coarse Marble (MC), Fine Marble (MF) and Plaster (PL).

Figure 3. PAH and PCB concentrations in the clam Abra nitida exposed to control sediment (CT) and the activated carbon thin-capping treatment (AC+clay) in Paper III (mean ± SD). Beneath the chart is capping efficiency (CE) presented (reduction in bioaccumulation) for the thin-capping treatments, as well as the results from the univariate analyses (performed on the real concentrations); * = significantly lower levels compared to CT; ns = non-significant.
Paper III:

Reduced bioaccumulation of PCBs and PAHs by *Hediste diversicolor* and *Abra nitida* following remediation in situ with activated carbon in the Trondheim Harbor, Norway.

The main objective of this paper was to study whether thin layer capping with activated carbon would reduce bioaccumulation of PAHs and PCBs in two different benthic organisms exposed to intact cores from a capping experiment in Trondheim Harbor, Norway. Three types of thin-layer capping methods with AC were compared: (i) activated carbon only (AC-only) (Figure 1c), (ii) activated carbon blended in clay (AC+clay) (Figure 1d) and (iii) activated carbon covered by sand in order to minimize cap erosion (AC+sand). From the *in situ* remediated fields sediment cores were sampled using transparent acrylic glass tubes. The tubes with intact sediment and overlying water were used as microcosms for a 31-34 days bioaccumulation study with the polychaete worm *Hediste diversicolor* and the clam *Abra nitida*. Changes in PAH concentrations in pore water and overlying water were also examined using passive samplers (POM). Condition of the organisms exposed to activated carbon was assessed with measurements of animal survival, wet weight and lipid content.

Reduced bioaccumulation was observed in the worm *Hediste diversicolor* and in the clam *Abra nitida* exposed to AC+clay treatment (Figure 3). PAH accumulation was on average 79% lower and PCB levels 59% lower in worms from the AC+clay treatment compared to the un-capped controls. AC-only also reduced bioaccumulation of PCBs in the worms (by 66%), however, no reduction of PAHs. No effect on bioaccumulation was seen in the AC+sand treatment. Reduced bioaccumulation in the clams was on average 81% for PAHs and 76% for PCBs in the AC+clay. The activated carbon treatments also reduced the pore water and the overlying water levels of PAHs.

Survival rate in the 31-34 days laboratory experiment was good for both organisms, no differences between treatments or uncapped control. Animal biomass was also similar among the treatments, though the clams showed a 23% and 27% decrease in wet weight after exposure to the control and AC+clay treatment, respectively. There was a significant reduction in lipid content in worms exposed to AC-only, and a non-significant similar trend in reduction for AC+clay.
**Paper IV:**

*Field experiment on thin-layer capping in the Grenland fjords, Norway – Effects on the benthic community 2009-2010*

In this large field study, capping with AC, clay and limestone was tested for the first time *in situ* on marine sediments at two different depths (30 and 95 meters), in the Grenland fjords in Norway. This study presents the effects of the capping treatments on benthic macrofauna. Capping field sites were chosen at locations in two arms of the Grenland fjords, the Eidangerfjord (95 m) and the Ormefjord (30 m), both of which are contaminated with dioxins and furans. At the Eidangerfjord site an experimental field of 200x200 m (i.e. 40 000 m²) was capped with a 1.5-2 cm thin clay slurry amended with AC (2 %), and was compared to two untreated reference fields at 80 meters and 95 meters depth respectively. At the more shallow Ormefjord (30 m depth) three thin-layer capping treatments, AC+clay, sediment clay (Clay) and crushed limestone (Lime), were compared with an un-capped reference sites. The field sites were 100x100m (i.e. 10 000 m²) each.

The AC+clay amendment caused large perturbations to the benthic community in both fjords with a significant decrease in numbers of species, organism abundance and total biomass. The negative effects were significant already one month after capping deployment both at 30 and 95 meters depth, suggesting an acute toxic effect and/or emigration of organisms from the AC+clay fields. After 14 months the negative effects were even more pronounced in the shallow (30 m) Ormefjord, indicating possible long-lasting effects on ecological processes like nutrient circulation and food supply to higher trophic levels. Initially the AC+clay treatment had its more severe impact on faunal functional groups like filter feeders and suspension feeder. After 14 months post amendment the AC+clay treatment also had affected deposit feeders and subsurface deposit feeders, and consequently the abundances of carnivores was also decreased. The number of species, organism abundance and total biomass in AC+clay after 14 months were all ca 80-90 % lower compared to REF and to Clay.
The absence of negative effect from Clay, as well as the relatively low perturbation from Lime, suggests that thin-layer capping can be used without causing large and long-term disturbances to the benthic communities.

