Dispersal and environmental impact of contaminants in organic rich, fibrous sediments of industrial origin in the Baltic Sea

Anna Apler
Abstract

The health of the Baltic Sea is negatively affected by hazardous substances such as metals and persistent organic pollutants (POPs), which include legacy pollutants that were banned decades ago, but still circulate in the ecosystem. Elevated levels of legacy pollutants, identified by HELCOM as key hazardous substances, have been found in accumulations of fibrous sediments, so-called fiberbanks and fiber-rich sediments, which derive from old pulp mills along the Swedish north coast. The fiberbanks are deposited in shallow water and bathymetrical models show evidence of their erosion, potentially caused by propeller wash, submarine landslides and gas ebullition. This thesis addresses the potential dispersal of key substances from three fiberbank sites located in a non-tidal Swedish estuary, in which metals and POPs are present in concentrations that may pose a risk for benthic organisms. Metals and POPs are partitioned to organic material and, as expected, show the highest partitioning coefficients (KD) in fiberbanks that have higher TOC levels compared to adjacent areas with fiber-rich sediments (natural clay sediments mixed up with fibers) or relatively unaffected postglacial clays. However, many analytes were found to be present in quantifiable concentrations in pore water, which indicates diffusion of substances from the solid phase to the aqueous phase. To assess the dispersive influence of an abrupt erosional event on dispersion, metals were measured in undisturbed bottom water and in bottom water disturbed by artificial re-suspension of fibrous sediments. The bioavailable, dissolved fraction of metals decreased in bottom water after re-suspension, probably due to the particle concentration effect. In contrast, the total concentrations of metals and number of quantifiable metals increased with particle concentration caused by re-suspension. At one station, the total concentration of chromium (Cr) was elevated to a level where it may lower the ecological status of the water body during periods of substantial erosion (e.g. spring floods or submarine landslides). Analyses of disturbed bottom water revealed, however, that minerogenic particles were preferentially re-suspended compared to organic. This suggests that physical erosion and re-suspension of fiberbank sediments might have a larger effect on dispersal of metals than on POPs.

Keywords: Fiberbank, fiber-rich sediments, metals, persistent organic pollutants, pore water, bottom water, dispersal, sorption, pulp and paper.
My dear colleagues at Marinen,
geologists,
Ocean Surveyor crew and technicians, who have worked by my
side all along,
this work is dedicated to you
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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The contribution of Anna Apler to the papers included in this thesis was as follows:

Paper I: The author was involved in the planning and achievement of the fieldwork, and wrote the paper

Paper II: The author was involved in the planning and achievement of the fieldwork, and contributed to the writing of the paper.
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Abbreviations

ACZA  Ammoniacal Copper Zinc Arsenate
AFS   Atomic Fluorescence Spectrometry
ANOVA Analysis of variance
AOX   Absorbable Organic halides
BAT   Best Available Technique
CCA   Chromated Copper Arsenate
CTD   Conductivity Temperature Depth
DDT   Dichlorodiphenyltrichloroethane
DDD   Dichlorodiphenyldichloroethane (transformation product of DDT)
DDE   Dichlorodiphenyldichloroethane (transformation product of DDT)
DOC   Dissolved Organic Carbon
DW    Dry Weight
EQO   Environmental Quality Objective
EQS   Environmental Quality Standard
ESP   Electrostatic precipitators
GM    Geometric Mean
HCB   Hexachlorobenzene
HELCOM Helsinki Convention (Baltic marine environment protection commission)
ICP-AES Inductively Coupled Plasma—Atomic Emission Spectroscopy
ICP-SFMS Inductively Coupled Plasma – Sector Field Mass Spectrometry
$K_D$  Sediment sorption coefficient
$K_{TOC}$ Organic carbon normalized sorption
LOQ   Limit of Quantification
OM    Organic Matter
PAH   Polycyclic aromatic hydrocarbon
PCB   Polychlorinated biphenyl
PCDD/F Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCP   Pentachlorophenols
POM   Polyoxymethylene
POP   Persistent Organic Pollutant
SDG   Sustainable Development Goal
SPM   Suspended Particulate Matter
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Term</th>
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<tr>
<td>SS</td>
<td>Suspended Solids</td>
</tr>
<tr>
<td>SwAM</td>
<td>Swedish Agency for Marine and Water Management</td>
</tr>
<tr>
<td>TBT</td>
<td>Tribetrytin</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>WDF</td>
<td>Water Framework Directive</td>
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</table>
Introduction

The Baltic Sea is one of the largest brackish seas in the world, relatively shallow (average water depth approximately 56 m) and connected to the Atlantic Ocean only via the narrow and shallow Danish Straits. As a result, water exchange is limited, with a relatively long residence time of several years in the central basins (Matthäus, 2006) that can negatively affect water quality. None of the sub-basins of the Baltic Sea are considered to have an acceptable environmental status and an integrated assessment of the ‘ecosystem health’ shows that very few coastal areas along the Gulf of Bothnia (Bothnian Sea and Bothnian Bay) can be considered healthy (HELCOM, 2010). Although measures and strategies to reduce the inputs of contaminants into the Baltic Sea have been undertaken, biota and sediments in all parts of the Baltic are still affected by hazardous substances (Bignert et al., 2007; Sundqvist et al., 2009; Miller et al., 2013; Sundqvist and Wiberg, 2013; Sobek et al., 2014, 2015; Nyberg et al., 2015). Organochlorines, such as dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) and their transformation products still contribute to poor reproduction among indicator species, such as sea eagles, decades after the substances were banned (e.g. Bignert and Helander, 2015; Helander et al., 2002). Contamination of fatty fish is also an ongoing problem. A large portion of the fish caught in the Baltic Sea exceeds EU thresholds in regulation EC No 1881/2006 (European Commission, 2006) and cannot be marketed within EU, although it can be placed on the national market. Persistent organic pollutants (POPs) listed under the Stockholm Convention (UNEP, 2008) are hydrophobic, bioaccumulative, and toxic, and can cause adverse effects on humans and animals. DDT and PCBs are included in this group of substances, and together with Hg are also listed as priority hazardous substances in the Directive 2008/105/EC on Environmental Quality Standards (European Commission, 2016). Key substances of current concern in the Baltic Sea and listed by HELCOM include; PCBs, heavy metals, tributyltin (TBT), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), DDT, polycyclic aromatic hydrocarbons (PAHs) and alkylphenols (HELCOM, 2010). Of these substances, PCBs, DDT and heavy metals such as Hg and lead (Pb) are considered legacy pollutants, i.e. a result of past use (EEA, 2011; ESF, 2011). In addition, offshore environmental monitoring of chemicals in sediments show that even though decades have passed since the ban of, for example, PCB, DDT and Hg within the business sector, these
pollutants still circulate in the aquatic system and occur in high concentrations in recently deposited sediments in the Baltic Sea (Apler and Josefsson, 2016).

The catchment area of the Baltic Sea consists of forest to an extent of 54% (HELCOM, 2007). The abundance of this natural resource in the area has resulted in a large forest industry sector that dates from the 19th century, with highest production in Sweden and Finland. In both countries, there have been several hundred forest industry sites, most of which were closed in the 19th and 20th centuries. The old, abandoned pulp and paper industry sites and many of those in operation are considered the most polluted in Sweden. In the 1990s the Swedish EPA started defining and developing strategies for contaminated land areas and the sites of old pulp mills were prioritized. In this management process, the pulp and paper industry was assigned the highest grade of contamination, risk class 1, together with e.g. the chemical industry, wood impregnation factories and glassworks.

