Organic pollutants pose a major risk to aquatic environments. These pollutants accumulate within the sediment, making it a primary target for remediation efforts. A cost-effective approach to sediment remediation is the reduction of contaminant bioavailability with in-situ application of activated carbon (AC). In this thesis, the remediation efficiency and adverse effects of AC-amendments are studied in field and laboratory. The findings are then used to improve the remediation method with the development of a new, AC-based remediation material.
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Sebastian Abel

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Methods for activated carbon-based sediment remediation. Applicability, remediation potential and adverse effects of conventional and novel sorbent materials under field and laboratory conditions

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ABSTRACT

Pollution is an ever growing concern for modern society. The rapid industrialization and technological advances in many parts of the world have led to the release of a wide variety of harmful substances into the environment. Many of these substances eventually accumulate in aquatic sediments, where they persist over long periods of time. Benthic organisms can take up and accumulate these sediment-associated contaminants, after which they can be passed on through the food chain. This can lead to significant exposure to humans, who are at the top of many food chains. The in-situ amendment of strong sorbents to sediments can prevent the uptake of contaminants right at the basis of the food chain. For this approach to remediation, the pollutant itself does not have to be removed from the ecosystem, but is rather bound strongly and thus rendered unavailable for uptake by organisms. Activated carbon (AC) has been identified as a promising sorbent material with exceptionally high remediation efficiency for hydrophobic organic contaminants (HOCs). However, there are signs that the sorbent itself may have ecotoxic effects. This thesis aims to study different AC amendments for their remediation efficiency and adverse effects to allow a balanced view on the potential and risks of the method. A pilot-scale field study was conducted in an HOC-contaminated lake in Finland and complemented by laboratory trials. The findings from the field study revealed several shortcomings of AC-based sediment remediation. As an application method for the field trial, AC thin layer capping (TLC) was chosen due to its simplicity and high remediation potential demonstrated in preceding laboratory trials. While laboratory tests conducted prior and following the field trial showed high remediation efficiencies of TLCs, this...
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This thesis aims to study different AC amendments for their remediation efficiency and adverse effects to allow a balanced view on the potential and risks of the method. A pilot-scale field study was conducted in an HOC-contaminated lake in Finland and complemented by laboratory trials.

The findings from the field study revealed several shortcomings of AC-based sediment remediation. As an application method for the field trial, AC thin layer capping (TLC) was chosen due to its simplicity and high remediation potential demonstrated in preceding laboratory trials. While laboratory tests conducted prior and following the field trial showed high remediation efficiencies of TLCs, this
could not be observed under field conditions. Major causes were identified to be poor retention of the AC cap on site, as well as an ongoing recontamination with sediment from adjacent, untreated sites during storm events. In laboratory tests, the adverse effects of the AC-cap were strong, with significant inhibition of growth of *Lumbriculus variegatus* and *Chironomus riparius*. Magnetizing the AC and stripping it from the sediment after the treatment could only mildly lower these effects, mainly due to incomplete AC-recovery rates. No ecotoxic effects of the AC TLC were observed during the field trial, indicating an overall low impact of the sorbent amendment since there was low AC retention in field sediments.

The experiences gathered from these trials were utilized to improve the remediation method. A novel, low-buoyancy AC-based material (ACC-G) was developed to improve the sorbent’s applicability from the water surface and increase its resistance to water turbulence. Initial laboratory tests showed high contaminant-binding capabilities of the novel material. Adverse effects were reduced compared to powdered ACs by granulating the ACC-G. This prevents the contaminant-binding capabilities of the novel material. Adverse effects were reduced compared to powdered ACs by granulating the ACC-G. This prevents the ingestion of AC particles by organisms, which has been suggested to be one of the major causes of AC-induced adverse effects. As a result, the newly developed ACC-G granules can serve as an advanced remediation material maintaining an improved field applicability and reduced adverse effects while maintaining high HOC-binding capacity.

*Universal Decimal Classification*: 502.174, 502.51(285), 504.5, 574.64

*CAB Thesaurus*: sediment; remediation; activated carbon; bioavailability; bioaccumulation; sorption; aquatic environment; pollutants; polycyclic hydrocarbons; polychlorinated biphenyls; benthos; toxicity

*Other keywords*: ecotoxicology; persistent organic pollutants; polycyclic aromatic hydrocarbons; benthic fauna; zoobenthos;

*YSA*: sedimentit; saasteet; järvet; pohjaelöstö; biosaatavuus; aktiivihiili; ekotoksikologia; vesistöjen kunnostus
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share amazing conference trip memories. Thank you for these experiences, and I sincerely hope there are more of these memories to be made in the future.

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Joensuu, October 2018
Sebastian Abel
LIST OF ABBREVIATIONS

AC             Activated carbon
ACC-G          Activated carbon / clay material, permanently fused and granulated
AFS            Artificial sediment
AFW            Artificial freshwater
ANOVA          Analysis of variance
BC             Black carbon
BFS            Benthic fauna survey
C_free         Freely dissolved fraction (concentration)
dw             Dry weight
fw             Fresh weight
GAC            Granular activated carbon
GC-MS          Gas chromatography – mass spectrometry
HOC            Hydrophobic organic contaminants
IC_{50}        Inhibitory concentration
KJ             Lake Kernaalanjärvi (sediment)
K_{ow} / logK_{ow} Octanol-water partition coefficient / logarithmic term of K_{ow}
LME            Linear mixed effect (model)
MagBio         Magnetic biochar
MagAC          Magnetic activated carbon
MNR            Monitored natural recovery
PAC            Powdered activated carbon
PAH            Polycyclic aromatic hydrocarbons
PCB            Polychlorinated biphenyl
PE             Polyethylene
RT             River Tyne (sediment)
sd             Standard deviation
SSA            Specific surface area
TEM            Transmission electron microscopy
TLC            Thin layer capping
TOC            Total organic carbon
ww             Wet weight
UoN            University of Newcastle
LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to by the Roman Numerals I-V.


III Abel S. and Akkanen J. A novel, activated carbon-based material for the in-situ remediation of contaminated sediments. *Manuscript*


AUTHOR’S CONTRIBUTION

I) All listed authors contributed to the planning phase of the study. The laboratory works were carried out by SA and IN. The results were evaluated and interpreted by SA. The first manuscript draft was provided by SA and proof-read and edited by all co-authors.

II) The field and laboratory follow-up experiments were planned and designed by SA and JA. Both authors conducted the practical works at the field site. Laboratory experiments were carried out by SA. Data analysis and writing the first draft of the manuscript were done by SA and edited together with JA.

III) The novel AC-clay pellets presented in this study were designed by SA and developed together with JA. The laboratory bioassays for the material’s initial testing were designed by SA and JA. Practical work, data analysis and writing a manuscript draft were carried out by SA, and edited with JA.

IV) The mainframe of the study was designed by ZH and DW. The magnetic AC was produced and tested for PAH-binding efficiency by ZH, BS, HK and DW. SA, IN and JA planned the ecotoxicity tests. The laboratory work and data evaluation were carried out by SA with help from IN. The major part of the first manuscript draft was written by ZH, with SA providing the ecotoxicity test documentation. All co-authors proof-read and edited the manuscript.

V) ZH and DW planned, designed and executed the study on contaminant binding efficiency tests of the sorbent materials. The ecotoxicity bioassays were planned by SA and JA, with the majority of practical works carried out by SAs. The first draft of the manuscript was written by ZH and SA provided the documentation of used methods and results in the bioassays. All co-authors participated in the proof-reading and editing process.

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INTRODUCTION

1.1 CONTAMINATION IN AQUATIC ENVIRONMENTS

The rapid development of heavy and chemical industries in the 20th century has led to a massive increase of the production of a wide variety of synthetic chemicals. Many of these substances were developed to increase the standards of living for people around the world. For example, pesticides have allowed more secure food supply, polymers enabled the advancing of technology and flame retardants provided safer work and living environments. However, many chemicals have been found to be toxic to the environment and humans (Connell 2005).

In many cases, the toxic effects are discovered after the substances have been in production and use for a long period of time. Until decisive actions, like a ban of the toxic substance can be issued, large amounts of data need to be collected, which can be a challenging and time-consuming process (Muir & Howard 2006).

Many of the substances banned in the Stockholm Convention of 2001 had by then been in use for several decades (UNEP 2001).

As long as a chemical is in production or use, it can be released into the environment. These releases can occur as accidental spills, continuous and unnoticed discharges or by improper disposal or storage (Tanabe 1988; Arukwe et al. 2012).

The long periods of time, during which many harmful substances have been in circulation, have thus led to significant amounts of these substances entering the environment. Water bodies are often a primary recipient of these contaminants, since producing industries often settle in the proximity of water bodies. Furthermore, a large fraction of hazardous material transport is still carried out by ship (US EPA 2005). In addition, the hydrological transport of contaminants from terrestrial areas is a secondary source of pollution for aquatic environments.