**Figure 4.** Abundance per m² for a) the Ormefjord and b) the Eidangerfjord, sampled 1 month and 14 months after capping deployment. (Mean ± SE). Susp, Suspension feeders; Filt.F, Filter feeders; Sub, Subsurface deposit feeders; Dep, Deposit feeders; Symb, Organisms with a symbiotic relationship which can be used for obtaining nutrients and/or energy; Pre, Predators and Scavengers.
Discussion

Thin layer capping

The relatively limited perturbations on benthic fauna by clay, sand and limestone (i.e. materials more similar to indigenous sediment) in Paper I, II and IV, suggest that thin layer capping as a technique (Figure 1e-f) can be used with moderate effects to benthic communities with these passive materials. However, these materials are at the same time the least efficient in terms of contaminant sequestration (Paper II). Such materials, for example clay, can on the other hand be a good carrier material for an active sorbent to be mixed with. It is, however, essential that the active sorbent itself is not toxic to the benthic fauna, as was the case in Paper IV.

The negative effects from the two marble treatments in Paper I, were probably due to the presence of toxic additives from the manufacturing process (e.g. the addition of tensides), since a purified version of the fine marble (named Lime in Paper II) showed no negative effect and neither did an additional, crushed limestone material (Paper II). The crushed limestone was also used in the large-scale in situ capping in the Ormefjord with only limited effects on the benthic community (Paper IV).

Capping efficiency, in terms of reduced bioaccumulation and lowered pore water levels of PAHs and PCBs (Paper III), was higher when AC was mixed into a bentonite clay carrier (Figure 1f), compared to capping with AC in its pure form (AC-only) (Figure 1e). Though such a comparison between a cap made of a pure sorbent and a cap made of a passive carrier amended with an active sorbent was not included in the ecological assessment in Paper I, the lipid loss in Hediste diversicolor when exposed to AC+clay was lower compared to when exposed to AC-only in (Paper III), and thus confirms the beneficial role of the carrier material. Less perturbation to the benthic communities were also seen in Trondheim Harbor by AC+clay compared to AC-only (Cornelissen et al. 2011), as well as less erosion.
Active sorbents

This thesis compares various materials suggested for thin layer capping and then focuses especially on activated carbon as an active sorbent for remediation of contaminated sediment. Activated carbon was chosen for its excellent sorption properties (Grathwohl & Kleineidam 2000, Cornelissen et al. 2005) and for its good results in contaminant sequestration in other studies (Zimmerman et al. 2004, 2005, Millward et al. 2005, Cornelissen et al. 2006, Cho et al. 2007, Sun & Ghosh 2007, McLeod et al. 2007). Kraft Lignin also has relatively good sorption properties compared to passive materials, however, far less than activated carbon (Paper II), and the negative effects from the coniferous (soft wood) Kraft lignin (Paper I and II) made this material less attractive than e.g. activated carbon. The higher oxygen respiration for the lignin treatment (Paper I and II) seems to be the main cause of the increased mortality (Paper I and II), most likely due to degradation of lignin monomers which would consume oxygen and have negative effects on the benthic community.

Reduced bioaccumulation and sediment-to-water contaminant fluxes

The results from Paper II and III show that thin-layer capping with activated carbon mixed with clay or limestone can significantly reduce bioaccumulation by marine benthic organisms of a variety of contaminants, such as PAHs, PCBs, polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene (HCB) and octachlorostyrene (OCS). The capping efficiency was measured in the deep digging omnivorous polychaete worm Hediste diversicolor, in the deposit feeding clam Abra nitida and in the omnivorous gastropod Nassarius nitidus, and was about 90 % for the dioxins, furans, HCB and OCS. The capping efficiency in reducing bioaccumulation of PAHs was approximately 80 %, and between 59-76 % for the PCBs.

Sediment-to-water fluxes of the same contaminants were also effectively reduced by the activated carbon treatments. The capping efficiency in terms of reduced release of contaminants to the overlying water was approximately 90% for dioxins, furans, HCB and OCS in the AC amended caps (Paper II), and up to 90 % for PAHs in the AC+clay
treatment (Paper III). The pore water concentrations were reduced by 80-95 % for all AC-treatments, AC+clay, AC-only and AC+sand. Interestingly, the reductions in aqueous and organism levels of contaminants are of the same magnitude.