Inventories of coastal and lake accumulations of fibers from pulp mill effluents were carried out by the Geological Survey of Sweden (SGU) between 2010 and 2017 (Apler et al., 2014; Norrlin et al., 2016; Larsson et al., 2017). The inventories revealed that 28 sites, estimated to cover approximately 29 km² in total, are covered with contaminated fibrous sediment where 2.5 km² are accumulations consisting solely of fiber (fiberbanks) (Norrlin et al., 2016). The dominating contaminants were found to be the legacy POPs and metals such as Hg, cadmium (Cd) and Pb. The inventories also revealed evidence of re-suspension of the fiberbanks by submarine landslides, sediment gas formation and propeller wash. These findings showed that there is a knowledge gap of sources of legacy POPs and metals to the Gulf of Bothnia, and in a broader perspective, the Baltic Sea. They also demonstrated the need for more knowledge on the processes governing the dispersal of these pollutants from contaminated sediment. This gap needs to be filled to achieve Swedish environmental quality objectives (EQOs), such as “A Non-Toxic Environment”, and “A Balanced Marine Environment, Flourishing Coastal Areas and Archipelagos”. In addition, The 2030 Agenda for Sustainable Development (UN, 2017) sustainability development goal (SDG) number 14 “Life below water” is directed towards marine environments, with the primary target to “By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution” (UN, 2018)
Aim and research questions

Substances banned decades ago are still in circulation in the ecosystem and there is reason to investigate if there is a link between the contaminated fiberbanks and the elevated levels of contaminants in sediments, water and biota of the Bothnian Sea (Fig. 1). This project aims to study the first link in this chain, the dispersal from sediment to water, and the papers of this thesis will increase our understanding of:

- how the concentrations of POPs and metals vary between the sediment types (fiberbanks, fiber-rich sediments and postglacial clays) and their degree of deviation from national backgrounds and available ecotoxicological thresholds for sediments (Papers I and II).
- the degree of mobilization of dissolved contaminants from the solid phase (sediment) to pore water and the partitioning between the two matrices (Papers I and II).
- to what degree metals, both particle bound and dissolved, are dispersed from the sediment to undisturbed overlying bottom water (Paper I).
- the effect of re-suspension of the sediments on the concentrations of metals, both dissolved and particle bound, in overlying bottom water (Paper I).

The fiberbank sediments, which contain cellulose and wooden fibers, are different in their texture and contain a higher content of organic matter compared to “natural” sediments in accumulation areas. In this study, three different fiberbanks, deriving from two different pulp industry types, have been studied and compared to each other.
Figure 1. As illustrated, the aim of this study is to investigate the dispersal of POPs and metals (Me) from sediment to pore water and from pore water to bottom water for metals. Both diffusive dispersal and dispersal from re-suspension have been studied.
The forest products industry and its waste products

The forest products industry can be divided into two main categories: the primary lumber and wood products industry, and the pulp and paper industry. The primary lumber and wood products industry includes facilities such as sawmills and plywood mills and cutting of timber to produce pulp wood. The pulp and paper industry, on the other hand, produces commercial pulp that is used to make paper and paperboard. The papermaking can be divided into three generalized steps: pulp making, pulp processing and paper/paperboard production. The first two steps are the most water consuming and chemical-intensive, generating the largest amounts of residuals of environmental concern within the sector (Svrcek and Smith, 2003). This thesis is, therefore, focused on the pulp industry where integrated pulp and paper mills are included.

The global pulp and paper industry is one of the largest industries in the world with major production in North America, Western Europe, Asia and South America. World production of paper and paperboard totals around 390 million tons a year where the European Union and North America account for about one-quarter each (Bajpai, 2013; Suhr et al., 2015). It has been estimated that 500 million tons of paper and paper products will be produced in the year 2020 (Ince, Cetecioglu and Ince, 2011).

The waste water from a typical pulp mill contains a range of different pollutants such as sludge, metals and fiber (Suhr et al., 2015) (Table 1). The discharges were emitted untreated or poorly treated to the receiving surroundings for long periods of time, resulting in pollution of air, water and land. Urged by environmental concerns and legislative pressure, along with technological developments and commitments from industry leaders, the emissions from this industrial sector have been reduced by 80-90% over the last few decades (Thompson et al., 2001).
Table 1. Summary of discharge sources from the pulp and paper industry (Suhr et al., 2015)

<table>
<thead>
<tr>
<th>Process</th>
<th>Examples of generated solid residues/waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood handling</td>
<td>Bark and wood fragments, sand, stone</td>
</tr>
<tr>
<td>Raw water treatment</td>
<td>Sludge from flocculation</td>
</tr>
<tr>
<td>Kraft (sulfate) pulping</td>
<td>Excess lime, dregs and grits from the recovery system; extracted electrostatic precipitator (ESP) ash; rejects and fiber from the fiber line</td>
</tr>
<tr>
<td>Sulfite pulping</td>
<td>Ash from the recovery boiler; sludge from the cooking liquor system; rejects and fiber from the fiber line</td>
</tr>
<tr>
<td>Mechanical pulping</td>
<td>Sand and wood fragments from chip washing; rejects and fiber from the fiber line</td>
</tr>
<tr>
<td>Processing paper for recycling</td>
<td>Rejects from stock cleaning (non-fiber rejects, e.g. sand, metal scrap), fiber rejects and deinking sludge</td>
</tr>
<tr>
<td>Papermaking</td>
<td>Rejects and fiber, fibrous sludge, coating pigments</td>
</tr>
<tr>
<td>Power boilers</td>
<td>Ash</td>
</tr>
<tr>
<td>Effluent treatment</td>
<td>Fiber sludge, biosludge and chemical sludge</td>
</tr>
</tbody>
</table>

Contaminants in pulp mill waste water

The characteristics of the waste water generated by the pulp and paper industry depend upon the type of process, type of raw material (e.g. hard wood or soft wood), process technology applied, management practices, internal recirculation of the effluent for recovery, and the amount of water used in each specific process (Svrcek and Smith, 2003; Pokhrel and Viraraghavan, 2004). Thus, pulp mill effluents are very complex mixtures with characteristics that differ from one mill to another. Prior to efforts to reduce polluting agents in waste waters, the pulp mill effluents were referred to as a Pandora's box of chemicals (Peck and Daley, 1994) pointing at the variety of elements and substances included. However, even though pulp processes have been the main sources of air and water pollutant outputs (Svrcek and Smith, 2003), significant amounts of residuals and contaminants have also been released into the environment by the primary wood products industries. For example, water bodies are affected by contaminants from bark and sawdust, including suspended solids (SS) and organic matter (OM), as well as runoff and waste from wood preservation sites storing wood treated with inorganic compounds such as chromated copper arsenate (CCA) and ammoniacal copper zinc arsenate.
(ACZA) or organic chemicals like pentachlorophenols (PCP) (Svrcek and Smith, 2003).

Wood-derived substances
Many of the problematic contaminants in pulp mill discharges are formed in the manufacturing processes as they are unavoidably extracted from the wood raw material (Svrcek and Smith, 2003). Wood is a natural organic material that consists of two main groups of compounds: carbohydrates (cellulose and hemicellulose) and phenols (lignin) (Pettersen, 1984). Wood also contains a group of substances referred to as wood extractives and inorganic elements such as calcium, potassium, magnesium, manganese and silica (Nascimento et al., 2013). The extractives consist of many diverse heterogeneous substances occurring in different ratios depending on the source of the wood, e.g. resin acids, fatty acids, alcohols and a variety of phenolic compounds. Waste water from pulp mills, therefore, contains complex mixtures of organic and inorganic compounds. Total suspended solids (TSS), a measure of the solid material in the waste effluent that does not pass through a 2 μm filter (Eaton, 2005), clouds receiving water and may settle and form fiberbanks, which results in bottom oxygen depletion and anoxia as the organic matter degrades. Lignin and its degradation products are responsible for problems such as discoloration of recipient water and high chemical and biological oxygen demand (Bajpai, 2013). Resin acids has been shown to have a toxic effect on a number of different organisms (Peng and Roberts, 2000). Even though the emissions of wood derived residues have drastically been reduced during recent decades, emission of TSS will remain a problem for the industry in the future (Suhr et al., 2015).

Chlorinated compounds
Chlorinated compounds associated with the pulp and paper industry find their way to the environment through different pathways, e.g. bleach plant effluents, from usage of impregnated wood, chlorinated biocides for prevention of insect infestation within the forest industry and accidental spillages (e.g. Apler et al., 2014; Bajpai, 2013; Hall, 2003; Owens, 1991; Svrcek and Smith, 2003). Organochlorines such as polychlorinated PCDD/Fs, hexachlorobenzene (HCB) and chlorinated pesticides are collectively referred to as absorbable organic halides (AOX). These have been a focus of environmental research and legislation during the past decades due to their toxic characteristics (Hall, 2003; Svrcek and Smith, 2003). Many of the substances within the AOX group can be associated with chlorine bleaching of pulp where chlorinated compounds form complex structures with the organic matter (e.g. lignin and humic acids) which degrade slowly in the environment (Håkansson et al., 1988). However, according to the Paris Convention for Prevention of Marine
Pollution for Land Based Sources and Rivers (PARCOM), twelve European countries signed an agreement in 1995 to limit general AOX emissions to 1 kg/ton of bleached chemical pulp. The discharge limits have then been lowered gradually to 0.3–0.5 kg/ton (Savant, Abdul-Rahman and Ranade, 2006). Today bleaching with no chlorine involved, Total Chlorine Free (TCF), and with chlorine dioxide, Elemental Chlorine Free (ECF), are adapted together with ozone and peracetic acid methods (Blanco et al., 2004; Bajpai, 2013).