Many contaminants released into water bodies are highly persistent and have a tendency to accumulate in the sediment. This makes aquatic sediment the primary storage compartment for a wide range of pollutants. Over time, substances associated with the sediment can be constantly released back into the water or be taken up by organisms living within the sediment (Beckingham & Ghosh 2013). Therefore, contaminated sediment can cause a substance to remain a risk to the environment and humans, even after all discharges to the environment have ceased (Reible 2014a).

When the contaminant levels in the sediment are low, the concentrations in the water phase may be barely measurable. This is especially the case in large water bodies, due to the effects of dilution. Nonetheless, the sediment can still be a risk factor due to the processes of bioaccumulation and biomagnification.
1 INTRODUCTION

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Bioaccumulation describes the uptake and accumulation of a substance within an organism. This is caused by the high affinity of many contaminants to organic tissue (especially biolipids), resulting in high uptake and slow elimination rates (El-Shahawi et al. 2010).

Bioaccumulation usually starts at the lowest trophic level with organisms that directly live within or feed on the sediment. The uptake can occur actively, by ingesting contaminants sorbed to sediment phases, or passively via dermal uptake from the sediment porewater (Leppänen & Kukkonen 1998c). From lower trophic levels, the contaminants are then passed on through the food chain. Biomagnification describes the process, when contaminant body burdens increase with each trophic level that they are passed through. Should harmful substances finally accumulate in organisms used as food, humans can become widely exposed and suffer from acute or chronic toxic effects (US EPA 2005).

### 1.2 HYDROPHOBIC ORGANIC CONTAMINANTS

Hydrophobic organic contaminants (HOCs) are substances with a high affinity to organic matter. Therefore they readily accumulate in sediments and organisms. The octanol water partition coefficient ($K_{ow}$, often expressed as logarithmic term $\log K_{ow}$) is a key value used to characterize HOCs. The higher this $K_{ow}$ value, the stronger the hydrophobicity of the substance. The $K_{ow}$ can be utilized to give a first approximation of a contaminant’s behavior in the environment. On the one hand, the rate at which an HOC is released from the sediment into the aqueous phase can be expected to be decreasing with increasing $K_{ow}$. Furthermore, the affinity at which these substances bioaccumulate rises with increasing hydrophobicity values (Lu et al. 2011). In addition to generally high bioaccumulation, many HOCs, especially those with a $\log K_{ow} > 5$, are biomagnifying substances (Gobas et al. 1999; Borgå et al. 2012).

The group of HOCs is made up of an extremely wide range of different substances. Many industrial organic chemicals and byproducts of combustion processes belong into this group. Two of the most important HOC-groups, due to wide-spread occurrence and associated toxicity, are polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

PCBs consist of an aromatic biphenyl body in which 1 to 10 hydrogen atoms have been replaced by chlorine (Figure 1), yielding a total of 209 congeners. The chemical properties and toxicity of the congeners largely depend on their degree of chlorination, as well as the position of the chlorine atoms. The $K_{ow}$ rises with an increasing degree of chlorination, leading to higher bioaccumulation (Lu et al. 2011) and stronger affinity to organic surfaces (Ghosh et al. 1999). For the toxicity of PC...
PCBs, both the number of chlorine atoms and their position on the biphenyl body are important. Toxicity generally rises with the degree of chlorination. However, when chlorines bind to the ortho-positions (2, 2’, 6 and 6’, see Figure 1) the toxicity is generally reduced. The most toxic congeners are those with no chlorine atoms occupying the ortho-positions. 12 of these congeners have high structural similarities and cause severe effects similar to dioxins (Bruner-Tran & Osteen 2010). Due to their persistence and toxicity, PCBs have been banned in many parts of the world during the second half of the 20th century. A world-wide ban ensued in 2001, when PCBs were included in the list of banned substances in the Stockholm Convention (UNEP 2001).

![Figure 1. Basic structure of PCBs (left). Chlorine atoms can substitute any number of the numbered, available positions on the phenyl rings. The highest toxicity is generally observed by the 12 dioxin-like congeners (e.g. 3,3′,4,4′ tetrachlorobiphenyl shown on the right)](image)

PAHs are common byproducts in the petrochemical industry and combustion processes. This unintentional production makes the banning of these substances hardly possible. Although their release may be lowered with the use of modern technology, they are likely to remain a burden to the environment (Manzetti 2013). PAHs are a group of hydrocarbons consisting of two or more aromatic rings (Figure 2) that have logKow ranging between 3 and 7 (Reible 2014b). They tend to accumulate to high levels in invertebrates, but have a lower tendency to biomagnify, due to higher metabolization rates in many vertebrates. However, the resulting PAH metabolites can be highly toxic to certain species. This can lead to stronger toxic effects in higher trophic levels even without significant biomagnification (Meador et al. 1995; US EPA 2005).

![Figure 2. Three examples for PAHs; anthracene (left), pyrene (middle) and benzo[a]pyrene.](image)
1.3 BIOAVAILABILITY AND MOBILITY

While chemical properties of a substance may give an indication on their behavior and toxicity in the environment, the actual risks that originate from a contamination case depend on a wide range of factors. The sediment characteristics are of major importance in this regard. Especially the organic fraction of a sediment, which may only make up a few percent of the total sediment mass, plays a key role. HOCs primarily bind to the surfaces of these organic particles. The adsorption strength to the particle surfaces largely determines the partitioning of a contaminant in between sediment and (pore-)water phases (Luthy 2004). In addition to surface adsorption processes, a smaller fraction of HOCs can be absorbed into amorphous organic matter. The relative importance of the two sorption processes depends on the composition of the sediment’s organic fraction (Cornelissen et al. 2005).

The organic fraction of a sediment can have strongly varying properties, depending on the origin of the organic matter. Highly degraded, complex matter, such as soot-like black carbon (BC) particles lead to several magnitudes stronger sorption than other organics (Bucheli & Gustafsson 2000; Ghosh et al. 2003; Cornelissen et al. 2005). Contaminants bound to surfaces of BC can be largely unavailable for the uptake by organisms. Therefore, bulk sediment concentrations, that are generally used to describe the severity of a contamination case, often do not adequately characterize the potential risk to organisms. High bulk sediment concentrations can cause relatively low ecotoxic effects, if the contaminant is bound strongly within the sediment (Gobas et al. 2009). The bioavailable fraction of a contaminant can be indicated by its freely dissolved concentration $C_{free}$. For example, the bioaccumulation of several HOCs could be explained with a product of their $K_{ow}$ and freely dissolved fraction in the porewater (Gschwend et al. 2011; Lu et al. 2011).

The mobility of a contaminant describes its ability to move in between compartments of an ecosystem (e.g. sediment to water flux) and on a larger scale in between geographic areas. PCBs with low degrees of chlorination, for example, are more mobile than their highly chlorinated counterparts. They dissolve more readily in the water phase and can be transported over longer distances with water streams (Hurme & Puhakka 1999). Some low-chlorinated PCBs as well as PAHs with low molar masses are volatile and can thus enter the atmosphere. This enables the extreme long-range transport of these contaminants that has, for example, led to the occurrence of PCBs in remote areas, such as the Arctic (Octaviani et al. 2015). The mobility of a contaminant, especially considering waterborne transport, is a direct result of its concentration in the aqueous phase. Therefore, contaminant mobility and bioavailability often correlate, as both are essentially driven by the desorption rate of a contaminant from the sediment.
2 REMEDIATION OF AQUATIC SYSTEMS

2.1 REMEDIATION METHODS

Both PCBs and PAHs can be highly stable in the environment and can persist as a threat to ecosystems for decades. Nonetheless, there is evidence that PCB dechlorination (and thus reduction of toxicity, albeit potentially increased mobility) occurs in natural environments, either driven by physicochemical processes or microbiological activity (Abramowicz 1990). Additionally, PAHs may break down naturally, continuously lowering contamination levels. These processes can be utilized for monitored natural recovery (MNR). This passive remediation approach is feasible in contaminated areas posing a low immediate risk and providing sufficiently high microbiological activity (Reible 2014a). However, these processes can be slow and require suitable sediment characteristics, such as appropriate oxygen levels and temperatures for the biodegradation of HOCs (US EPA 2005; McDonald & Knox 2014). In addition, the intensity and depth to which benthic organisms dwell through and mix the sediment (bioturbation) can delay MNR by increasing the release of contaminants from deeper sediment layers (Reible et al. 1996). Hence active remediation methods are required to improve the situation in many sites. These remediation methods can be classified as ex-situ (off-site) or in-situ (on-site) methods.

