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Spreading of Persistent Organic Pollutants from Fiber Bank Sediments

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Department of Aquatic Sciences and Assessment
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Spreading of Persistent Organic Pollutants from Fiber Bank Sediment in English

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Abstract

Discharge of untreated wastewater from paper and pulp industries have led to large environmental impacts on the coastal sediments in Västernorrland, Sweden. Dissolved fibers caused the formation of large fiber banks and fiber influenced sediment areas, which proved to be highly affected by contamination with persistent organic pollutants (POPs). Concentrations of hexachlorobenzene (HCB), 21 polychlorinated biphenyls (PCB) congeners and 6 substances of the dichlorodiphenyltrichloroethane (DDT) group were determined in sediment, pore water (extracted with polyoxymethylene (POM) strips) and two benthic biota species (*Marenzelleria ssp.*, *Saduria entomon*). Contaminants were extracted using Soxhlet (sediment), shaking with acetone:*n*-hexane (POM) and cold column extraction (biota). Multilayer clean-up columns were used for sediment and biota, before instrumental analysis with GC-MS/MS.

Several sediment samples were classified with very high contamination levels for HCB and PCB_7, which is an indicator value of the seven most common PCBs in nature. Different contaminant distribution patterns at the investigated sites indicated that contaminant composition varied at different local sources. Pore water concentrations were higher for less hydrophobic contaminant groups (HCB, DDT and its derivates (DDX)). Sorption (log K_d) increased significantly with increasing hydrophobicity (log K_{ow}) and was significantly higher in fiber bank sediments than in fiber rich sediments and less affected sediments. Bioaccumulation, measured with biota-sediment-accumulation factors (BSAF), seemed to have a bell-shaped distribution for *Marenzelleria* BSAFs when related to contaminant hydrophobicity; however, results observed were not significant. For *Saduria entomon*, bioaccumulation increased linearly with increasing contaminant hydrophobicity. Significant positive correlations between contaminant concentrations in biota and sediment or pore water was observed between concentrations in *Marenzelleria* on a lipid weight basis and concentrations in sediment on a dry weight basis.

Keywords: persistent organic pollutants, PCB, DDT, HCB, fiber bank, paper and pulp, sediment, POM, log K_d, log K_{ow}, bioaccumulation, pore water concentration, *Marenzelleria* ssp., *Saduria entomon*

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Popular science summary

Sweden is among the world leaders in the production of paper and pulp. However, this industry generates large quantities of wastewater that get discharged into the Baltic Sea and thus potentially affects the aquatic environment. Effluent water from the paper and pulp production contains contaminated cellulose or wood fibers that can accumulate on the seafloor and lead to the formation of so called fiber banks. Depending on the extent of fiber impact, these sediments can be categorized into 3 types: fiber bank sediment (consisting of 100% fibers), fiber rich sediment and less affected sediment. The substances that have been investigated in this study belong to the group of persistent organic pollutants (POPs) which are difficult to degrade (persistent), can accumulate in living organisms (bioaccumulative) and can be toxic. They are also hydrophobic, which means that they are repelled by the water phase. Consequently, these contaminants prefer to sorb to particles and fat in living organisms. The contaminants analyzed in this study were 21 polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and its 5 closely related substances (all together named DDX) as well as hexachlorobenzene (HCB). All contaminants had various applications (e.g. insulation, pesticide) but all of them were also related to the paper and pulp production. Although their production is banned nowadays, they are still found in the environment due to their persistence. Concentrations of these pollutants were analyzed in the sediment, in the sediment pore water and in sediment biota in fiber bank areas near Kramfors, Västernorrland. Generally, relatively high levels of contamination were found in the fiber banks. In sediment and biota, the PCBs concentrations were especially high. In the pore water, the less hydrophobic pollutants (HCB, DDX) were found in higher concentrations, compared to the more hydrophobic ones (i.e. PCBs). Moreover, the strength of the sorption of the contaminants and the tendency to accumulate in animals (bioaccumulation) was determined. The sorption was higher in fiber bank sediments than in fiber rich sediments and less affected sediments because of differences in organic carbon content. The sorption of the contaminants increased with increasing hydrophobicity. The bioaccumulation of contaminants in the biota *Marenzelleria* and *Saduria entomon* generally increased with increasing hydrophobicity, but declined again for the most hydrophobic ones in *Marenzelleria*, possibly because the most hydrophobic contaminants are strongly sorbed to the sediment. Reasons for the differences in bioaccumulation between the two species could be due to differences in the feeding behavior.