PCBs are another group of chlorinated compounds that can be associated with the pulp and paper industry. PCBs have never been active chemicals in pulping, but have been found in high concentrations in fibrous sediments in vicinity of pulp mills (Gullbring and Hammar, 1993; Gullbring et al., 1998). One well documented source of PCBs within the pulp and paper industry is the sludge from the de-inking process of recycled paper used in many places (Suhr et al., 2015). DDT was a common insecticide used in the forest industry for decades in the middle of the 1900s mostly to prevent infestation of the wood living beetle *Hylobius abietis* (Stoakley, 1968). DDT and its transformation products dichlorodiphenyldichloroethene (DDE) and dichlorodiphenyldichloroethane (DDD) have been found in elevated concentrations in sediments outside old pulp mills (Paper II). Many of the AOX are substances that persist in the environment for long periods of time and have negative impacts on organisms (e.g. Bignert and Helander, 2015; Helander et al., 2002; Helle et al., 1990; Jensen, 1972; Letcher et al., 2000).

**Metals**

There is scant scientific documentation on metal contamination related to the pulp and paper industry. However, the wastewater from a typical mechanical pulp mill contains heavy metals such as Pb, Cd, chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn). Analyses of kraft (sulfate) pulp residues consisting of lime mud, green liquor sludge etc., show that these discharges contain calcium oxide and calcium carbonate, potassium salts and different amounts of metals such as barium (Ba), Cr, Cd, Cu, Pb, Ni and Zn (Svrcek and Smith, 2003; Monte et al., 2009; Suhr et al., 2015). The amount of metals discharged varies between production of bleached and unbleached kraft pulp, where bleached kraft pulp emissions contain higher concentrations of heavy metals (Suhr et al., 2015). Heavy metal emissions have also been associated with pyrite ash from historical sulfuric acid production within the sulfite pulp process (Jerkeman and Norrström, 2018). Pyrite ash consists mainly of iron oxides but can also contain heavy metals originating from the minerals in the ore (Nordbäck et al., 2004). Arsenic (As), Cu, Hg, Zn, Ni, Pb, gold (Au), silver (Ag) and cobalt (Co) are some of the metals that have been detected in in pyrite ash (Tugrul et al., 2003; Nordbäck, Tiberg and Lindström, 2004; Jerkeman and Norrström, 2018). In 1989, the Swedish EPA estimated that between the years 1890 and 1980, 110 tons of Hg were released in air emissions
and 40 tons were released into water with a discharge maxima around 1950 when 3 tons of Hg were emitted from ‘roasting’ of pyrite ores (Jerkeman and Norrström, 2018). Mercury has also been used intentionally in different processes in the pulp industry: as a catalyst in the chlor-alkali process that produce chlorine gas for bleaching (Lindqvist et al., 1991; UNEP, 2013; Wiederhold et al., 2015), as a slimicide to prevent fouling in process tubes (Lindqvist et al., 1991; Wiederhold et al., 2015; Jerkeman and Norrström, 2018) and to protect pulp fibers from microbial degradation in mechanical pulp mills (Skyllberg et al., 2007; Jerkeman and Norrström, 2018).

The discharges of heavy metals from pulp mills are difficult to avoid. As the major present day source for the emissions of the metals is the wood used for pulping, a reduction in discharges of metals is probably possible by increasing the degree of process closure, while options for external treatment to reduce metal emissions are very limited (Suhr et al., 2015). Research funded by the Swedish Forest Industries Federation proposed that the metal load from the Swedish pulp and paper industry was 95 tons per year for Zn, 0.6 for Cd, 7 for Cu and 4 for Pb (Enell, 1996). These numbers equal 7%, 21%, 3% and 9% respectively of the total load of each element to the Baltic Sea (Enell, 1996). The estimated total amount of Hg emitted to air and water from pulp mills until the ban of use of the metal in pulp processes in 1967, is over 500 tons (Jerkeman and Norrström, 2018).

Nutrients

Discharges of organic materials that contain nutrients, such as nitrogen (N) and phosphorus (P), can cause eutrophication and are also components of pulp and paper mill effluents (Hall, 2003; Blanco et al., 2004). These two nutrients derive not only from the wood used in pulping but also from nutrients added to the secondary waste water treatment systems where microorganisms degrade organic matter before discharged into receiving waters. It is common to add ammonium and phosphate or urea to the waste water to enhance microbiological processes (Hynninen and Viljakainen, 1995; Suhr et al., 2015). Since it is difficult to match the consumption of nutrients by microbes with accuracy, the fertilizers are added in excess, which results in an excess of nutrients being discharged in the treated effluent (Hynninen and Viljakainen, 1995; Svrcek and Smith, 2003; Bird and Talberth, 2008). Just like the suspended solids, reducing nutrient emissions remains a challenge for the industry (Suhr et al., 2015).

Investigated contaminants

Legacy pollutants are still circulating within the Baltic Sea environment and in this project, metals and organic contaminants from this group have been
investigated. The heavy metals Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn have all been found in high concentrations in fiberbanks (Apler et al., 2014; Norrlin et al., 2016). Arsenic, which is a semi-metal, frequently occurs in high concentrations and is included in the selection of metals. The targeted POPs in this study are PCBs, DDT and HCB (Fig. 2), which also occur in high concentrations in fibrous sediments (Gullbring and Hammar, 1993; Gullbring et al., 1998; Apler et al., 2014; Norrlin et al., 2016). The PCB group includes twenty congeners: four planar (CB-77, -81, -126, -169), eight co-planar (CB-105, -114, -118, -123, -156, -157, -167, -189) and eight non-planar (CB-28, -52, -101, -138, -153, -170, -180, -209) congeners. The sum of the analyzed twenty PCBs is abbreviated $\Sigma_{20}$PCBs and the sum of the seven indicator PCBs (CB-28, -52, -101, -118, -138, -153, -180) is abbreviated $\Sigma_{7}$PCBs. The DDTs ($o,p'$-DDT and $p,p'$-DDT) and the transformation products DDE ($o,p'$-DDE, $p,p'$-DDE) and DDD ($o,p'$-DDD, $p,p'$-DDD) have also been included and are referred to as $\Sigma_{6}$DDX.

**Figure 2.** Molecular structures of the legacy POPs. DDT and its transformation products DDE and DDD, PCBs and HCB have been analyzed in this project.
Fibrous sediments

Fibrous sediments are products of losses of fibers to the receiving waters during pulp manufacturing. Before primary treatment plants were established for removal of solids and other pollutants, fibrous waste water was discharged untreated into receiving waters outside pulp mills in different parts of the world (Hall, 2003; Svrcck and Smith, 2003; Norrström, 2015). The emitted fibrous residues and solids were either deposited close to the terminus’ of the wastewater pipes forming accumulations of cellulose fiberbanks, or remained in suspension until they settled further away in deeper, sediment accumulation zones, mixing with natural sediments and thus forming fiber-rich sediments (Apler et al., 2014). Canadian studies have shown that discharged organic material in mill effluent undergoes coagulation and flocculation and are transported as agglomerates rather than individual particles in receiving waters (Krishnappan, 2000; Young and Smith, 2001). This flocculation process is enhanced by different factors e.g. the content of pulp fiber, amount of sodium (Na), calcium (Ca) and hydrolytic lignin, and has a negative impact on ecosystems close to the outfall of the mill due to the buildup of fiberbanks (Young and Smith, 2001).