2.1.1 Ex-situ

Ex-situ methods are perhaps the most straightforward approach to sediment remediation, as the contaminants are physically removed from the site by means of sediment dredging. These operations require heavy machinery, as well as the adequate treatment of the excavated, hazardous material. This includes the transport, dewatering and final disposal at a suitable landfill. In many cases, an additional treatment step, e.g. incineration or chemical destruction of contaminants, has to be carried out before the sediment can be safely disposed (Palermo & Hays 2014). This makes the ex-situ sediment remediation both cost- and labor-intensive, reducing their economic feasibility (Kupryianchyk et al. 2015). In addition, the success is often limited or can even cause an increased release of contaminants (Cornelissen et al. 2008). Lastly, dredging large volumes of sediments can strongly disrupt benthic organisms due to physical habitat destruction (Ghosh et al. 2011).
2.1.2 In-situ

For in-situ remediation methods, the contaminant is not physically removed from the site, but treated right at the site. Conventional in-situ methods focus on the physical isolation of the hazardous substance from the surrounding environment. This is achieved by capping the sediment with inert, clean material, such as sand or clay. Often, large amounts of capping material are needed to successfully separate the contaminated sediment from the overlaying water phase. The required cap thicknesses largely depend on the site characteristics, such as the intensity of water upwell through the sediment, as well as contaminant concentration and mobility. Bioturbation can also have a negative impact on cap integrity (Reible & Lampert 2014) and may require caps of several tens of centimeters, resulting in high costs and the need for special equipment (US EPA 2005). Thinner caps (< 5 cm) are applied as well, but bear an increased risk of low long-term remediation success (Cornelissen et al. 2011; Samuelsson et al. 2015). Although potentially less severe compared to dredging, damages to benthic communities can also be caused by in-situ capping (Samuelsson et al. 2017).

Less conventional in-situ methods are based on the active degradation or immobilization of contaminants. Bioremediation, for example, utilizes organisms with metabolisms capable of degrading hazardous substances. These methods include the introduction of suitable organisms or the improvement of their growth conditions with the addition of nutrients (Yang et al. 2009). As with MNR, site-specific characteristics can be a limiting factor. Especially in cold regions, metabolic activities may be too low for a successful remediation in a reasonable timeframe (Yang et al. 2009; McDonald & Knox 2014). The immobilization of contaminants with the amendment of active materials is a relatively new method in sediment remediation. These methods are based on lowering C_free and bioavailability of contaminants by strongly binding them. Frequently utilized binding mechanisms are complexation (Ding et al. 2007) and surface adsorption to sorbents (McLeod et al. 2004). One of the most promising materials for the active in-situ remediation of sediments is activated carbon (AC), which has undergone extensive research (Rakowska et al. 2012; Kupryianchyk et al. 2015).

2.2 ACTIVATED CARBON

2.2.1 Mechanism and application methods

The in-situ amendment of AC takes advantage of the high affinity of HOCs to complex organic surfaces (Ghosh et al. 2003). The extremely low polarity of AC
surfaces causes strong sorption and facilitates the transfer of contaminants from sediment particles to the sorbent. To obtain a highly porous material, the AC production process generally uses high temperatures (< 500 °C) and an ensuing activation process that can include the use of steam or chemicals (Gergova et al. 1993). The high porosity results in a large specific surface area (SSA), which can be well in excess of 1000 m² per g of AC (Zimmerman et al. 2005). Due to the high SSA, small doses of AC can bind large amounts of HOCs (Chen et al. 2008). Therefore, lower amounts of material are required, increasing the economical feasibility of the method (Ghosh et al. 2011). Another advantage is the flexibility in AC raw material choice. A wide range of petrogenic, as well as biogenic materials can be used (Lillicrap et al. 2015). Using biogenic waste materials, such as coconut shells, can improve the sustainability and carbon footprint of the remediation works (Sparrevik et al. 2011).

The in-situ application of AC can be carried out by two major methods. Mixing the sorbent particles actively into the sediment is laborious, but stabilizes the AC against water turbulences and reaches a homogenous dispersal within the sediment. Using this method under field conditions requires specialized equipment to prevent an unintended spread of the applied sorbent and reduce physical disturbance of the benthic ecosystem (Beckingham & Ghosh 2011). However, utilizing an active mixing method in tidal zones (Cho et al. 2009) or drainable waterbodies (Kupryianchyk et al. 2013) can be relatively easy. Thin layer capping (TLC), on the other hand, is relatively simple in execution for most water bodies. The low density of the porous AC materials poses an obstacle with TLC application. Slow sinking speeds require measures to prevent an unintended spread or loss of AC, especially with increasing water depths. Pumping the sorbent layer directly down to the sediment has been successfully tested, but adds to the method’s costs (Cornelissen et al. 2012; Samuelsson et al. 2017).

2.2.2 Remediation potential and risks

AC has been widely tested for its remediation potential. Under laboratory conditions, mixing the sorbent into the sediment can greatly reduce the mobility and bioavailability for different HOCs. Reductions in bioaccumulation in benthic organisms have been reported to reach 70 - 98 % for mussels (McLeod et al. 2004; McLeod et al. 2007), oligochaetes (Beckingham & Ghosh 2011), polychaetes (Janssen et al. 2010) and chironomid larvae (Nybom et al. 2016b). Due to a reduced bioaccumulation in these lower trophic levels, organisms higher up in the food chain also exhibit reduced contaminant uptake (Kupryianchyk et al. 2013). The high remediation potential is likely a direct effect of the reduction by AC of a contaminant’s desorption rate and C_{inwv}, that has been demonstrated both
experimentally (Zimmerman et al. 2004; Nybom et al. 2015) and in models (Werner et al. 2006; Hale & Werner 2010). In addition, field studies found high remediation efficiencies, although reductions in \( \text{C}_{\text{free}} \) and bioaccumulation have not always been as conclusive as demonstrated in laboratory studies (Cho et al. 2007; Beckingham & Ghosh 2011). In both laboratory and field studies, small doses of AC below 5% of sediment dry weight (dw) have been found to be effective.

TLC is studied to a lesser extent than the mixing treatments. Several studies found that TLC can also effectively reduce the bioavailability and release of HOC from sediments. However, the observed effectiveness tends to be lower both under laboratory (Lin et al. 2014) and field conditions (Cornelissen et al. 2011).

Although the in-situ amendment of AC is a promising remediation method, there are potential risks associated with it. Especially in laboratory trials severe ecotoxic effects of AC particles have been observed for certain benthic species (e.g. *Lumbriculus variegatus* and *Chironomus riparius*). Amongst the observed adverse effects are lowered growth, biomass losses or reduced survival (Jonker et al. 2009; Nybom et al. 2012; Nybom et al. 2016a). However, the magnitude of these effects seems to be species-dependent, with some benthic organisms showing no measurable adverse reaction to AC amendments (e.g. *Gammarus pulex* (Kupryianchyk et al. 2011). As for the remediation potential, under field conditions, the magnitude of adverse effects can vary strongly. Observations range from greatly reduced species richness and diversity (Samuelsson et al. 2017) to almost no measurable adverse impact (Cho et al. 2009). The potential adverse effects of AC amendments have been reviewed in detail by Janssen & Beckingham (2013).

### 2.2.3 The dilemma of particle size

ACs are most often classified as granular (GAC) when the particle distribution is 90% larger than 180 \( \mu m \). When the majority of particles is primarily below 180 \( \mu m \), it is referred to as powdered (PAC) (Rakowska et al. 2012). The particle size of AC is a key factor that influences both the remediation efficiency and adverse effects of AC (Janssen & Beckingham 2013). This causes a dilemma, as coarser GAC has lower ecotoxic potential (Nybom et al. 2012) than PAC, but at the same time might not be able to sufficiently sequester contaminants (Zimmerman et al. 2005), at least under desirable time-frames. For this reason, the potentially riskier PAC option is often preferred in remediation trials.
2.4 AIMS OF THIS STUDY

The major objective of this study was to investigate and improve the potential of AC amendments. Both the remediation efficiency and adverse effects to the benthic community were considered to obtain a method that is both effective and safe. The focus was set to a practical application scenario under realistic field conditions. Therefore the central part of this study was a field trial in Lake Kernaalanjärvi, southern Finland. Laboratory studies with *Lumbriculus variegatus* and *Chironomus riparius* were used to support and follow-up the field study.