In conclusion, the high pollution levels of POPs in the fiber banks and the high accumulation in biota show that the fiber banks are an environmental concern. More research is needed, in order to better understand and determine the impacts of the spreading of these contaminants from fiber banks, as well as the related risks for environment and society.

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Abbreviations

∑PCBs	Sum of the 21 PCBs analyzed in this study
Ah	Aryl hydrocarbon (Ah receptor)
BSAF	Biota-sediment-accumulation factor
C_{free}	Freely dissolved concentration
C_L	Subcooled liquid solubility
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DDX	Sum of the six DDT related compounds analyzed
dw	Dry weight
FB	Fiber bank (sample name abbreviation)
FRS	Fiber rich sediment (sample name abbreviation)
GC	Gas chromatograph
HCB	Hexachlorobenzene
IS	Internal standards
K_d	Solid-water partition coefficient
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
K_{POM}	POM-water partition coefficient
LOD	Limit of detection
LOI	Loss on ignition

LOQ	Limit of quantification
LW	Lipid weight
MS	Mass spectrometer
MW	Molecular weight
OC	Organic carbon
OPB sampler	Orange peel bucket sampler
PCB	Polychlorinated biphenyl
PCB_7	Indicator parameter that sums up the most common PCBs in nature (PCB 28, 52, 101, 118, 138, 153, 180)
PE	Polyethylene
PES	Performance evaluation standard
POM	Polyoxymethylene
POP	Persistent organic pollutant
RS	Recovery standards
S/N	Signal to noise ratio
SED	Less affected sediment (sample name abbreviation)
SGU	Swedish Geological Survey (Sveriges geologiska undersökningar)
SLU	Swedish University of Agricultural Sciences (Sveriges lantbruksuniversitet)
SPME	Solid phase microextraction
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TEF	Toxicity equivalent factor
v/v	Volume per volume
ww	Wet weight

1 Introduction and objectives

1.1 Introduction

The forest industry is one of the main industries in Sweden and plays an important role in Swedish economy. Various subindustries are comprised under this term: forestry, pulp and paper industry, sawmill industry, carpentry industry, wood board industry, manufacturing of refined wood fuel as well as the packaging production from wood, paper and board. All together the forest industry in Sweden provides around 55000 jobs (Swedish Forest Industries Federation, 2014). Among the different parts of forest industry, the paper and pulp industry is the largest. In 2014, the production of 41 pulp mills summed up to a total production of 11.5 million tons (Swedish Forest Industries Federation, 2014). Almost 90 per cent of the paper and pulp is exported, and combined with the sawn wood products, this made Sweden the third largest exporter globally (Swedish Forest Industries Federation, 2014).

However, the pulp and paper industry is not only accountable for jobs and economic contribution, but also for the generation of pollutants. The high water demand during the production process leads to the generation of large quantities of waste water (Pokhrel & Viraraghavan, 2004). These polluted effluents impact the environment, when not or insufficiently treated before being discharged into receiving waters.

On the seafloor around pulp and paper mills in Västernorrland, Sweden, large accumulations of fibers have been observed. These so called fiber banks are formed from fiber residues in the discharged wastewater. As part of the *Fiberbank project*, the Swedish geological survey (SGU) mapped and sampled these fiber banks. Within the scope of this master thesis, samples from the Formas project TREASURE were analyzed in order to investigate the potential spreading of per-

sistent organic pollutants (POPs) from these fiber banks. However, sampling was conducted within TREASURE before the start of this thesis project. This thesis work consisted of chemical extraction of the contaminants, sample clean-up and analysis, and analysis of the results.

1.2 Objectives

The aim of this project was to investigate the presence and fate of persistent organic pollutants in three different fiber bank areas. The objective was to determine how available the pollutants in the sediment are for uptake in living organisms and transport to the water column. In order to do this, the amount of POPs was investigated in different matrices, namely sediment, sediment pore water and biota.