In Sweden, there is no scientific literature and very little other information available documenting the amount of emissions before 1980s. However, it has been estimated that the discharges of SS increased significantly in 1880s when the first machine based mills were founded and reached two maxima, one in the 1930s and one between 1965 and 1975, when approximately 300 000 tons of SS were released per year (Jerkeman and Norrström, 2018; Norrström, 2015). Norrström (2015) estimated a net loss of up to 10% of cellulose fibers during pulp production until the period 1965-1975, after which the emissions were drastically reduced as a result of the modernization of the industry, which included closed water systems and the establishment of primary treatment in all mills during this time period. The amount of fibers released from a pulp mill was proportional to the water consumption in the mill, resulting in increased loads of fibers with increasing water consumption (Norrström, 2015). As mentioned earlier, the pulp and paper industry has reduced its environmental impact drastically during the recent decades, but even though almost half a century has passed since the discharge maxima of SS between 1965 and 1975 (Norrström, 2015), the residues from historical emissions remain on the seafloor along the Swedish north coast (Apler et al., 2014; Norrlin et al., 2016; Larsson et al., 2017).
Fiberbanks

The fiberbanks are characterized by massive cellulose deposits with high contents of water and cellulose or/and wooden fibers (Apler et al., 2014; Norrlin et al., 2016). The high load of terrestrial organic matter results in deficiency of dissolved oxygen in the sediment, making the environment inside the fiberbank anoxic, due to the consumption of oxygen as the organic matter degrades. The anoxic conditions generate formation of methane, carbon dioxide and hydrogen sulfide due to complex fermentation processes in the sediment (Leschine, 1995). These gases are released to the atmosphere as emerging bubbles (Smook, 2002; Apler et al., 2014). The gas seeps are visible as pockmarks at the sediment surface (Fig. 3A and B). However, since many fiberbanks are deposited in shallow waters, water circulation is usually adequate to keep the bottom water oxygenated. Yet, no benthic fauna was encountered during sampling in anoxic fiberbank accumulations (Apler et al., 2014; Norrlin et al., 2016). There is no scientific literature available on degradation rates of cellulose deposits in marine environments, but according to Smook (2002), sludge blankets of organic solids emitted from pulp factories are degraded very slowly due to the high content of tannins and lignin with complex molecular structures.
Figure 3A and B. The fiberbanks display rolling surface structures covered with pock-marks and the sulfur reducing bacteria Beggiatoa. Photo: SGU.

Fiber-rich sediments

Fiber-rich sediment is the term used for naturally deposited postglacial sediments composed of silty clay mixed with cellulose and/or wooden fiber from pulp production (Apler et al., 2014). These sediments are thought to be formed
when suspended solids in effluents are transported from the source and settle in calm environments where they are mixed with the postglacial sediments within the recipient (Judd et al., 1996; Krishnappan, 2000; Apler et al., 2014).

Sediments containing a high content of organic matter tend to appear as sapropels in the inventoried fiberbank areas (Norrlin et al., 2016). However, it has been proven difficult to differentiate a sediment with organic content deriving from anthropogenic sources such as pulp mills, from a sediment in which the organic components are "natural".
Transport processes

To understand and quantify transport mechanisms in sediments, it is important to comprehend sediment geochemical processes. Dispersal of pollutants from fibrous sediments to surrounding waters can occur through different dispersal mechanisms:

**Diffusion**: Diffusion is a chemically driven process by which matter is transported from one part of a system to another via random motion. Net diffusion (more matter transported in one direction than the other) occurs as a result of concentration gradients. The diffusion transport can be divided into two sub-processes: i) Eddy diffusion (= turbulent diffusion) is when a concentration gradient is equaled out by motions in the matrix, e.g. due to motions in pore water. This process is faster than ii) molecular diffusion, which occurs in stagnant waters e.g. over the diffusive boundary layer at the solid-water interface in an aquatic system. Diffusion arises within the same matrix or between two matrices with different chemical activity e.g. a molecule of a substance adsorbed to a sediment particle dissolves into water with lower chemical activity. Diffusion is often used to describe the movement of the contaminants, but can also be used to describe the movement of particles.

In this project the diffusion transport mechanism is relevant for the studies of pore water concentrations where molecules or ions are desorbed from particles in the sediment and dissolved into porewater. The same process also forms the basis for passive sampling of pore water contaminants (Paper II). Diffusion is also relevant when contaminants move from the fibrous sediment to the bottom water (Paper I).

**Advection**: The process of advection is simply described as passive transport of a substance by a moving medium e.g. a fluid, gas or particles by the medium’s bulk motion. In an aquatic system for example, it would be the transport of a contaminant, dissolved or carried by a particle, by bulk water flow.

In this project, the advective transport mechanism is relevant for the study of metal concentrations in bottom water that have been affected by re-suspension of underlying sediment. Relevant for this study is particle re-suspension triggered by ship traffic, currents, wind generated waves and submarine landslides.
**Dispersion** is a broader term that includes both advection and diffusion. The term is defined by Sly (1989) as:

the net result of numerous interactions between confining factors such as bathymetry and size and shape of an aqueous environment, and the differential response by particulates of various sizes and suspended load concentrations.

In short, dispersion is the dilution and settling of matter, either adsorbed on particles or freely dissolved, in a plume as it advects or diffuses from a point source.

In this study, dispersal is used as the overall term for transportation of contaminants from fibrous sediments to the surrounding aquatic system.
Material and methods

Detailed descriptions of all presented methods are found in Paper I and II.

Study area – Ångermanälven river estuary

The study areas are located in the inner part of the Ångermanälven river estuary (Fig. 4A and B) on the northern Baltic coast of Sweden. The Ångermanälven river estuary is a non-tidal estuary that extends approximately 50 km inland from the Bothnian Sea where the 450 km long Ångermanälven river discharges. The fresh water of the Ångermanälven river is positioned over the brackish waters that come from the Bothnian Sea (Cato, 1998). A sill, which rises to approximately 10 m depth, exists halfway along the estuary and divides it into two. The area between this sill and the river outlet constitutes the inner, fjord-like part of the water body with a maximum basin depth of 100 m where the studied water bodies are located. Several pulp and paper industries were located along the sides of the Ångermanälven estuary during the 19th and 20th centuries, generating a multitude of fiberbanks on the sides of the estuary (Apler et al., 2014).

Three fibrous sediment sites (Väja, Sandviken and Kramfors) and a reference site were sampled during the study, in total 25 stations. The three fibrous sites had been surveyed in previous investigations by SGU (Apler et al., 2014) and were chosen as study areas due to their differing geological and hydrographical conditions, e.g. the steepness of the river sides onto which the fiberbanks are deposited and the type of organic matter in the fibrous sediments. The study sites are located within two basins that failed to achieve good ecological and chemical status due to sediment mercury pollution after classification of surface waters in accordance with Water Framework Directive (WFD) (European Community, 2000).
Figure 4A. The study area (rectangular box) in Ångermanälven river estuary on the northern Baltic coast of Sweden.
Väja

The Väja site contains a fiberbank located outside an active mill (Fig. 4B; Fig. 2A in Paper I) that has manufactured unbleached kraft pulp since 1914/15.
Given that the Väja factory manufactured unbleached kraft pulp, it was long considered a minor culprit in terms of emissions of contaminated waste water (Valeur, 2000). However, in the end of the 1980s the seafloor outside the mill had become the largest anoxic, dead area of all pulp mill recipients along the Swedish north coast, and in 1990 the managing company was sentenced by a court ruling to reduce its emissions of oxygen depleting agents and SS by 50% within 5 years (Valeur, 2000). The earlier emissions of SS have given rise to a fiberbank situated at a water depth of around 15 m. It is estimated to cover an area of around 70 000 m² and is split in two due to a process water outfall that eroded the bank. The fiberbank consists mainly of cellulose fibers and patchy occurring wooden splinters down to a sediment depth of at least 6 m in some locations (Paper I). The fiberbank was, at the time of all performed surveys, anoxic at the sediment surface and down to the maximum level recovered during sampling. The fiber-rich sediment outside Väja covers an estimated area of around 800 000 m² and consists of reduced clays with high content of fibers and wooden debris on top of postglacial clays (Paper I). During the sampling in 2015, it was found that the delineation between the fiberbank and the fiber-rich sediments was not accurate, resulting in reclassification of the sediment from fiberbank to fiber-rich sediment at one sampling station. The Väja study area has been investigated concerning dispersal of POPs and metals (Papers I and II).