The specific aims of this study were to:

1) Investigate the remediation potential and adverse effects of AC TLC amendments, for which relatively little data existed. This was done as a series of experiments utilizing different application methods and AC variants to precede the field trial (I)
2) Test AC TLC under field conditions in a boreal, contaminated lake. The aim was to gather experience for an environment in which AC amendments had not yet been extensively tested (II)
3) Gain knowledge about the feasibility of AC amendments in areas where contaminant deposition onto a site cannot be prevented (II)
4) Develop and test novel, AC-based materials for remediation of sediments. The aim was to improve the application to the sediment under field conditions (III) and to reduce adverse effects of the material, either by stripping it from the sediment after treatment (IV and V) or by increasing particle sizes without sacrificing remediation potential (III)
MATERIALS AND METHODS

3.1. LABORATORY STUDIES

Microcosm setup

The microcosms used for the laboratory bioassays were set up to represent the natural benthic environment. A layer of sediment was applied to glass vessels and covered with artificial freshwater (AFW) (OECD 1992) with a hardness of 0.5–1 mM (Ca + Mg). The aeration of the water phase through a pasteur pipette was started after letting the systems settle overnight. This general design was used for all microcosms and scaled to the demands of the respective experiments. For contaminant bioaccumulation tests, larger amounts of sediments ranging from 100–250 g wet weight (ww) were required in order to accommodate a sufficient amount of organisms for analytics. Adverse effects tests were carried out with fewer organisms and less sediment (10–50 g ww) in each microcosm to allow the complete recovery of all surviving individuals. The specifications of the microcosms and number of replicates used for the different studies are given in the corresponding papers.

3.1.2 Sediments

Natural, contaminated sediments were used for both adverse effects and bioaccumulation studies. The PCB-contaminated sediment (KJ) for papers I–III was obtained from Lake Kernaalanjärvi, southern Finland. The lake and contamination case are characterized in more detail in section 3.2.1. For papers IV and V, PAH-contaminated sediment (RT) was obtained from River Tyne at Gateshead in Newcastle upon Tyne, Great Britain. RT was sampled by the researchers at the University of Newcastle (UoN), and treated with sorbents at the UoN prior shipping to the University of Eastern Finland for ecotoxicological tests. In paper III and for preliminary tests carried out for paper I, clean, artificial sediment (AFS) was used. This sediment was prepared according to the OECD guideline 225. Ground Urtica powder, mixed into the sediment at 0.5 % (of sediment dw) was used as a food source. (OECD 2007). AFS was used exclusively to investigate the adverse effects of AC. The sediments were characterized for dw content, total organic carbon (TOC), BC and contaminant concentrations (Table 1). TOC and BC were measured with an N/C 2100 analyzer (Analytik Jena, Jena, Germany) after a method described by...
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Grossman & Ghosh (2009) or as loss on ignition (LOI; only used in III) at 550 °C (Heiri et al. 2001). PCB and PAH concentrations were quantified using coupled gas chromatography / mass spectrometry systems (GC-MS). Two models were used; a Hewlett-Packard series 6890 GC / 5973 MS detector (I – III) and a Agilent 7890A GC / 5975C MS detector (UoN; IV, V).

Table 1. Characterization of all sediment batches used for the experiments. Natural sediments from Lake Kernaalanjärvi (KJ) and River Tyne (RT), as well as artificial sediment (AFS) were used.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Publication</th>
<th>TOC [g/kg]</th>
<th>BC [mg/kg]</th>
<th>PCB [mg/kg]</th>
<th>PAH [mg/kg]</th>
<th>dw [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KJ</td>
<td>I (prelimin.)</td>
<td>7.56 ± 1.0</td>
<td>2.7 ± 0.3</td>
<td>6.6 ± 0.4</td>
<td>-</td>
<td>59.1</td>
</tr>
<tr>
<td></td>
<td>r</td>
<td>36.0</td>
<td>1.1</td>
<td>8.6 ± 0.5</td>
<td>-</td>
<td>50.9</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>29.1 ± 0.9</td>
<td>-</td>
<td>4.0 ± 0.2</td>
<td>-</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>52.5 ± 0.6 a</td>
<td>-</td>
<td>1.8 ± 0.1</td>
<td>-</td>
<td>53.5</td>
</tr>
<tr>
<td>AFS</td>
<td>III</td>
<td>35.9 ± 1.1 a</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67.7</td>
</tr>
<tr>
<td>RT</td>
<td>IV</td>
<td>64.0 ± 1.0 a, b</td>
<td>-</td>
<td>-</td>
<td>16.9 ± 0.6</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>30.0 ± 2.4</td>
<td>-</td>
<td>-</td>
<td>6.1 ± 0.4</td>
<td>42.3</td>
</tr>
</tbody>
</table>

a LOI method  b Siavalas et al. (2013)

3.1.3 Activated carbon amendments
Several different AC variants were tested. The effect of raw material used for the AC production was tested by comparing petrogenic PACs (based on coal) and one biogenic PAC made from coconut shells (I). Magnetized AC (MagAC) and biochar (MagBio), which can be stripped from the sediment after sequestrating contaminants, were tested in papers IV and V. These magnetic materials were produced at the UoN by precipitating iron hydroxides to the surfaces of PAC particles (Oliveira et al. 2002). Coal-based PAC was used to create TLCs. It was applied pure (I, II) and in mixtures with clean Kaolin (I). The novel remediation material (ACC-G, III) is based on coal-based PAC. The production process of ACC-G is described in detail in section 3.2.1. The AC materials were characterized for TOC (I – III) with the same methods used for sediments. Table 2 contains a list of all tested AC materials, their particles sizes and application method.
3.1.4 Test organisms

Two benthic test organisms were used throughout the laboratory studies: *C. riparius* (II, III) and *L. variegatus* (I – V). Both of these organisms and their close relatives are commonly found in many aquatic ecosystems, where they are part of the basis of the aquatic food web. They are well researched and widely used in standardized...
bioassays (OECD 2004; OECD 2007). Both of the two species complement each other well for sediment toxicity studies due to their different behaviors.

Sediment-dwelling oligochaetes, such as L. variegatus are known to cause stronger and deeper bioturbation in sediments (i.e. observed to 45 mm depth in I) (Reible et al. 1996; Lin et al. 2014). C. riparius larvae on the other hand inhabit the sediment surface exclusively. Only the upper few millimeters of sediment are affected by the larvae (Naylor & Rodrigues 1995).

The organisms were reared at the University of Eastern Finland in cultures with 0.5 mM AFW. Cut cellulose tissues were used as culture substrate for L. variegatus (OECD 2007) and clean sediment for C. riparius.

### 3.1.4 Measured endpoints

Measured endpoints for L. variegatus were the PCB-bioaccumulation (I – III), feeding rate (I, IV), growth / reproduction rates (I – V), gut microvilli condition (I) as well as lipid content (I, III). For C. riparius the PCB-bioaccumulation, growth, survival rates (II, III), and the lipid content (III) were measured.

The growth and reproduction endpoints were measured by weighing and counting the organisms before and after the exposure. C. riparius was applied to the microcosms as freshly hatched larvae 1 – 3 days post hatching. The starting biomass of this organism was therefore approximated as zero. L. variegatus were pre-selected from the cultures to be of similar sizes. This was done to minimize the impact of a random effect to the organisms’ reproduction, which in turn can affect feeding and growth rate (Leppänen & Kukkonen 1998b). This random effect occurs because larger individuals are likely to reproduce at an earlier point in the exposure, regardless of treatment (Leppänen & Kukkonen 1998a). The lipid content was initially (I) measured gravimetrically after Parrish (1999), but was replaced by a more rapid and reliable spectrophotometric micro method (III) developed by van Handel (1985). The L. variegatus feeding rate was measured as egested feces (Leppänen & Kukkonen 1998a). Microvilli measurements were conducted on transmission electron microscopy (TEM) images of central gut cross-section. The images were taken with a JEM 2100F TEM (JEOL, Tokyo, Japan).

The effects of the AC materials on contaminant bioavailability (remediation potential) was assessed by measuring PCB body burdens in the test organisms after the given exposure times (I – III) and by determining C\textsubscript{free} with polyethylene (PE) passive samplers at UoN (IV, V). After recovery from the sediment, the organisms were allowed to depurate their gut contents (6 – 8 hours), frozen and stored for later analysis (-20 °C). The extraction procedures differed slightly between the studies. When only small sample sizes were available, a micro method as described
by Jones et al. (2006) was used, whereas larger sample sizes allowed the use of a simpler method as described by Mäenpää et al. (2011).

The exposure times for *L. variegatus* was 14 days when only feeding rate was measured (I), and 28 days in all other setups (I – V). *C. riparius* larvae were exposed to the sediment for 10 days in growth and survival exposures (III) and 12 (II) to 13 (III) days in bioaccumulation studies. The amount of organisms depended on the measured endpoint and experimental setup (Table 3).

Table 3. General microcosm setups (sediment amount and number of organisms at the start of exposure) and measured endpoints. *L. variegatus* PCB-bioaccumulation tests were started with a set biomass, hence the approximation in number.