AC applied in a thin cap on contaminated sediment in a recent study (Beckingham & Ghosh 2011) showed reduced PCB bioaccumulation and aqueous concentration in a freshwater oligochaete worm Lumbriculus variegatus. The reduced bioaccumulation and aqueous levels of PCBs and PAHs in Paper III and dioxins and furans, HCB and OCS in Paper II, confirms these findings, and also generalize the capping efficiency of thin layer capping with AC to be valid in marine systems. Together with reduced sediment-to-water fluxes measured in situ in the Grenland Fjords and in Trondheim Harbor (Cornelissen et al. 2011, 2012) these results suggest that thin-layer caps amended with activated carbon can significantly hamper the two important routes for transfer of organic contaminants from sediments to higher trophic levels.

**Ecological effects from AC amendment**

The strong negative effects from activated carbon on benthic community in Paper I and especially in the large field study (Paper IV) are troublesome in the search for a suitable capping material to be used in the Grenland fjords and other polluted marine sediments.

Negative effects of carbonaceous materials on ecological or physiological endpoints have been reported in other studies, e.g. reduced lipid content in the fresh and brackish water oligochaete Limnodrilus sp. exposed to soot-amended sediment (Jonker et al. 2004), and behavioral effects in the marine amphipod Corophium volutator avoiding sediment with 30% coal and charcoal (Hellou et al. 2005). Negative effects have also been seen in organisms exposed to activated carbon. The most severe effects are seen in pure and high concentrated AC and moderate or less severe perturbations in low AC concentrations. Pure AC showed to be lethal to the freshwater invertebrates Lumbriculus variegatus, Daphnia magna, and the marine mud shrimp Corophium volutator (Jonker et al. 2009), but no lethality was seen in 25% AC:sediment content. Preference tests in the same study showed avoidance to
high AC content (15-25%) but generally not to sediment with lower AC content. Reduced relative lipid content and altered feeding behavior in *Lumbriculus variegatus* were observed already at low AC content. Nybom et al. (2012) confirmed that the AC concentration is a determinator, but more importantly that larger negative effects were related to smaller particle sizes of AC in *L. variegatus* (Nybom et al. 2012). Fine particle AC (90% < 63 µm) had negative effects on feeding, growth, lipid content and reproduction already at low AC concentrations.

Both Nybom et al. (2012) and Jonker et al. (2009) showed that also sediment type influences the results. Moreover, Sun & Ghosh (2007) detected no change in relative lipid content in *L. variegatus* exposed to AC amendment. Obviously the type of organism, particle size of the AC mode of AC distribution (e.g. AC-content), nature of the sediment and type of end points will influence whether negative effects are seen or not. The negative effect on lipid content was statistically significant in the omnivorous worm *Hediste diversicolor* exposed to AC-only, but not when exposed to the AC+clay treatment (Paper III). Moreover, this effect was not observed in the deposit feeding *Abra nitida* (Paper III). Other studies also show different results for different organisms. Reduced growth rate was seen in the sediment ingesting polychaete *Neanthes arenaceodentata*, but not in the particle-browsing amphipod *Leptochirus plumulosus*, exposed to sediment amended with activated carbon (Millward et al. 2005), and reduced wet weight was observed in the freshwater filter-feeding bivalve *Corbicula fluminea*, but not in the deposit-feeding bivalve *Macoma balthica*, exposed to activated carbon (McLeod et al. 2008). Many other studies, showing no negative effects from AC amendment (e.g. Cornelissen et al. 2006, Cho et al. 2009, Beckingham & Ghosh 2011, Kupryianchyk et al. 2012), are adding to an inconclusive picture. However, small but non-significant differences in single species endpoints, may add up to larger structural perturbations on benthic communities, similar to the negative effects on benthic communities observed here in Paper I, IV and in Cornelissen et al. (2011).

In the studies on benthic communities in Paper I and IV the negative effects from AC were rather clear. Especially remarkable were the negative effects on the benthic community exposed to AC+clay in the Ormefjord. Initially it mostly affected filter
feeders and suspension feeders, but subsequently also the other functional groups, deposit feeders, subsurface deposit feeders and carnivores. Large scale reductions or loss of filter feeders and suspension feeders may have implications on bacteria and phytoplankton dynamics and might lead to large plankton or cyanobacteria blooms, since higher abundances of pelagic plankton and bacteria have been related to the loss of suspension feeders (Elmgren et al. 1980).

The experimental area in Ormefjorden is dominated by the bioturbating suspension feeding brittle star *Amphiura filiformis* which accounts for up to 80 % of the oxygenation the sediment. The large negative effects on *A. filiformis*, and on the overall abundances of organism, will certainly reduce the bioturbation leading to decreased oxygenation of the sediment and altered recirculation of nutrients. However, the reductions in mobile species like the brittle stars may be due to migration. Nevertheless, after a full scale remediation refuges for migrating organisms may not be available.