As a basis for this research, three hypotheses were formulated:

1. There is a correlation between contaminant physical-chemical properties and sorption to sediment as well as between physical-chemical properties and bioaccumulation. Sorption is lowest for compounds with low hydrophobicity. Bioaccumulation is highest for compounds with medium hydrophobicity.

2. There is a relationship between the sediment composition and sorption as well as between sediment composition and bioaccumulation. High fiber impacted sediments exhibit high organic carbon content and therefore sorption is high and bioaccumulation low.

3. Pollutant concentrations in biota correlate better to pore water concentrations than to total sediment concentrations.

2 Background

2.1 Fiber banks

The forest industry is an important industry in Sweden. It has provided work and generated export incomes, but it has also affected the environment. For example, the high density of pulp and paper factories in Västernorrland county has had serious impacts on the coastal environment in the area. Wastewater from the industries was discharged without cleaning for a long term period. The production-related wood and cellulose fibers that were suspended in the water accumulated and formed fiber banks in the water outside the factories. The Swedish Geological Survey (SGU), in cooperation with the Västernorrland county administration, identified and examined the fiber bank areas within the *Fiberbank project* (Apler *et al.*, 2014). In addition to looking at the spatial distribution of the banks, levels of pollutants were determined. The fiber banks proved to be contaminated with e.g. persistent organic pollutants (POPs) with levels classified as very high contamination (Apler *et al.*, 2014). Contaminants found, e.g. polychlorinated biphenyls (PCB) and dichlorodiphenyltrichloroethane (DDT), are linked to usage in forestry as well as to pulp and paper production. Apler *et al.* (2014) differentiates between pure fiber banks, which consist of 100% fiber material, and fiber rich sediments. The fiber banks are usually located close to the factories, but can also be present further away from the shoreline due to dredging activities to facilitate ship traffic to the factories (Apler *et al.*, 2014).

The Västernorrland coast, also known as the High Coast, lies within the region that exhibits the fastest uplift of land (8-10 mm/year) nationwide (Apler *et al.*, 2014). This will cause the fibers banks to rise closer to the water surface and consequently be more prone to erosion from for example waves. In consequence, it might lead to resuspension and spreading of the accumulated contamination. Furthermore, landslide scars and erosion channels have been detected by SGU in some of

the fiber banks in shallow water indicating that the pollutants present in the fiber banks can disperse suddenly and in high amounts.

Apler *et al.* (2014) linked the contamination of the organic pollutants that are also investigated in this work directly with the pulp and paper mills. Therefore the level of contamination can be assessed as the impact of the local sources. Nevertheless, high levels of pollutants not directly related to the paper production have been detected as well. Saw mills, which are also present in the area, could be additional potential pollution sources (Apler *et al.*, 2014).

The contamination of the area combined with the described geological circumstances pose a serious risk for the coastal ecosystem in the area and the ecosystem in the Gulf of Bothnia (Apler *et al.*, 2014). It is to be suspected that areas around other current or former paper mills are likely to have the same formation of fiber banks, and fiber banks are therefore likely to be present along the northern Baltic Sea coast, where the forest industry has been important. Despite the fact that the impacts of fiber banks are a highly pressing issue and should be focused on, no research or further investigations have been conducted on this topic so far. For this reason the investigations of this project regarding the presence and fate of pollutants in the fiber banks is of high relevance for the society.

2.2 Target analytes and properties

All the contaminants investigated in this thesis are toxic organic chemicals that are classified as Persistent Organic Pollutants (POP) according to the Stockholm Convention (United Nations Environment Programme, 2004). Although many different POPs exist, they exhibit some common characteristics: they are persistent, bioaccumulative and toxic. Partitioning of these compounds usually takes place to solids, especially organic matter, in aquatic ecosystems and into lipids in organisms avoiding the aqueous milieu. This is due to their hydrophobicity and lipophilicity, which in combination with their persistence leads to the ability for accumulation in organisms (bioaccumulation) and along the food chain (biomagnification) (Jones, 1999). Bioaccumulative and biomagnifying properties contribute to render POPs to pollutants of major concern regarding impacts on top predators, which includes humans (Jones, 1999).