<table>
<thead>
<tr>
<th>Test organism</th>
<th>Major endpoints</th>
<th>Sediment (wet) [g]</th>
<th>Organisms / replicate</th>
<th>Other endpoints</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>L. variegatus</em></td>
<td>Feeding</td>
<td>25</td>
<td>5</td>
<td>biomass, reproduction</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>PCB-bioaccumulation</td>
<td>250</td>
<td>ca. 60 - 80</td>
<td>biomass, lipid content (I, III)</td>
<td>I - III</td>
</tr>
<tr>
<td><em>C. riparius</em></td>
<td>Growth &amp; survival</td>
<td>10</td>
<td>1</td>
<td>developmental stage (instar)</td>
<td>II, III</td>
</tr>
<tr>
<td></td>
<td>PCB-bioaccumulation</td>
<td>100</td>
<td>35 - 40</td>
<td>biomass, lipid content (I, III)</td>
<td>II, III</td>
</tr>
</tbody>
</table>

3.2  FIELD STUDY

3.2.1 Lake Kernaalanjärvi

Lake Kernaalanjärvi is a PCB-contaminated waterbody located in southern Finland (60°85′44″ N, 24°64′ 21″ E). The source of the contamination was a continuous, unnoticed spill in a paper mill between 1956 and 1984 that released over 1000 kg of PCB oil (containing mostly lower chlorinated congeners) into Lake Kernaalanjärvi’s tributary River Tervajoki. The discharge of contaminated sediment from this river has led to high PCB-levels at the river’s mouth. Over time the PCBs have spread throughout the lake, thus diluting local concentrations (Hurme & Puhakka 1999). However, decades after the spill, concentrations in fish remain high enough to warrant a ban of commercial fishery and consumption advisories for private individuals (Koponen et al. 2003; Figueiredo et al. 2014). Although not considered highly contaminated (see for example Table 1), Lake Kernaalanjärvi is an example of how bioaccumulation and biomagnification can increase the risk of even relatively low levels of contaminants, making the lake a suitable target for remediation.
3.2.2 Activated carbon amendment and monitoring

In 2015, a small area (300 m²) of sediment was amended with a TLC of an AC-clay mixture with a target concentration of ca. 1.7 kg AC/m² (Figure 3). Pressed AC-clay pellets (Sedimite™), designed to sink quickly through the water column and disintegrate at the bottom was used to allow the AC application from the water surface (Menzie et al. 2016).

Figure 3. Sediment core showing the AC TLC amended in Lake Kernaalanjärvi (one day after the AC was applied).

Monitoring was carried out over a period of 14 months at the AC-amended test plot and pristine reference sites at distances of ca. 100 m to the plot. During this period, the adverse effects of the AC cap over time were assessed with benthic fauna surveys (BFS). The remediation potential was measured as the bioaccumulation of PCBs in the field collected organisms with the same methods as used for the laboratory studies. The results were normalized to the sediment PCB and TOC content at each of the test sites to account for the strong spatial heterogeneity of the lake’s sediment (Hurme & Puhakka 1999).

A more detailed description of the setup, location and monitoring work is given in the materials and methods section of paper II.

3.2 DEVELOPING NOVEL, AC-BASED REMEDIATION PELLETS

3.2.1 Production process

The newly developed AC-clay granules (ACC-G) consist of a clay matrix, into which PAC is embedded (depicted in III / Figure 1). The base for ACC-G is a slurry of equal parts clay and PAC and a small amount of NaHCO₃ in ultrapure water. The slurry is filled into aluminum trays and dried over several hours at increasing temperatures up to 200 °C. During this process, the NaHCO₃ disintegrates, facilitating the formation of pores in the drying material. Following the drying, the material is baked at high temperatures (increasing in small increments to 580 °C) to “fire” the clay and form a stable solid that can be broken up into granules of the desired size (Figure 4).

Nonetheless, a loss of about 1/3 of the material due to AC-oxidization could not be avoided with the current production process. At this state, this increases the production costs of ACC-G by about 33 % compared to conventional AC-clay mixtures. By further reducing the oxygen content in the oven chamber, however, these additional costs could be reduced significantly. Other, additional costs in the production of ACC-G are relatively minor factors (energy consumed by ovens, NaHCO₃ and equipment / labor to grind the material into granules).

Figure 4. AC materials used in experiments described in publications (I – III). The picture shows from left to right PAC (< 100 µm), clay granules, GAC and ACC-G (all 400 – 1000 µm). The Macroscope images of ACC-G show the material’s sandstone-like structure, consisting of PAC embedded in a clay matrix.

3.2.2 Initial testing

The performance of the material of ACC-G was tested and compared to GAC of the same particle size, as well as PAC (Table 2). Laboratory bioassays as described in 3.1 were used to test adverse effects and remediation potential. By measuring the recovery of ACC-G after being used in the exposure tests, the stability of the granules after application was assessed. The advantages of ACC-G in a practical field application scenario are hard to test in the laboratory. A simple buoyancy test...
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was carried out to determine the sinking speed and theoretical retention on top of the sediment in turbulent waters.

3.3 STATISTICS

The data was analyzed using SigmaPlot (Systat software) and R. The used methods were one- and two-way analysis of variance (ANOVA). Normality and equal variances of the data were generally tested visually (QQ- and residuals plots) due to the low number in replicates. Linear mixed effects models (LME) were used where a significant random effect was expected. This was the case in the adverse effects setup for the ACC-G tests (III). The large amount of total microcosms made it necessary to split the experiments over multiple days (sub-runs). Each of the separate sub-runs was subject to daily variation, caused e.g. by a different batch of organisms. This can cause random variance that has to be regarded in the data analysis. The fit of the LME models was tested visually (fitted values vs. residual plots and QQ-plots). The lme4 R-package was used for the LME models and significance levels were obtained with the multcomp-package. The materials and methods sections of the corresponding papers contain more information about specific statistical tests. Standard significance levels (p < 0.05) were used in all tests. Graphs were created with GraphPad Prism (GraphPad Software).
4 RESULTS AND DISCUSSION

4.1 LABORATORY STUDIES

4.1.1 Adverse effects of AC amendments

The preliminary tests with AFS for paper I were carried out to test for the degree of adverse effects of TLC on *L. variegatus*. Pure AC was used in two grain sizes, PAC < 100 µm and a slightly coarser AC of 63 – 200 µm, which had been shown to exhibit milder adverse effects to the test organisms when mixed into the sediment by Nybom et al. 2012. However, when applied as a TLC in doses of 0.9 and 1.8 kg/m², the differences in adverse effects on *L. variegatus* growth rate were small and only weakly significant (p = 0.029, two-way ANOVA). As both ACs caused a significant loss in biomass in both doses (Figure 5), the benefit of using the larger particle size was considered insignificant for TLC amendments. Therefore it was decided to continue with the smaller particle size below 100 µm to focus on maximizing the remediation potential. Interestingly, no significant effect of the TLC thickness was observed, leading to the assumption that the strongest adverse effects of both materials were reached already with the lower dose of 0.9 kg/m². Hence the doses were slightly reduced for the main experiments.

![Figure 5](image)

Figure 5. Growth rate of *L. variegatus* in sediments amended with TLCs made from a fine and intermediate PAC (< 100 µm and 63 – 200 µm particles size, respectively). Growth rates were higher in AFS than in natural KJ sediment, despite the lower AC doses used in the latter. Negative growth rate values refer to a loss of weight during the experiment. The test could not be conducted with *C. riparius* due to mortality. The graph shows mean values and standard deviation (sd).
Figure 6. Adverse effects of a PAC TLC (1.2 kg/m²) after simulated recontamination. An additional layer of contaminated sediment in varying thicknesses was applied following the TLC amendment. The deep dwelling L. variegatus were highly exposed to the AC and showed reductions in growth and reproduction. Partial mortality of L. variegatus occurred in some cases with just the TLC applied (marked), but survival was not negatively affected in other treatments. Shallow dwelling C. riparius larvae were isolated from the PAC more quickly, which alleviated adverse effects (reduced growth and survival). The data was obtained from PCB bioaccumulation (closed symbols) and adverse effects (open symbols) experiments. Values are relative to the corresponding control group growth of each experiment. Mean and sd are shown.

The adverse effects were more severe in the natural KJ sediment, despite slightly reduced doses as a consequence of the preliminary tests (I). The application of a 1.2 kg/m² TLC of pure PAC led to the only observation of significant L. variegatus mortality (Figure 6). Although this was only observed in one experimental setup, it raises concern about the possible magnitude of adverse effects caused by TLC amendments. C. riparius did not survive any of the TLC treatments and could thus not be included in the study. However, once new sediment was added on top of the AC layers, the adverse effects quickly decreased for C. riparius, but not for L. variegatus (Figure 6), due to their different dwelling behaviors (II). The freshly
hatched chironomid larvae stay on the surface of the AC layer after being introduced to the test vessel (Naylor & Rodrigues 1995). While this likely caused their mortality on a fresh TLC, even a small amount of sediment covering the AC isolated the larvae from it. The deep-dwelling oligochaetes (Reible et al. 1996; Lin et al. 2014) are more exposed to the sorbent when they burrow through the TLC, but can reach the underlying sediment, allowing their survival.