Sandviken

The fiberbank at Sandviken is located outside an old kraft pulp mill that produced unbleached kraft pulp between 1926 and 1979 (Fig. 4B; Fig. 2B in Paper I). The deposit is situated at a water depth of around 12 m. The facilities were demolished and deposited in situ between 1982 and 1984. According to inventory protocols produced by regional authorities, it is possible that the landfill still holds instruments containing, for example, Hg. This landfill is situated in the slope towards the Ångermanälven river estuary side. The emissions from Sandviken mill have generated a fiberbank that covers an area of approximately 55 000 m². The deposit is located outside an old wooden quay and consists of wooden splinters and chips down to a sediment depth of around 6 m. Unlike the Väja fiberbank, this fiberbank is covered with a layer of approximately 10 cm of recently deposited laminated clay. The fiber-rich sediments associated with this site cover an estimated area of approximately 500 000 m² and consist of reduced clays mixed with fiber and wooden debris (Paper I). Just like in Väja, it was found that the delineation of this fiberbank was not accurate, resulting in reclassification of the sediments at one sampling station. The Sandviken study area has been investigated concerning dispersal of POPs and metals (Papers I and II).
Kramfors

Kramfors sulfite mill was funded in 1907 and produced unbleached sulfite pulp until the closure in 1977. The facility was never extended with primary treatment and hence, the waste water was emitted untreated into the recipient until the end (Valeur, 2000). The accumulated material was deposited along the river sides of the industrial area (Fig. S1 in Paper II). However, several submarine landslides, documented on bathymetrical models of the seafloor, have caused the fiberbanks to slide from the sides and redeposit further out from the shoreline. In addition, fiberbank material has been dredged and dumped further out and patches of fiberbank material can be identified. The total area of the isolated fiberbank accumulations are around 135 000 m². The fiberbank material at Kramfors consists of water saturated cellulose fibers (Apler et al., 2014). The fiber-rich area covers an area of 2.4 km². The Kramfors study area has only been investigated concerning the dispersal of POPs (Paper II).

Reference sites

The reference station is located at a water depth of around 70 m in the river basin east of Sandviken (Fig. 2B in Paper I). The sediment consists of reduced postglacial clay with a minor organic component and is today considered relatively unaffected by the forest products industry that operated upstream, although it may have been affected during previous decades. The reference station is equivalent to the International Ocean Discovery Program (IODP) site M0062 (Andrén et al., 2013; Hyttinen et al., 2017).

As a reference for the current load of metals to the Bothnian Sea, concentrations of metals in the sediment of an offshore monitoring station (SE-2) east of the mouth of Ångermanälven river estuary have been used (Fig. 4A).

Sampling and analyses

Conductivity, temperature and oxygen measurements

Prior to sediment sampling, salinity and temperature were measured with a conductivity-temperature-depth (CTD) sensor from the water surface to the bottom of the water column. Oxygen levels were measured with an oxygen sensor to provide an estimation of the concentration of dissolved oxygen concentration in the bottom water.
Sediment sampling

All stations, except the ones located in fiberbanks, were sampled using a GE-MAX corer (a larger version of the device described by Niemistö (1974)). The surface sediments, 0-4 cm, were stored in plastic jars in a freezer (−18 °C) until analyses of total sediment metal concentrations. Sediments for pore water extraction were stored cool (+4-8°C) in plastic bags until extraction.

Due to the highly unconsolidated nature of the water saturated fiberbank sediments, sampling was carried out with a boxcorer (L 30 x W 30 x H 50 cm) in the Väja fiberbank and bulk samples (0-30 cm) were taken. In Sandviken and Kramfors, an Orange Peel Bucket (OPB) was used and bulk samples (0-40 cm) were obtained. Sediment samples for analyses of POPs were attained at 24 different sampling stations whereas metal samples were taken at 10 stations.

Pore water extraction

Pore water for analyses of metals was extracted from the sediment using centrifugation in tubes for 15 min at 2500 relative centrifugal force (rcf; Eppendorf centrifuge 5810). The obtained pore water was withdrawn using plastic syringes and transferred into plastic flasks provided by the analytical laboratory, then frozen (-18 °C) until analysis. Pore water for dissolved metal analyses was filtered through 0.45 µm Acrodisc syringe filters with Supor membrane. Two laboratory blanks with millipore water instead of sediment were included in the batch.

Concentrations of freely dissolved POPs in pore water were measured using polyoxymethylene (POM) strips according to the method described in (Hawthorne, Miller and Grabanski, 2009). Each sample was shaken for 28 days using an end-over-end shaker, after which the POM strips were retrieved, wiped clean from sediment particles and POPs extracted by shaking with organic solvents.

Bottom water sampling

Bottom water sampling was conducted at one station at each fiberbank and fiber-rich sediment in Väja and Sandviken, plus at the reference station using a Ruttner water sampler mounted on the previously mentioned camera cage. Bottom water was collected in two different ways: (i) with the sediment surface undisturbed and (ii) with sediment surface particles re-suspended. A weight was suspended underneath the camera cage, thus causing sediments to re-suspend when lowered to the seafloor surface. A remotely controlled mechanism released the Ruttner sampler to collect the bottom water at around 30 cm above the seafloor. Samples for total concentrations of metals, TOC, dissolved metals and dissolved organic carbon (DOC) were collected in plastic
bottles. For dissolved samples, the water was filtered using Acrodisc syringe filters with 0.45 µm supor membrane (Pall Life Sciences) immediately after sampling. Samples were stored in a freezer at -18 °C until shipping to the laboratory. In addition, 1 L water was sampled for determination of suspended particulate matter (SPM). The analysis of POPs in bottom water is not included in this thesis.

Suspended particulate matter determination
Suspended particulate matter (SPM) was determined with a gravimetric method based on the Swedish Standard SS-EN 872 where water samples were filtered through glass fiber filters (Whatman GF/F, 0.7 µm). The filters were then stored frozen (-18°C). Before the filtering, the filters were rinsed with ultra-pure water, dried at 105°C overnight, cooled in a desiccator and weighed. After filtering, the filters were dried again at 105°C, cooled in a desiccator, and weighed. To correct for weight loss, blank filters were used.

Sediment and POM analyses of POPs
Sediment concentrations of POPs were analyzed at the Swedish University of Agricultural Sciences (SLU at the laboratory of the Department of Aquatic Sciences and Assessment) using Soxhlet extraction based on US EPA method 3540C. Samples were mixed with sodium sulfate (Na₂SO₄), spiked with isotope-(13C)-labeled internal standards and extracted with acetone:n-hexane for around 24 hours. After extraction, activated copper was added to remove sulfur. The extracts were then cleaned up on multilayer columns composed of activated silica (SiO₂), sulfuric acid treated silica (40% H₂SO₄:SiO₂) and sodium sulfate (Na₂SO₄).

Each POM strip was extracted with acetone:n-hexane for 2 x 24 hours using an end-over-end shaker. Prior to extraction isotope-(13C)-labelled internal standards were added. After extraction, isotope-(13C)-labelled recovery standards were added and the sample volume reduced to 100 µL of n-tetradecane.

Analyses of extracts from sediments and POMs were performed on a gas chromatograph (Agilent Technologies, 7890 A) coupled to a triple quadrupole mass spectrometer (Agilent Technologies, 7010, GC/MS Triple Quad).

Sediment and water analyses of metals, TOC and DOC
Metals were analyzed at ALS Scandinavia AB, accredited for all analyses. Sediment samples were extracted using partial microwave assisted digestion with 1:1 HNO₃:water in closed Teflon vessels and the final analysis was done with inductively coupled plasma – sector field mass spectrometry (ICP-SFMS).
The sediment TOC was determined at SLU (laboratory of the Department of Soil and Environment) by elemental analysis using a TruMac Series Macro Determinator. In short, air dried (40 °C) sediment (0.5-2 g) was combusted at a temperature of 1350°C to analyze total carbon. To differentiate between inorganic (carbonates) and organic carbon the sample was first combusted at 550°C to remove the organic fraction. Quantification was done after elemental analysis.

Pore and bottom water samples were treated in HNO₃ in an autoclave followed by detection using ICP-SFMS or inductively coupled plasma—atomic emission spectroscopy (ICP-AES). Mercury was analyzed using atomic fluorescence spectrometry (AFS). TOC and DOC concentrations in water samples were analyzed at ALS Czech Republic using IR detection.

Calculations and data evaluation

The sediment pore water concentration (Cₚw) of each analyzed POP was calculated using the equation:

\[ C_{pw} = \frac{C_{POM}}{K_{POM}} \]  

(1)

Where \( C_{POM} \) is the concentration in the POM strip after shaking and \( K_{POM} \) is the established POM-water partitioning coefficient for each target compound (Hawthorne, Miller and Grabanski, 2009; Endo et al., 2011).