2.2.1 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls are a group of anthropogenic toxic pollutants that consists of 209 congeners. The basic structure is a biphenyl that after being chlorinated incorporates between one to ten chlorine atoms instead of hydrogen atoms. The different congeners are distinguished by different numbering according to the position of their chlorine atoms on the biphenyl rings (Baird & Cann, 2012) (Figure 1). Due to their chemical and physical stable characteristics, PCBs found a wide range of applications. The main application was in capacitors and transformers as electrical insulating fluids as well as for heat transfer and lubrication. Among others, PCBs were also used in carbonless copy paper, paints and plastics (Erickson & Kaley, 2011). Even though PCBs are no longer intentionally produced in the world, the combination of their persistence together with widespread use and inappropriate disposal has made PCBs significant pollutants in the environment still today (Baird & Cann, 2012). Being suspected of being endocrine disruptors as well as carcinogenic, PCBs are recorded on several lists including the US EPA List of Priority Pollutants and the Stockholm Convention (Tehrani & Van Aken, 2014).

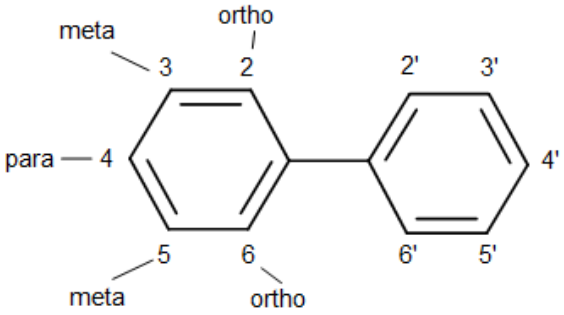


Figure 1: Chemical structure of a biphenyl molecule with numbers indicating positions for configuration.

The toxicity of PCBs is connected with their three-dimensional structure determined by the position of the chlorine atoms and their consequent ability to bind to a cellular receptor in animals and humans. Planar congeners are dioxin-like and therefore exhibit the same binding function to the aryl hydrocarbon (Ah) receptor, which is connected to different toxic effects (Erickson & Kaley, 2011). PCB congeners that take on planar configuration and bind to the Ah receptor have at least four chlorine atoms incorporated but none of them in the *ortho* position which is the carbon atom next to the one that binds to the second aromatic ring. Similarly, mono-*ortho* PCBs bind to the Ah receptor but less strongly. They also have at least four chlorine atoms in any position but only one in an *ortho* position (Erickson &

Kaley, 2011). The twelve congeners that exist in these configurations have been given toxicity equivalent factors (TEF) which express their binding ability to the Ah receptor and therefore their toxicity in relation to TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin), the most toxic dioxin (Van den Berg *et al.*, 2006).

2.2.2 Dichlorodiphenyltrichloroethane (DDT) and its metabolites DDE and DDD

DDT

The chemical formula of dichlorodiphenyltrichloroethane (DDT) is $C_{14}H_9Cl_5$. It is a substituted ethane, where at one of the carbon atoms all hydrogen atoms are replaced by chlorine atoms and two benzene rings substitute two hydrogen atoms at the other carbon as shown in Figure 2 (Baird & Cann, 2012). DDT is an organochlorine insecticide that has been used vastly for public health purposes for example to fight malaria and other pests by killing mosquitos, fleas, and, lice. In even higher amounts it was used as a pesticide in agriculture and forestry (Turusov *et al.*, 2002). In the environment, levels increased strongly due to overuse during the 1950s and 1960s (Baird & Cann, 2012). Due to its hydrophobic character it tends to bind to organic matter and bioaccumulate in lipids. In the environment it can therefore accumulate in tissues and in soils, which exhibit a strong sorptive capacity for this compound (Turusov *et al.*, 2002). DDT is not acutely toxic (Turusov *et al.*, 2002) but due to ecological concerns and toxic effects on freshwater and marine organisms as well as on birds, Sweden banned the usage of DDT in 1970 and many other countries followed (Turusov *et al.*, 2002). Nevertheless, it is still used for public health purposes in some developing countries (Turusov *et al.*, 2002).