The mix treatments tested for PAC (I, III) and MagAC (IV, V) showed consistent results, with strong adverse effects caused by even small doses of AC (Figure 7). As little as 0.1% PAC could lead to a significant reduction in L. variegatus feeding rate (I, IV), with an almost complete cessation of feeding activity at concentrations of 1% and higher. This was accompanied by significant growth reductions or losses in biomass (I – V). Across all experiments conducted for this study, the overall IC₅₀ for PAC was 0.12% (R² = 0.77). These findings are in line with many publications focusing on adverse effects of AC amendments under laboratory conditions to L. variegatus (Jonker et al. 2009; Nybom et al. 2012; Nybom et al. 2015). Although MagAC was removed from the sediment before the ecotoxicity tests, the residues were high enough (> 1%) to cause significant adverse effects, with their magnitude depending on the particle sizes. The finely powdered MagAC variant (> 64 µm; IV) caused reductions in L. variegatus growth as would be expected from PAC, while the coarser MagAC material (75 – 300 µm) resulted in milder adverse effects. C. riparius tolerated lower AC doses better than L. variegatus, with severe adverse effects starting at concentrations of 2% and more (III). This species-dependent magnitude of adverse effects caused by AC can be seen throughout the available literature. Low to moderate toxicities are e.g. reported for C. riparius (Nybom et al. 2016a; Nybom et al. 2016b), Asellus aquaticus (Kupryianchyk et al. 2011), Neanthes arenaceodentata (Millward et al. 2005; Janssen et al. 2012) and Macoma balthica (McLeod et al. 2007). Besides for L. variegatus, strong adverse effects have also been observed in Gammarus pulex (Kupryianchyk et al. 2011). One potential reason for the species-dependent magnitude of adverse effects are the different feeding strategies of the organisms. While more selective feeders, such as G. pulex (Kupryianchyk et al. 2011) or C. riparius (Naylor & Rodrigues 1995) can avoid the ingestion of AC particles to some extend, this is more difficult for unselective feeders like L. variegatus (Leppänen & Kukkonen 1998a).
Figure 7. Summarized biological effects of all tested AC materials (mixed into the sediment) on *L. variegatus* and *C. riparius* growth. AC-induced adverse effects were observed for all materials (except GAC) and their magnitude depended mainly on AC particle size. MagBio and standard biochar caused low adverse effects, despite small particle sizes. Mean and data range (where more than one experiment using the same AC dose was conducted) are shown. Data obtained from I–V.

The AC variant used did not have a measurable impact on the results. Neither magnetizing (IV) nor different raw materials and manufacturers (I) significantly worsened or improved the response of *L. variegatus*. Unlike the ACs, MagBio, which is based on non-activated biochar, was milder (no significant effect seen for MagBio in IV). A preliminary experiment found similar results for non-magnetized biochar (Figure 7). These findings suggest that the activation process and its effect on chemical and physical surface structures (Gergova et al. 1993), have a large impact on the ecotoxicity of sorbent materials.

Despite the extensive research conducted, the mechanisms that cause AC-induced toxic effects in benthic invertebrates remains somewhat unclear. The observations made in the research presented here can help to identify the causes of these adverse effects.
Figure 7. Summarized biological effects of all tested AC materials (mixed into the sediment) on L. variegatus and C. riparius growth. AC-induced adverse effects were observed for all materials (except GAC) and the magnitude depended mainly on AC particle size. MagBio and standard biochar caused low adverse effects, despite small particle sizes. Mean and data range (where more than one experiment using the same AC dose was conducted) are shown. Data obtained from I–V. The AC variant used did not have a measurable impact on the results. Neither magnetizing (IV) nor different raw materials and manufacturers (I) significantly worsened or improved the response of L. variegatus. Unlike the ACs, MagBio, which is based on non-activated biochar, was milder (no significant effect seen for MagBio in IV). A preliminary experiment found similar results for non-magnetized biochar (Figure 7). These findings suggest that the activation process and its effect on chemical and physical surface structures (Gergova et al. 1993), have a large impact on the ecotoxicity of sorbent materials. Despite the extensive research conducted, the mechanisms that cause AC-induced toxic effects in benthic invertebrates remains somewhat unclear. The observations made in the research presented here can help to identify the causes of these adverse effects.

One hypothesis that has been made is the effect of an unintended binding of nutrients to the sorbent amendment. The affinity of organic substances to AC surfaces is not selective to HOCs. Nutrients could be sequestrated in similar ways as the contaminants, making them inaccessible to organisms. Although the actual availability of nutrients to organisms has not been extensively investigated, it has been shown that organic carbon readily adsorbs to AC (Schreiber et al. 2005). Evidence for a nutrient-limiting effect of sorbent amendments are the lower adverse effects in AFS compared to natural KJ sediment. For TLC amendments, for example, L. variegatus showed better growth in AFS, despite higher AC-doses, (Figure 5). Nybom et al. (Nybom et al. 2012) directly compared the two sediments and found a similar effect for AC mixed into the sediment. Due to the short equilibrating time (one week) used for AFS, the Urtica powder remains an easily accessible food source of high quality to benthic organisms. This allows significantly higher growth rates of L. variegatus and C. riparius in AFS compared to natural sediments, where nutrients might be harder to access (Figure 8). When AC is introduced to these naturally poor sediments, the effect of nutrient binding might have a larger impact than in the rich AFS (Nybom et al. 2012). Still, there are findings that contradict the theory. Janssen et al. (2012) found that AC could bind nutrients only from an aqueous suspension, but not from natural sediments. This would affect the relatively loosely bound nutrients in AFS to a greater extent after an AC amendment, thus bringing the magnitude of adverse effect in both sediments closer together.
There are further indications that the binding of nutrients is at least not the major cause for the ecotoxic effects of AC. The TEM images of L. variegatus showed significant reductions in microvilli density after exposure to AC-amended sediments. This led to the assumption that AC-particle ingestion could cause severe damages to the organism’s gut (I). Similar observations were made for L. variegatus by Nybom et al (2015), providing evidence that AC can be directly harmful to benthic organisms. The observed cessation in feeding following the sorbent amendments (I, IV) support the conclusion of the direct adverse effects. Visual observations of C. riparius exposed to TLC treatments (II) showed that PAC particles had adhered to the larvae, almost completely covering some individuals (Figure 9). It is a possibility that this could directly induce toxic effects, e.g. hindering dermal oxygen uptake.

![Figure 9. C. riparius larva covered in PAC particles after exposure to sediments amended with an AC TLC.](image)

External feeding of C. riparius larvae with Tetramin® could not prevent their high mortality on TLC treatments. Although a share of this applied food source might be adsorbed and thus become unavailable quickly (Janssen et al. 2012), it would be expected that larger food particles remain at least partly accessible. This would especially be the case with small amounts of sediments in between the applied food particles and the AC layer, suggesting a quicker decline of adverse effects than what was observed (II, Figure 6). The occurrence of mortality in L. variegatus with AC-only TLC provides additional support for the hypothesis of toxic effects caused by direct contact to the sorbent rather than indirect processes. During the MagAC tests, the organisms showed no mortality for 28 days when feeding was essentially ceased (IV). Based on these results, even if nutrients would become completely inaccessible, L. variegatus should still be able to survive the exposure time. Lastly, GAC was shown to adsorb contaminants, but no adverse effects were observed for either of the two test organisms in doses up to 7.5 % (III).
For higher doses, Nybom et al. (2012) found adverse effects to also occur with GAC. However, this could also be caused by an abrasion of GAC particles during the mixing process. The application of such large GAC amounts can then lead to the formation of PAC in sufficiently high doses to cause adverse effects by ingestion.

MagAC was developed to tackle the direct toxic effects of AC to organisms, as the sorbent removal from the sediment should alleviate the amendment’s negative impact. This is supported by the observed reduction in adverse effects in sediments from which MagAC (V) has been recovered. However, the recovery was not complete, leaving behind enough AC to still cause adverse effects. Low recovery rates (<55%) for magnetized ACs were also reported by Choi et al. (2016). A near-complete stripping of AC particles from the sediment might be possible, as seen for MagBio (V) and eliminate all adverse impacts. Nonetheless, this can be hard to achieve reliably, especially under field conditions.

The findings presented in papers I, II, IV and V strongly influenced the development of the novel ACC-G remediation material. To reduce the ingestion of this material and thus its toxicity, ACC-G consists of PAC clustered into larger particles outside of the ingestible particle size of organisms like *L. variegatus* and *C. riparius* (see section 4.3.1).