Sediment-water distribution coefficients (\( K_D \)) for each metal and POP was calculated using equation 2, based on the measured pore water concentration (\( C_{pw} \)) and sediment concentration (\( C_{sed} \)).

\[ K_D = \frac{C_{sed}}{C_{pw}} \]  

(2)

Sorption of hydrophobic organic contaminants is mainly dependent on the fraction of organic matter in the sediment. The organic carbon normalized sorption (\( K_{OC} \)) coefficient was calculated for each POP using equation 3, where \( (f_{OC}) \) is the fractional amount of organic carbon in the sediment.

\[ K_{TOC} = \frac{K_D}{f_{OC}} \]  

(3)

Chemical sediment data are assessed using two different systems. The most extensive classification system used for marine sediments was developed by the Swedish EPA (Swedish EPA 1999) and has been revised for classification of POPs by Josefsson (2017). This system groups the assessed elements and POPs into classes or criteria based on the statistical distribution of concentrations from surface sediment samplings in Swedish coastal and offshore waters.
In a scale of five groups, class 1 represents the natural background for the specific element. For organic substances class 1 represents the lowest 5th percentile of measured concentration in the database. Subsequent classes describe a successively larger degree of deviation from the natural or less polluted environmental state. Class 5 means a clear influence from pollution sources. Environmental assessment criteria are available for all metals and POPs analyzed within this study. For POPs, the criteria for HCB, Σ7PCBs and Σ3p,p’-DDX (p,p’-DDT, p,p’-DDE and p,p’-DDD) were used.

Since 2013, there are also environmental assessment criteria for water management based on toxicological studies on benthic organisms. These criteria are set by the Swedish Agency for Marine and Water Management (SwAM) and are presented in the regulation on classification and environmental quality standards regarding surface water HVMFS 2013:19 (SwAM, 2013). These criteria were developed for the participating countries within the EU to facilitate their adaptation of the environmental monitoring to local conditions. Effect-based criteria are set for two metals: Cd and Pb (HVMFS 2013:19). Due to the lack of Swedish ecotoxicological assessment criteria for the POPs studied in this project, Norwegian sediment criteria for HCB, Σ7PCBs and p,p’-DDT were used. These were developed by Norwegian authorities for classification of environmental status in water, sediment and biota (Norwegian Environment Agency, 2016).

Chemical water data were assessed using the EQS set in the EQS set in the Priority Substances Directive (EQSD) (2008/105/EC) under the WFD (2000/60/EC) applicable for river, lake, transitional and coastal waters (European Community, 2000). For As, Cu, Cr and Zn, national Swedish criteria for classification of ecological status (HVMFS 2013:19) were used.

Statistical analyses
Measurement uncertainties for metal analyses are expressed as an expanded uncertainty calculated with a coverage factor of 2 which gives a confidence interval of 95%. In the blank samples for pore water analysis all metal concentrations were below the limit of quantification (LOQ).

For calculations of the geometric mean (GM) and the sum parameters for the targeted POPs (Σ3p,p’-DDX, Σ6DDX, Σ7PCB and Σ20PCB), values below LOQ were given the value LOQ/2. One-way ANOVA tests were carried out to compare significant differences between the groups of samples. To differentiate pollution patterns between the three different sediment types and sampling areas, principal component analysis (PCA) was conducted.

Potential sources of PCBs were investigated using a cluster analysis following Ward’s method. Sediment samples were grouped by their relative concentration of the different congeners constituting 12 technical PCB products.
Results and discussion

Paper I presents the results of the distribution and dispersal of metals in fibrous sediments. For detailed descriptions of mobilization of metals between sediment, pore water and bottom water, see Paper I. The distribution and partitioning of POPs in sediment and pore water are presented in detail in Paper II. This section provides a synthesis of the two papers.

Sediments

The highest concentrations of POPs are found in the fiberbank sediments in all studied sites, with lower levels in the fiber-rich sediment and the postglacial clay (Paper II). The highest measured levels of $\Sigma_7$PCB and $\Sigma_3$p,p’-DDX are found in the Sandviken fiberbank where the geometric mean (GM) concentrations of the two substance groups lie within class 4 according to the Swedish EPA classification system (Josefsson, 2017). The higher $\Sigma_7$PCB levels in Sandviken cannot be ascribed to the former pulp making process but might be caused by leakage from the old landfill. The levels of $\Sigma_6$DDX are slightly higher in the Sandviken fiberbank but still in the same concentration range as Väja. The high concentrations of $\Sigma_6$DDX may be associated with former handling of timber impregnated with DDT to prevent insect damage to the tree raw material (Stoakley, 1968). The highest measured HCB concentration was found in the Kramfors fiberbank where the single sample contains levels within class 5. Similar to PCB, HCB cannot be associated with any of the processes within the old mill in Kramfors because bleaching of pulp was never undertaken there. In comparison with the offshore station, the fiberbank levels of all targeted POPs are higher in the fiberbanks, whereas the fiber-rich sediments and postglacial clays contain concentrations in the same range as the offshore sediment (Apler and Josefsson, 2016).

The metals that occur in concentrations with the largest deviation from background levels are Cd, Cr, Hg and Pb, all in the Sandviken fiberbank. However, metal concentrations do not differ as much between sediment types as the POPs. For instance, As and Co levels are lower in fiberbanks than in fiber-rich sediments and the postglacial clay. The high values of Cd, Cr, Hg and Pb in the Sandviken fiberbank are not observed in the Väja fiberbank, where the concentrations are lower and in the same order of magnitude as in
the other sediment types. The higher levels at Sandviken may partly be explained by the higher TOC level in one of the Sandviken fiberbank samples (26% of DW) in which the highest concentrations of metals have been detected (Table I in Paper I), but the higher levels may also reflect leaching from the landfill at the site. As mentioned earlier, according to the inventory protocols produced by regional authorities, it is possible that the landfill contains, for example, Hg from old instruments. In the postglacial clays outside Sandviken, the metals occur in approximately the same concentration range as the national background. The Väja fiberbank contain elevated levels of Cd (class 4) whereas the fiber-rich sediments are somewhat enriched (class 3) in the metals that are known to have been discharged in larger quantities by the Swedish pulp and paper industry: Cd, Cu, Pb and Zn (Enell, 1996). The elements As, Co and Ni occurred in higher concentrations in the offshore sediment than in any of the sampled stations within this study.

The fiberbank enrichment of POPs is easier to explain due to the hydrophobic character of the analyzed substances, which causes contaminant sorption to the organic fraction in the sediment. The Σ7PCB concentrations in the three investigated fiberbanks are several orders of magnitudes higher than in fiber-rich sediments and the postglacial clays. Also, Σ6DDX and HCB show higher concentrations in fiberbanks than in the other types of sediments. When the concentrations of the POPs are normalized to the fraction of TOC in the sample, concentrations are evened out but are still higher in fiberbanks. The Väja and Sandviken fiberbanks are enriched in Σ7PCB and Σ6DDT whereas HCB levels are more evenly distributed between stations and sediment types after normalization to TOC. This result indicates that diffusive pollution plays a more important role in the study area for HCB than for Σ7PCB and Σ6DDX. The more even distribution of HCB is also coherent with the fact that bleaching of pulp was never undertaken at any of the three mills.

The distribution pattern of PCB congeners (Σ20PCB) shows that different types of commercial PCB products have been used at Sandviken compared to Väja and Kramfors. Since recycled paper has not been in the production lines at any of the studied mills, it is likely that the PCBs in the fiberbanks come from other sources within the facilities, such as disposed electronic components, plastics or caulks in construction material (Ericksion and Kaley, 2011). The Σ6DDX distribution profile shows that the transformation products of DDT (DDE and DDD) dominate all three sites. This reflects historical (legacy) use of DDT. At Väja and Sandviken, the fraction of DDD is higher in the fiberbanks than in the fiber-rich sediment and postglacial clays, which likely is due to the anoxic conditions in the fiberbanks (Macalady, Tratnyek and Grundl, 1986; Huang, Liu and Kuo, 2001).
Pore water

Similar to the sediment concentrations, pore water levels of metals are higher (µg L⁻¹) than those of POPs (pg L⁻¹). There are few studies on pore water concentrations of metals and organic pollutants in the Bothnian Sea area and this study (Paper II) is the first to report DDX concentrations in pore water from sediment in the Baltic Sea. Σ₇PCB and Σ₆DDX concentrations in pore water within this study reflected sediment concentrations with maximum values in the fiberbank samples. HCB, on the other hand, did not show the same pattern but were more evenly distributed between sites and sediment types, just like the sediment concentrations of this substance. The levels of PCBs were found to be similar to pore water concentrations measured in the Stockholm archipelago (Jahnke, Mayer and McLachlan, 2012) but higher than reported concentrations in pristine areas of the Baltic Sea (Cornelissen et al., 2008) and in the Gulf of Bothnia (Sobek et al., 2014). The measured concentrations of Σ₆DDX in pore water were higher than those of Σ₇PCB even though the Σ₇PCB occurred in higher concentrations in the sediment matrix. This result is probably best explained by the lower average hydrophobicity of the Σ₆DDX compared to Σ₇PCB. The PCB congeners and Σ₆DDT compounds with lowest hydrophobicity dominated the substance distribution within the pore water samples. HCB occurred in concentrations in the same order of magnitude as the Σ₇PCB in pore water although the sediment concentrations were much lower. This result is probably also explained by the lower hydrophobicity compared to many of the Σ₆DDX and PCBs, which results in higher dissolution into the water phase.