DDE

By elimination of HCl, DDT can be metabolized or degraded to dichlorodiphenyldichloroethene (DDE), shown in Figure 2 (Baird & Cann, 2012). This metabolite of DDT has been linked to eggshell thinning for birds (Baird & Cann, 2012; Jones, 1999). DDE persists even longer in the body and is more relevant regarding bioaccumulation than DDT, therefore the presence of DDE is an indicator for chronic exposure to DDT (Jaga & Dharmani, 2003).

DDD

Another environmental degradation product of DDT that is also studied in this project is dichlorodiphenyldichloroethane (DDD) (Figure 2). One of the three chlorine atoms that bind to one of the carbon atoms in DDT is substituted with a hydrogen atom in DDD. Due to their similarities regarding shape and size, DDD is

likewise toxic to insects and therefore was earlier also applied as an insecticide (Baird & Cann, 2012).

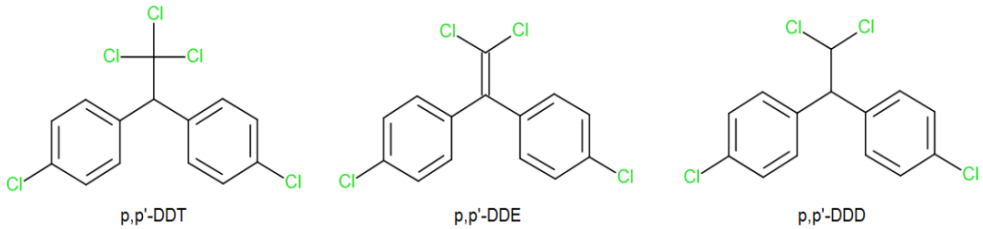


Figure 2: Chemical structures of the three *para, para* configured DDX compounds.

The most important difference between these three compounds is their three-dimensional structure. DDT and DDD are very similar and propeller-shaped, while DDE has a more planar structure due to its carbon double bound. It does not interfere with the insects' nerve channel and consequently has no insecticidal function (Baird & Cann, 2012).

For each of the three contaminants, two isomers were analyzed. The name of the isomer corresponds to the configuration of the molecule. The positions of the chlorine atom on the ring are named *ortho*, *meta* or *para*, as for the PCBs. For all compounds in this project the isomers with chlorine atoms on either both *para* positions (p,p'-DDT, p,p'-DDE, p,p'-DDD) (Figure 2) or chlorine atoms on *ortho* and *para* positions (o,p'-DDT, o,p'-DDE, o,p'-DDD) were examined.

2.2.3 Hexachlorobenzene (HCB)

Hexachlorobenzene with its chemical formula C_6Cl_6 (Figure 3), is a chlorinated aromatic hydrocarbon. HCB is very persistent in the environment due to its long half-lives in different media (air, water and sediment) (Mackay *et al.*, 2006). Compared to PCBs and many other POPs, HCB has a lower octanol-water partition coefficient indicating a lower sorption and a higher likelihood for recycling of this contaminant in the environment (Barber *et al.*, 2005b). Nevertheless, it is still sufficiently hydrophobic to sorb to particulate matter and sediments in the aquatic environment.

HCB has been used both in industry and agriculture. It was utilized as a fungicide and to disinfect seeds, replacing seed disinfectants based on organomercury compounds (Baird & Cann, 2012). Furthermore, it has been applied for example in military pyrotechnics, in aluminum fluxing and as a wood preserving agent (Barber *et al.*, 2005b; Bailey, 2001). Even though its production has ceased in

most parts of the world (Bailey, 2001), HCB is still formed unintentionally as a by-product or impurity in the chemical industry, as well as in combustion processes (Baird & Cann, 2012; Barber *et al.*, 2005b).

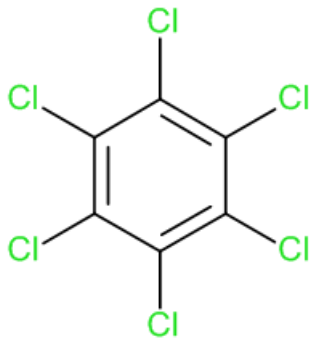


Figure 3: Chemical structure of hexachlorobenzene (HCB).