### 4.1.2 Remediation efficiency of AC amendments

In all treatments where PAC was mixed into the sediment, the remediation efficiencies were extremely high. Reductions in HOC-bioavailability were significant at 0.1% PAC and could reach up to 93% for *L. variegatus* (I) and up to 97% measured with PE passive samplers (IV) (Figure 10). Reductions of more than 90% with this type of AC-treatment are not unusual for laboratory studies (Sun & Ghosh 2008; Janssen et al. 2010; Nybom et al. 2015). However, this is limited to PACs. The coarser GACs underperformed, with PCB-body burdens reduced by less than 45% (III). The potentially poor remediation efficiency of GAC has also been demonstrated by Zimmerman et al. (2005), who found no significant effect on Cfree reductions of PAHs. This shows that the adverse effects of most currently available AC materials correlates strongly with their remediation potential (Figure 11). This seems to be true with biochar as well, although results are less conclusive. On the one hand, there was only a minor difference in Cfree reductions of PAHs between MagAC and MagBio of PAHs. This is in line with observations made by Silvani et al. (2017), who found biochar to be more effective than GAC. However, in comparison to PAC, and especially when bioaccumulation into organisms is regarded, biochar is often the less effective sorbent (Figures 10 & 11) (Chai et al. 2012; Beckingham & Ghosh 2017). The discrepancy between bioavailability as predicted by Cfree and observed bioaccumulation in organisms can be explained by
a lower adsorptive strength of biochars in the presence of digestive fluids (Zhang et al. 2015; Hilber et al. 2017). The higher the relative importance of ingested particles as a potential contaminant exposure source becomes in comparison to passive uptake from the pore water, the further C_free and actual bioaccumulation might diverge from each other. This can depend on either the examined organism, or abiotic factors, such as a contaminant K_ow and its sorption strength to sediment or sorbent particles (Leppänen & Kukkonen 1998c; Lu et al. 2004). As the desorption resistance of contaminants tend to be higher when bound to AC, the phenomenon might be more clearly observed with biochar. Good agreement between C_free and PCB-bioaccumulation in L. variegatus was found e.g. by Nybom et al. (2015).

Figure 10. Summarized remediation efficiency of all tested AC materials (mixed into the sediment). PAC and ACC-G showed the highest potential reductions in HOC-bioavailability, while GAC’s efficiency was low, even in high doses. Bioavailability was measured as PAH-uptake in PE passive samplers for MagAC and MagBio, and as PCB-bioaccumulation in L. variegatus and C. riparius for other AC materials. Mean and range (where more than one experiment using the same AC dose was conducted) are shown. Data obtained from I–V.

Figure 11. Positive correlation of adverse effects (organism growth) and remediation potential (bioavailability of PCBs / PAHs) of AC amendments. The higher line for ACC-G illustrates less of a trade-off, i.e. to reach the same remediation potential as with PAC, less adverse effects are caused. The slope for GAC does not differ significantly from zero due to the low adverse effects of this amendment. Data for PAC: mean results from I, II, III, other sorbents as replicate results from II and III.
The high remediation efficiencies observed in the tests conducted for this thesis did not depend on the tested AC type. As observed with the adverse effects, there was no significant impact of magnetization or AC raw material on the contaminant binding potential. Nonetheless, it has to be noted that the coating of AC particles with iron hydroxides can slow down the speed at which contaminants are adsorbed and thus short-term remediation potential (IV). However, after 3 or more months, both conventional AC and MagAC are highly effective in reducing $C_{\text{free}}$ of PAHs in sediments. The contaminant uptake in PE passive samplers was 67 – 97 % (IV, V, respectively) lower in sediments treated with MagAC compared to the unamended control sediment. This is in line with an 89 % reduction reported for magnetized ACs in Choi et al. (2016), who also found no significant difference depending on whether petrogenic or biogenic raw materials were used for the production of ACs.

Figure 12. Remediation efficiency of a PAC TLC (1.2 kg/m²) after simulated recontamination, where the AC layer was covered with increasing amounts of contaminated sediment. The bioaccumulation of PCBs could be effectively reduced with the applied TLC. The AC-cap’s efficiency, however, depended on bioturbation. With *L. variegatus*, the sorbent retained its efficiency for significantly longer than with *C. riparius* larvae. Values are relative to the corresponding control group growth of each experiment. Mean and sd are shown.

Applying the AC as a TLC on top of the sediment was shown to significantly lower PCB-bioaccumulation (I), even when recontamination of the amended site was simulated (II). There were clear signs of *L. variegatus* dwelling through the AC-layer, mixing it with the underlying sediment, as well through the layer of contaminated sediment settling after the application of the TLC (Figure 12). This bioturbation helped to retain the AC-caps efficiency in binding contaminants not only from the sediment below the amendment, but also in the newly deposited material. Consequently, this was not observed with the low dwelling-intensity caused by *C. riparius*. Lin et al. (2018) reported similar results, showing that *L.*
*variegatus* bioturbation could reduce the contaminant flux from freshly deposited, contaminated sediment to the overlying water by up to 90%. Findings of retained AC TLC effectiveness, despite recontamination of the amended site, were also made under field conditions (Cornelissen et al. 2015).

A direct comparison of the remediation efficiency of TLC and mixing treatments is difficult, as different doses and equilibration times were used. The TLC treatments might have been further away from reaching an equilibrium state than microcosms where the AC was mixed into the sediment (Beckingham & Ghosh 2011). However, the results from the laboratory tests (I), as well as findings from field studies (Cornelissen et al. 2011; Cornelissen et al. 2012) showed that the TLC remediation method can be successful. This conclusion provided the foundation for the planning and design of the field trial (II).

### 4.1.3 Scaling up: moving from laboratory to field

The decision to use an AC-clay TLC for the field trial (II) was based on the findings of a successful PCB-bioaccumulation reduction with this amendment, the reduced adverse effects compared to pure AC caps (I) and the simple application of a TLC with Sedimite™ (Menzie et al. 2016). Determining the dose to be applied in the field based on the findings in the laboratory posed some difficulties. Increasing the TLC thickness (0.6 to 1.2 kg AC/m²) seemed to worsen the adverse effects to a greater extent than it improved the remediation efficiency. Nonetheless, a higher target dose of 1.2 kg AC/m² was determined beneficial for the field trial, since there can be other organisms that would benefit more from an increased TLC thickness than *L. variegatus* (Josefsson et al. 2012). Furthermore, the magnitude of effects of AC amendments, both beneficial and negative, can be exaggerated under laboratory conditions (Cho et al. 2009). The targeted dose was set to 1 – 1.2 kg AC/ m². To account for the potentially high losses of AC under field conditions (Cornelissen et al. 2011; Menzie et al. 2016), the practically applied dose was set higher (1.67 kg AC/ m²).

### 4.2 FIELD STUDY

#### 4.2.1 Impact of AC amendment under field conditions

The impact of the AC layer was less significant under field conditions than observed in the laboratory. A reduction in PCB-bioaccumulation was observed 2 months after the TLC amendment, but the effect diminished over the following months. AC induced adverse effects were not observed at any point. While less
conclusive results than obtained under laboratory conditions were expected (Cho et al. 2009; Cornelissen et al. 2011), the observed success of the remediation was considered insufficient. This was largely caused by poor retention of the AC on the site, a recontamination from untreated, adjacent sites, as well as slow mixing of sediment and AC due to a lack of bioturbation.

Although the clay addition to the AC-layer was shown to stabilize the TLC in some sites against cap erosion (Cornelissen et al. 2011; Menzie et al. 2016), this effect was not sufficient in Lake Kernaalanjärvi. Several storm events have contributed to a loss of the material from the site, which could not be prevented by the stabilizing properties of the clay addition to the TLC due to the relatively shallow water depth of the lake. High losses of clay-stabilized AC during storm events were also reported for one amended site by Menzie et al. (2016). An additional sand cap on top of the AC, as employed by Cornelissen et al. (2011) could further stabilize the TLC against water turbulence. However, this model was considered unsuitable for Lake Kernaalanjärvi, as the added sand layer would provide a barrier between AC and contaminated sediment deposited post-capping. Detailed results on AC-retention, adverse effects and PCB-bioaccumulation during the field trial in Lake Kernaalanjärvi are presented in paper II.