Metal concentrations in pore water were low (compared to EQS values from WFD) and in many samples below LOQ. Hg and Cd, the two metals that deviated most from the national background in the sediment samples, were not quantifiable in any of the analyzed pore water samples but these are also the metals occurring in lowest total concentrations in the sediments. Measurements of DOC in the pore water samples reveal that the lowest concentrations of DOC seem to be associated with the lowest number of quantifiable dissolved metals. One exception is the Väja fiberbanks where pore water contained the highest DOC concentration (148 mg L⁻¹) but a low number of quantifiable metals. The low concentrations and high numbers of analytes below LOQ can be ascribed to factors that involve reactivity to inorganic ions in the sediments. Metals tend to form insoluble sulfides under reducing conditions (Di Toro et al., 1992; Chapman et al., 1998). The sulfides metacinnabar (HgS) and greenockite (CdS), for example, are less soluble than millerite (NiS) (Di Toro et al., 1992), which in combination with the low sediment concentrations of Hg and Cd in the sediment may explain why Ni is found in all pore water samples. It is also shown that stations further out from the fiberbanks contain the highest numbers of detectable metals in pore water. This may be attributed
to the lower concentrations of both TOC (an important controlling factor mobility between phases in sediments (Mahony et al., 1996; Santschi, Lenhart and Honeyman, 1997) and S in the sediments which could possibly increase partitioning of metals to the water phase. The Väja fiberbank sample, however, is deviating from the general pattern with a measured DOC concentration almost three times higher than the second highest value, from Sandviken fiberbank, but with a low number of detectable dissolved metals.

Sorption

To evaluate the degree of sorption of metals and POPs to the solid phase in the sediments, the sediment-water distribution coefficients ($K_D$) have been calculated using equation 2. For calculations of metal sorption, pore water samples where metals concentrations are below LOQ are excluded from the calculations. $K_D$ values for POPs are based on average $K_D$ values calculated for each congener or transformation product that was detectable. The results show that $K_D$ values for POPs are higher than those of metals in the fiberbanks at Väja (FBV) and Sandviken (FBS), and the fiber-rich area of Väja (FRV), whereas sorption is in the same range for both POPs and metals at the post-glacial clay in Sandviken (PGCS; Fig. 5). Co and Ni are the only metals occurring in concentrations above LOQ in both pore water and sediment samples for all types of sediment (allowing calculations of $K_D$), whereas Cr could not be detected in pore water from fiber-rich sediment in Väja. Only one $K_D$ value for HCB is available for Väja and Sandviken and is therefore left out from the comparison.

Of the POPs, PCB showed the highest affinity for the solid phase whereas $\Sigma_6$DDX and HCB demonstrated the same values as the strongest sorbed metals. Due to the hydrophobicity of the POPs, it would be expected that the organic compounds would be sorbed stronger to the sediments with higher TOC content than the metals. Metal partitioning to the solid phase is also affected by the organic fraction in the sediment through sorption to and within organic molecules (Ramamoorthy and Rust, 1978; Santschi, Lenhart and Honeyman, 1997) but is also subjected to a number of other factors such as clay particle adsorption and precipitation with sulfides under anoxic conditions, all resulting in increasing $K_D$ values. For POPs and metals, sorption is higher in the fiberbank samples than in those from fiber-rich and postglacial clays, which was expected because of the higher TOC content in the fiberbanks. When looking at the organic carbon normalized sorption ($K_{TOC}$) coefficient, calculated using equation 3, the sorption is evened out between sediment types and stations which emphasizes the importance of TOC for partitioning of hydrophobic compounds to the sediment phase. Metal $K_D$ patterns were less clear and showed that the content of TOC was not a dominating factor for partitioning to the sediment. For example, in Sandviken, Cr and Ni demonstrated
higher sorption to the postglacial clay than to the fiberbank (Fig. 5). Comparing the two fiberbanks, Väja and Sandviken, $K_D$ values could be estimated for Co, Cr and Ni in pore water from both sites, and values were always lower at Sandviken even though TOC levels were higher in this fiberbank. There is a possibility that the weaker sorption in Sandviken is a result of the difference between the types of organic matter in the two fiberbanks. The Väja fiberbank consists of relatively long cellulose pulp fibers whereas the Sandviken fiberbank has a higher proportion of small wooden splinters and chips (Apler et al., 2014). For example, it is possible that the fiber deposits at Väja, deriving from cellulose emissions, contain a larger fraction of lignin. Lignin is a possible adsorbent for both metal ions and organic pollutants and studies have showed that lignin deriving from kraft pulping can be an adsorbent for metals over a wide concentration range (Crist, Crist and Martin, 2003; Guo, Zhang and Shan, 2008). The stronger sorption at Väja may also be associated with higher S concentrations and thus, increased precipitation of sulfides, in the sediments where sorption is higher.

Figure 5. $K_D$ values show that the sorption of POPs is higher than that of metals in fiberbank samples from Väja (FBV) and Sandviken (FBS) and the fiber-rich sediments of Väja (FRV). Sorption is in the same range for POPs and metals in the postglacial clay outside Sandviken (PGCS).
Bottom water concentrations of metals

Bottom water concentrations of total and dissolved metals were analyzed at five stations: one station in each fiberbank of Väja and Sandviken, one station in the fiber-rich sediment of Väja, one in the postglacial clay close to Sandviken fiberbank and one at the reference station in the river basin outside Sandviken. As for the pore water, bottom water concentrations of both total and dissolved metals were low and often below LOQ (Fig. 4 in Paper I). Samples collected in the fiberbanks and the fiber-rich sediment of Väja after resuspension of the underlying sediment contained higher total concentrations and a larger number of quantifiable metals than the samples taken from undisturbed bottom waters. The higher concentrations were expected since particles were re-suspended and particle bound metals were included in the analysis. However, at the stations with postglacial clay, the opposite relationship was found, with no quantifiable total metal concentrations in the Sandviken station and only one quantifiable metal (Ni) at the reference station. The minerogenic sediments at these two stations contain low total concentrations of metals, which may be one reason, but it is also possible that the cohesive nature of clay decreases the degree of re-suspension resulting in lower total concentration of metals in the water. This supposition is confirmed by the SPM levels that show values orders of magnitudes higher at the fiberbank and fiber-rich stations compared to the postglacial clays in Sandviken and at the reference station. However, the TOC levels in the samples stayed within the same concentration range for all stations irrespectively of the degree of re-suspension (Fig. 4 in Paper I). This indicates that the increased SPM levels at the fiberbank and fiber-rich stations are caused by re-suspended minerogenic particles.

The concentrations of dissolved metals were low or below LOQ in all five samples, both after re-suspension and during undisturbed conditions. Compared to pore water, a smaller number of metals were quantifiable and the concentrations were lower in bottom water samples. The explanation for this result is probably a low diffusion rate of metals from the sediment or when the sediment is re-suspended, the particle concentration effect, which means that a larger number of particles in the water causes increased metal adsorption to surfaces and thus lower dissolved concentrations (O’Connor and Connolly, 1980; Benoit and Rozan, 1999). As for the TOC levels, DOC concentrations were in the same range in samples from all five stations. The DOC levels were also found to be in the same concentration range as TOC, which means that the organic matter in the bottom water mainly occurs in a dissolved fraction and that re-suspension causes the minerogenic fraction to suspend in the water. An explanation for this pattern remains to be found. Even though the dissolved fraction of metals decreased after re-suspension, earlier research has shown that re-suspension events leads to aeration of sediments resulting in oxidation of sulfides with a potential increased fraction of dissolved species...
in the water as a consequence (Huerta-Diaz and Morse, 1992; Zhuang, Allen and Fu, 1994).