According to several studies compiled by Barber *et al.* (2005a), HCB emissions have also been detected from pulp and paper mills, but were suspected to be caused by the use of HCB contaminated products, rather than with the actual production of this hazardous compound.

2.3 Biota species studied

Two biota species were found in the samples taken in this study: The isopod crustacean S*aduria entomon* and the polychaete worm *Marenzelleria* spp. Organisms were sampled in this study in order to measure contaminant concentrations in biota. Both biota types are benthic species and dig in the sediment they live in (Josefsson *et al.*, 2010; Haahtela, 1990). While the predator *Saduria entomon*, feeds on other benthic fauna (Haahtela, 1990), *Marenzelleria* is a surface deposit-feeder but can also make use of suspended particles in the water phase (Dauer *et al.*, 1981).

2.4 Processes affecting the fate of POPs in the aquatic environment

Many POPs started to be synthesized in the 1930/1940s and were thereafter widely used. Due to concerns about their persistency and their accumulation in the food chain, many POPs were banned or restricted in usage between the 1970s and 1990s (Jones, 1999). However, due to their persistence they can still be found ubiquitously in the environment, where they are subject to various processes.

2.4.1 POPs in sediments

A major part of the POPs in the environment is found in soils and sediment (Jones, 1999). In the aquatic environment, the pollutants are mostly sorbed to particles due to their hydrophobicity and consequently deposit in the sediment. Sediments can function as a sink for these contaminants as they can become buried in areas where sediment accumulates.

The amount of pollutants in the sediment is influenced by various processes. Biological or abiotic degradation decrease the amount of pollutants, and ageing effects can make the compounds less extractable with increasing time (Jones, 1999). Stronger sorption, or bound forms, decreases the proportion of POPs that is available for transportation processes in the environment, including possible transfer into the food chain.

Regarding sorption and desorption to and from sediment particles, it has been shown that organic matter content and particle porosity play a major role. The former being very heterogeneous leads to a variation in sorption affinities (Birdwell *et al.*, 2007), which is natural, considering that hydrophobic compounds prefer to sorb to organic matter instead of being dissolved in water.

The partitioning of the chemicals between the different phases in sediment, and therefore their behavior, is dependent on the chemicals' hydrophobicity. Besides compound solubility (Reid *et al.*, 2000), the octanol-water partition coefficient (K_{ow}) is a commonly used parameter to evaluate their behavior in environmental systems (Hawker & Connell, 1988). It describes the ratio between the compound concentration in octanol to its concentration in water, at equilibrium (i.e. its solubilities). Values are usually expressed as log K_{ow} and can be used to derive other compound properties as well (Hawker & Connell, 1988). Two other partition coefficients give information about the partitioning of the compound between organic carbon and water (K_{oc}) and between solids and water (K_d). All three of them corre-

late and can be calculated from each other theoretically (Birdwell et al., 2007). However, K_{oc} and K_d can also be calculated empirically from environmental data.

2.4.2 Bioavailability

Sorption has an influence on contaminant bioavailability. The definition of this term varies within different research areas (Alexander, 2000). According to Reichenberg and Mayer (2006), the prevalent way is to understand bioavailability as the part of the total concentration that is not irreversibly bound, and therefore is, or can, be available for processes like biodegradation or uptake into biota. It needs to be mentioned that the bioavailable fraction is subject of changes over time. Besides removal processes, compound availability can be reduced by intra-soil processes (Reid *et al.*, 2000). These can cause an increase of the irreversibly bound fraction of the contaminant. This effect influences bioavailability in soils and sediment and is termed chemical ageing (Hatzinger & Alexander, 1995).