4.2.2 Potential remedies to shortcomings of conventional ACs

The poor AC-retention observed in Lake Kernaalanjärvi was suspected to be caused mainly by the high buoyancy (low density). The AC particles suspend readily in the water column and become subject to transport off the site. The experiences on shortcomings of AC-based sediment remediation gathered during the field trial were the main motivator to develop the novel ACC-G material. The main objective therein was to reach a significantly higher density of the granules compared to conventional ACs. While the clay added to Sedimite™ as a bulking agent has a similar purpose, the material disintegrates quickly after contact with water as designed. This could reduce its applicability in deeper water bodies, as the disintegration of the AC-clay pellets might start before the sorbent has reached the sediment. Wet weather conditions during application activities bear an additional risk, as the pellets have to be protected from moisture. The ACC-G granules, on the other hand, are designed to not disintegrate over long periods of time to allow application in deeper and turbulent waters. The low buoyancy of the granules is retained and can be modified by altering the clay – AC ratio or particle size. This is aimed at providing additional resistance against sorbent losses due to turbulent waters as observed in Lake Kernaalanjärvi (II) and other studies (Cornelissen et al. 2011; Menzie et al. 2016).
4.3 NOVEL, AC-BASED REMEDIATION PELLETS

4.3.1 Performance of the sorbent pellets

The ACC-G pellets proved to be highly effective in lowering PCB-bioaccumulation in both *L. variegatus* and *C. riparius*. When considering the same doses, they significantly outperformed GAC. Although PAC can achieve highest remediation efficiency in laboratory tests at very low doses (I, Nybom et al. 2015; Sun & Ghosh 2007), the ACC-G granules could reach comparable results in AC doses commonly used in field-scale applications (Ghosh et al. 2011). This was not observed with GAC, which might have to be applied in doses exceeding the 7.5 % used for the tests presented in manuscript III. Adverse effects of ACC-G were still observed, but with lower severity than seen with PAC (Figures 8 and 11).

As discussed in section 4.2, the practical applicability and long-term retention of AC at a treated site can depend on the buoyancy of the sorbents. Whether the ACC-G granules are generally tackling this issue was tested with a simple, preliminary setup measuring their sinking speed through a water column. In this test, the dry ACC-G granules sank more than 60 % faster than the GAC that was shortly pre-soaked (< 1 hour). The test setup does not allow for strong conclusions, but serve as a good indicator for the materials’ behavior in the environment.

Pre-soaking the GAC for longer time (for as long as 8 hours) could further improve its settling speed through the water column (Patmont et al. 2015). However, this increases costs by raising energy and equipment requirements of the operation, since the additional water-weight has to also be transported. Pre-soaking the sorbent directly at the application site requires larger transportation vessels equipped with suitable containers. Furthermore, the pre-soaking time is added to the overall duration of the works. ACC-G granules, on the other hand, can be applied dry without further pre-treatment. The higher density of the granule could also improve the retention of the sorbent to a site in turbulent waters, although further tests are required.

4.3.2 Development potential and outlook

The major target for improving the production process should be to increase the short- and long-term stability of ACC-G. Although only minor losses of AC from the granules was measured, the adverse effects of even small residues of PAC in sediment have been clearly demonstrated. Different ratios of AC and clay in the granules, other clay materials, and higher firing temperatures can be tested to further improve the post-amendment material integrity. It has to be considered that raising the production temperature of the material increases the importance of
excluding oxygen from the firing chamber to prevent the AC from burning off (Buettner et al. 2014).

The high base-density of the material can be further improved with established methods, such as soaking the sorbent over longer time (Patmont et al. 2015) or in salt water with a higher salinity than the water in the target waterbody (Cornelissen et al. 2012). However, these are laborious methods and, in the case of increasing the materials salinity, more suited to larger waterbodies or saltwater systems. In smaller freshwater systems the added salt could lead to adverse environmental impacts. An easier approach to increasing ACC-G’s density lies in the modification of the production process. Choosing different clay materials and increasing the firing temperature can not only improve the stability of the clay granules, but also significantly increase their density (Baumann & Keller 1975). Furthermore, by incorporating additives of higher densities than clay (generally around 1.3 – 2.7 g/cm³; Baumann & Keller 1975), the buoyancy of sorbent material can be reduced as well. Nevertheless, it has to be assured that the additives are not released from the granules over longer periods of time, or that they are of no concern to the environment. Additives can further be used to completely alter the technical properties of ACC-G and its potential application range. Magnetizing the granules by incorporating iron oxide and hydroxides (Oliveira et al. 2002) would allow for contaminant extraction and recovery, including the potential reuse, of the sorbent material. Sorbents optimized for the sequestration of nutrients (phosphorus or nitrogen) can be added to obtain a material for the treatment of eutrophic aquatic ecosystems. Suitable sorbents for this purpose are for example certain biochars (Kizito et al. 2015) or hydrated ferric oxides (Pan et al. 2009), the latter of which could be easily combinable with the idea of a retrievable, magnetized material. Incorporating heat resistant metal binding substances before firing, or applying them by coating post-firing could extend the application range to metal contaminated sediments. Bisphosphonates (Iде et al. 2011) or chitosan (Ding et al. 2007) could be suitable for this purpose. The AC can be retained in the granules to strongly bind these metal complexors (Venault et al. 2008), which could help reduce their loss by dilution in the water phase. Incorporating the metal complexors into larger ACC-G particles further prevents their ingestion by benthic invertebrates, which has been shown to reduce remediation efficiency due to chemical instability of the metal-complexes in the organisms’ guts (Väänänen 2017).
CONCLUSIONS
The results of the research project have demonstrated the high potential of AC-based sediment remediation, but also identified risks and potential shortcomings for application in the field. The adverse effects shown in the laboratory studies should not be neglected in the future development of AC-based remediation methods. The potential severity of adverse effects observed in this study is concerning, especially when AC is applied as TLC amendments. Even with a lower magnitude of adverse effects under field conditions, this could still cause major problems in vulnerable ecosystems. Nevertheless, this study has shown that AC-amendments are a sediment remediation method with great potential. The high contaminant binding efficiency of the tested sorbents was clearly shown in the laboratory experiments and supports previous studies in the published literature. The possibility of almost completely eliminating not only the release of HOCs from the sediment into water but also their bioaccumulation in organisms is remarkable. The results obtained in the laboratory, as well as from the initial stages of the field trial, have shown that AC TLC amendments provide a simplified yet effective alternative to actively mixing the sorbent into the sediment. The correlation of adverse effects and the remediation efficiency shown in this study has illustrated the dilemma for decision makers tasked with planning remediation work. This potential tradeoff has to be carefully evaluated before large-scale application is conducted. It was shown that site-specific factors, such as water depth, vulnerability to resuspension events, bioturbation activity or potential recontamination can have a great impact on both remediation success and adverse effects. Therefore, the suitability of AC-amendments to a contaminated site or the potential risks to the ecosystem can hardly be generalized. The need for further development of the AC-amendments was highlighted by the quick decline of remediation efficiency in the field, practical application issues of conventional ACs and the potential risk for adverse effects. The use of magnetized sorbents (such as MagAC) that can be recovered has shown to reduce the adverse effects of the amendments to some extent. However, the difficulties of magnetic sorbent recovery from sediment under field conditions, as well as the incomplete recovery rates, limit the application scope of MagAC at the present time. As a result, the development of a novel sorbent-material, ACC-G, was initiated. This AC-based material is still at a very early development stage, but has already been demonstrated to reduce the sorbent’s ecotoxic impact and to simplify its delivery to the sediment. At the same time, ACC-G has been shown to retain the...
5 CONCLUSIONS

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Nevertheless, this study has shown that AC-amendments are a sediment remediation method with great potential. The high contaminant binding efficiency of the tested sorbents was clearly shown in the laboratory experiments and supports previous studies in the published literature. The possibility of almost completely eliminating not only the release of HOCs from the sediment into water but also their bioaccumulation in organisms is remarkable. The results obtained in the laboratory, as well as from the initial stages of the field trial, have shown that AC TLC amendments provide a simplified yet effective alternative to actively mixing the sorbent into the sediment.

The correlation of adverse effects and the remediation efficiency shown in this study has illustrated the dilemma for decision makers tasked with planning remediation work. This potential tradeoff has to be carefully evaluated before large-scale application is conducted. It was shown that site-specific factors, such as water depth, vulnerability to resuspension events, bioturbation activity or potential recontamination can have a great impact on both remediation success and adverse effects. Therefore, the suitability of AC-amendments to a contaminated site or the potential risks to the ecosystem can hardly be generalized.

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As a result, the development of a novel sorbent-material, ACC-G, was initiated. This AC-based material is still at a very early development stage, but has already been demonstrated to reduce the sorbent’s ecotoxic impact and to simplify its delivery to the sediment. At the same time, ACC-G has been shown to retain the
great contaminant binding efficiency of PAC. With further improvements to the production process, ACC-G could become an alternative to conventional ACs, especially in waterbodies with turbulent waters. Furthermore, it is highly suited to projects with budget constraints, or in areas unsuitable for heavy equipment.
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Organic pollutants pose a major risk to aquatic environments. These pollutants accumulate within the sediment, making it a primary target for remediation efforts. A cost-effective approach to sediment remediation is the reduction of contaminant bioavailability with in-situ application of activated carbon (AC). In this thesis, the remediation efficiency and adverse effects of AC-amendments are studied in field and laboratory. The findings are then used to improve the remediation method with the development of a new, AC-based remediation material.