Ecotoxicological relevance
The GM concentrations of $\sum_7$PCB in fiberbank samples from all three sites are classified as levels that may cause chronic effects on aquatic or sediment dwelling organisms at long term exposure (category III) according to the Norwegian criteria (Norwegian Environment Agency, 2016). In some samples from Väja and Sandviken, the levels exceed category III and are enough to cause acute toxic effects at short time exposure. The $p,p'$-DDT and HCB levels are within category II, which suggests no toxic effects according to Norwegian standards. However, these quality standards were developed based on sediment data from fine grained sediments with lower TOC content (1% of DW). This may result in an overestimation of the toxic effects due to a lower fraction of dissolved POPs in the fiberbanks due to the higher TOC content and thus, stronger sorption to the solid phase. Yet, bioaccumulation of POPs in benthic organisms (*Marenzelleria* spp. and *Saduria entomon*) in fiber-rich sediment from the same areas has been assessed (Dahlberg et al., in prep) and shows that the possibility of negative impact on marine organisms cannot be ruled out.

Sediment concentrations of Cd and Pb are below the threshold set by SwAM (HVMFS 2013:19) in all samples except one in the Sandviken fiberbank. At this station the Cd level of 5910 µg kg$^{-1}$ DW is well over the threshold value of 2300 µg kg$^{-1}$ DW and Pb exceeds its threshold of 120 000 µg kg$^{-1}$ DW. Thus, the levels of Cd and Pb at this station may cause negative impact on benthic organisms. The dissolved bottom water concentrations of the metals with available EQS values were found to be below threshold values for each respective metal. However, Cr exceeds the threshold value for total concentrations in bottom water from the fiberbank in Väja after re-suspension of sediment, according to thresholds evaluating ecological status (HVMFS 2013:19). This result indicates that Cr concentrations may lower the ecological status during periods of re-suspension e.g. spring floods. It is not possible to assess the metals concentrations that have been reported as below their respective LOQ. The elements As, Cu and Zn occur in concentrations below LOQ at all stations, but their respective LOQ is above the assessment criteria for ecological status. Therefore, it cannot be ruled out that As, Cu and Zn occur in concentrations that are harmful to pelagic organisms.
Conclusions and future perspectives

This study has focused on three fiberbank affected areas along the Swedish north coast. However, approximately 315 land areas are contaminated by the pulp and paper industry according to the Swedish national database for contaminated areas (EBH-stödet) (Fig. 6). Only a few of these areas have been investigated in respect to adjacent receiving waters. To obtain a full understanding of the fiberbanks’ impact on local and regional waters as well as on the Baltic Sea, further inventories of contaminated sediments must be carried out. This study has contributed new knowledge of the distribution and dispersal of POPs and metals in two types of fiberbank in a Swedish brackish estuary system. The main conclusions are:

- POPs and metals occur in concentrations that deviate from national background data and for PCBs are high enough to cause chronic effects on aquatic organisms according to Norwegian assessment criteria (Norwegian Environment Agency, 2016). Furthermore, the Cd and Pb concentrations exceed the national ecotoxicological assessment criteria at one of the studied fiberbanks (HVMFS 2015:14).

- POPs and metals show signs of dispersal from sediment to pore water, where POP levels in pore water are higher in fiberbank sediment than in fiber-rich sediment and postglacial clays. Metal concentrations are low or below the LOQ in many samples from all types of sediments, regardless of the total sediment concentration of the individual metals.

- Metal and POP partitioning to the sediment, $K_D$, is generally strongest in fiberbanks where the POPs showed higher correlation to TOC than the metals.

- Dispersal of dissolved metals from sediment to overlying bottom water was low in undisturbed bottom water and in bottom water affected by artificial re-suspension. After re-suspension of underlying sediments, metals in bottom water increased both in numbers and in total concentrations. The total Cr concentration at one station exceeded its threshold for ecological status after re-suspension.
• TOC and DOC levels in bottom water do not differ between stations and sediment types and do not change after re-suspension even though the SPM levels increase showing that minerogenic particles were preferentially re-suspended compared to organic particles. This result was unexpected.

The analyses of bottom water show that the concentrations of the freely dissolved, bioavailable fractions of metals are low, both during undisturbed and disturbed conditions. The levels of total, particle bound fraction on the other hand, increased in bottom water samples from fiberbanks after re-suspension indicating an increased dispersion of metals during periods of massive re-suspension such as spring floods. This process may result in transportation of suspended particle bound metals by currents to accumulation areas offshore where different chemical conditions prevail. Changes in the aquatic chemical conditions such as redox, salinity and pH may affect metal mobilization (e.g. Ingri et al., 2014; Zhuang et al., 1994). Climate change with increased precipitation and river discharge may result in increased erosion of fiberbanks in this area. The isostatic land uplift of around 8 mm/year in this region will continue to contribute to erosion due to decreasing water depth. Environmental feedbacks associated with climate change and land uplift must be taken into consideration in future work on fiberbank impact on the aquatic environment.

The type of organic matter in the fiberbanks needs to be further investigated. If suspended organic solids tend to flocculate when emitted in receiving waters it is likely that the fibers are bound to one another and thus, more resistant to re-suspension than recently settled minerogenic fines like clay and silt. Given that metals adsorb to the surfaces of clay minerals, physical erosion and re-suspension of fiberbank sediments may have a greater effect on dispersal of metals than on POPs.

There is a knowledge gap in the field of bioaccumulation of the fiberbank contaminants in benthic biota. The less hostile fiber-rich sediments are a habitat for benthic organisms that have bioaccumulated POPs (Dahlgren et al., in prep.) but bioaccumulation of contaminant metals has not been studied, so it cannot be ruled out. This link between the sediment and living organisms needs to be studied closer in the future to evaluate the contaminated fibrous sediments’ contribution to marine top predator health.

Remediation of contaminated sediments has been in focus within Swedish marine and water management the last few years but up to this date, there are no proven remedial techniques that fit the water saturated, organic rich fiberbanks (Jersak et al., 2016). This study shows that metals are more strongly sorped to the fiberbank in Väja than to the one in Sandviken. The difference in sorption
of metals between the two fiberbanks may be reflected by the different types of organic matter. It is possible that the cellulose fibers characteristic of the Väja fiberbank adsorb more contaminants than the wooden chips characteristic of the Sandviken fiberbank. If remediation is needed, it is of importance that the characteristics of the organic material are known, so that optimal remediation methods are used.

Figure 6. Approximately 315 land areas are contaminated by old pulp and paper mills in Sweden (data from EBH-stödet).
Acknowledgements

This project was financed by the Swedish Research Council for Environment (FORMAS) grant no. 214-2014-63 (for project TREASURE) and the SGU research grant no. 362-1493/2013. SGU also contributed by giving me the opportunity to be enrolled as an industrial PhD student at the Department of Earth Sciences according to the SGU agreement no. 411-1578/2013.

Just like most projects happening around the world, this one is not a one woman’s show but assigned to a whole bunch of competent, wonderful people that have my fullest gratitude:

Formed General Director at SGU, Jan Magnusson, who initiated the opportunities to become an SGU-doktorand.

Present General Director at SGU, Lena Söderberg, for letting me finish part 1 (licentiate degree) of my project.

Former avdelningschef, Anna Åberg, for supporting my project from the start.

My boss, the head of department of Marine environment and planning, Lovisa Zillén Snowball, for believing in me from the start and for helping me take the first step into research. I will be grateful forever!

My main supervisor, Ian Snowball, for support, patience, guidance and several good laughs. I hope we get the chance to continue this fibrous journey. Otherwise it’s about time to go out and look for new old sins at the muddy bottoms of the sea.

Sarah Josefsson, my co-supervisor, college and friend, thank you for being the kindest perfectionist and scientific leader imaginable!

Karin Wiberg, my co-supervisor at SLU, thanks for putting up with this hopelessly inorganic student!

Kevin Bishop, my other co-supervisor at SLU for positive feedback and cheering on.
All my colleges at Marinen, both land and sea based, you have all contributed to this work and should all be credited for it. Thank you for being the best colleagues in the world!

The members of TREASURE group for all the support and work hours on deck.

Freddan, for scripting, IT support, love and for teaching me that the oceans are the outer space on earth.

Colleague and IT expert Masi for helping me with my computer over and over again.

Johan S and Tone for all the help with figures and graphics.

Hans Norrström (ÅF consult), Reine Morin (SÖDRA) and Kristina Wiklund (SSVL) for sharing information, knowledge and experience from the Swedish forest industry.

Iréne Hedlund och Karin Jönsson at Länsstyrelsen i Västernorrland, for being my partners in fiber since the beginning of time.

My family: Mammut, for being my mum and for helping with molecules and graphics. Papp for being my dad and for helping with Mr Chatterbox on Fridays.

My Ikigai (my reason for being): my son, Arvid.
References