The remaining community in the AC+clay field showed a large share of tolerant and opportunistic species. Taking the 80-90% reduction in species, abundance and biomass into account, the benthic community had the characteristics typical for a highly disturbed successional state (Pearson & Rosenberg 1978).

The strong negative response by the benthic community to AC in the Ormefjord questions the resilience in this system. The lower resistance compared to the Eidangerfjord may be related to the community composition, e.g. larger portion of filter feeders and suspension feeders which appeared to be highly sensitive to the small particle AC. The large effects can also hypothetically be due to historical losses of species and lowered diversity and redundancy already before addition of the capping material.

The difference in responses between the Ormefjord and the Eidangerfjord in (Paper IV), the marine communities analyzed in the boxcore in Paper I and in Trondheim harbor (Cornelissen et al. 2011) and the limited affected fresh water communities in Gras River (Beckingham et al. 2013) and in Veenkampen, Netherlands
(Kupryianchyk et al. 2012) may be connected to a variety of potential factors. Interactions between environmental factors, contaminants, community composition, properties and distribution of the capping material may determine the response to a capping material.

Interestingly the above mentioned studies show a degree of disturbance that was inversely related to the total organic carbon (TOC) in the system (Figure 5). Since AC has been shown to sequester organic nutrients (Aitcheson et al. 2000, 2001) and organisms to display reduction in lipid content and body mass (e.g. Nybom et al. 2012), AC can be suspected to lower the overall carrying capacity in food limited marine sediments.

Figure 5. Conceptual chart over the degree of Disturbance in benthic communities exposed to activated carbon and the total organic carbon in the sediment. ‘add’, refers to the regular addition of food in this experiment; m = meters depth; a. (Kupryianchyk et al. 2012); b. (Beckingham et al. 2013); c. Paper I; d. (Cornelissen et al. 2011); e. Paper IV
The affected communities in **Paper I, Paper IV** and in Trondheim harbor (Cornelissen et al. 2011) also shared other factors; e.g. fine particle AC, marine system and larger number of defined taxonomic elements, which probably also influenced the response and the outcome of the assessment.

**Challenges and Recommendations**

Contaminant sequestration and reduced toxicological risk are the main goals for a remediation. However, benthic recovery and recolonization of capped areas should also be the intention in large capping areas. A meta-community perspective may help in determine appropriate preconditions. Suitable areas could preferably be left temporarily uncapped, to function as refuges for sensitive species and sources for subsequent dispersal of organism to recolonize the capped areas. Such untreated areas might be left uncapped or capped further down the road after a successful recolonization of the capped areas has been documented. Connectivity between such refuges and capped areas need to be evaluated for different species regarding larval and adult dispersal modes (swimming, walking, drifting, spawning), physical conditions (distance, currents, pycnoclines, fjord sills etc) and time (e.g. season) before large areas e.g. entire fjords are to be remediated by thin layer capping. Evaluations of the rate of benthic recovery in the field may take several years and also vary among locations and species.

In order to minimize the negative effects in the capped fields it would also be important to consider factors which have been documented in the literature and also discussed in this thesis. For example, balancing the concentration of activated carbon against the TOC content and the food input in the system. Particle sizes of AC up to 300µm are documented to be effective for sorption in sediment remediation (Zimmerman et al. 2005). Managers could thus consider using fine granular activated carbon instead of powdered AC in order to lower the risk of large-scale negative effects in the system, such as degradation of seafood production and outbreaks of phytoplankton and cyanobacteria blooms. Timing can also be crucial for a successful remediation, with the identification of an optimal time of low biological activity and minor potential stressors such as high temperature in order to avoid disturbing
biologically active events such as reproduction, spawning and settling, or critical foraging periods (e.g. after algal blooms).

Moreover, initial disturbances of the benthic community following various sediment remediation options is the rule rather than the exception. Compared to the deleterious effects associated to conventional remediation options initial negative effects of thin-layer capping with AC or other sorbents may be acceptable. An essential question is how long-lasting the negative effects are and how long it takes for the benthic community to recover after the capping.

**Conclusion**

The results in this thesis suggest that remediation of contaminated sediments using thin layer capping is highly effective in reducing the bioaccumulation and aqueous concentrations of organic contaminants ([Paper II](#) and [III](#)), but that it is associated with severe negative effects on benthic communities ([Paper I](#) and [IV](#)) at least initially. This thesis highlights the need for further studies in order to adjust the sorbent type in order to be less toxic. There is also a need for a more comprehensive cost-benefit assessment of this technique, both in terms of environmental costs and benefits and in terms of societal costs and benefits.

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