In order to be able to measure bioavailability, Reichenberg and Mayer (2006) define the term even further by distinguishing between accessibility and chemical activity. Differences in chemical activity are the driving factor for the processes that determine the partitioning and mobility of the pollutant. One option to assess chemical activity is the measurement of the freely dissolved concentration of a specific compound (Reichenberg & Mayer, 2006). It can be determined analytically by the method of passive sampling. The samplers measure the chemical activity when in equilibrium with the sampling device. This gives insight about the concentration of pollutant that is freely dissolved in the water or soil or sediment pore water (Lydy *et al.*, 2014). Sampling devices for this purpose are coatings, thin films or membranes. Polyethylene (PE), polyoxymethylene (POM), solid phase microextraction (SPME) or polymer-coated vials and jars can be used in order to assess freely dissolved contaminant concentration in pore water (C_{free}). C_{free} is the bioavailable concentration, since it is not bound to particles and is therefore available for uptake into biota.

In this study, passive sampling with POM was used in order to measure pore water concentrations, i.e. the bioavailable, freely dissolved concentrations. The freely dissolved concentration in pore water was used, together with the concentration in sediment, to calculate corresponding K_d values. The determination of compound sorption (log K_d values) thus provided insight in bioavailability.

2.4.3 Uptake in biota, bioaccumulation and biomagnification

POPs can be taken up by biota via gills or dermally and through the gastrointestinal tract (Boese *et al.*, 1990). Once taken up by biota, POPs partition into tissue, which functions as storage for the compounds (Jones, 1999).

While bioconcentration describes the accumulation of a compound in organisms from the environmental medium it is exposed to, e.g. from the water for fishes (Meylan *et al.*, 1999), bioaccumulation takes all exposure pathways into account, including feeding (Burkhard, 2003). An empirical measure for bioaccumulation of compounds for sediment-dwelling organisms is the biota-sediment-accumulation factor (BSAF). It describes the tendency of an organic compound to partition into organisms from the sediment. For benthic invertebrates, this factor can be applied to assess potential bioaccumulation of contaminants present in sediment (National Research Council of the National Academies, 2003). It needs to be noted that this parameter is site- and species specific (Burkhard, 2003; Lake *et al.*, 1990) due to differences in for example food web structure, organism trophic level or compound bioavailability in the surrounding water (Burkhard, 2003).

Besides accumulation of contaminants in one organism, this process takes place in the food web as well. The increase in concentrations along the food chain is known as biomagnification. This process is driven by the fact that POPs are excreted or metabolized slowly (Braune *et al.*, 2005). Biomagnification has been shown to be food web specific (Kelly *et al.*, 2007). For example, biomagnification tends to be higher in aquatic food webs, where more trophic levels exist compared to terrestrial food webs (Dietz *et al.*, 2000). When magnified along food chains, the compounds may reach concentrations that can harm organisms at high trophic level (Kelly *et al.*, 2007). Evidently, this also concerns humans.

3 Material and methods

3.1 Chemicals and materials

3.1.1 Target analytes

In total, 28 compounds were analyzed: HCB, six DDT compounds and 21 PCBs. They are listed in Table 1 with compound characteristics. Included characteristics are the chemical formula, molecular weight (MW), water solubility, log K_{ow}, and the partition coefficient between POM and water (log K_{POM}). The water solubility is given as subcooled liquid solubility (C_L) to enable comparison of solubility values between different congeners (Shiu & Mackay, 1986). For comparison of results between studies, seven PCB congeners are commonly summed up. This indicator, named PCB_7, includes PCB 28, 52, 101, 118, 138, 153, 180. Throughout this thesis work the sum of the six DDT compounds is referred to as DDX.

Table 1: Target analytes and their characteristics

Compound	Chemical formula	MW [g/mol]	C_L [mmol/m^3]	Log *K*ow *c*	Log K_{POM} *d*
HCB	C_6Cl_6	284.8	0.002 *a*	5.50	4.96
o,p'-DDD	$C_{14}H_{10}Cl_4$	320.0	- *a*	6.00	5.46
o,p'-DDE	$C_{14}H_8Cl_4$	318.0	1.35×10^{-3} *a*	5.80	5.26
o,p'-DDT	$C_{14}H_9Cl_5$	354.5	4.96×10^{-4} *a*	6.98	6.45
p,p'-DDD	$C_{14}H_{10}Cl_4$	320.0	1.08×10^{-3} *a*	5.50	4.96
p,p'-DDE	$C_{14}H_8Cl_4$	318.0	5.40×10^{-4} *a*	5.70	5.44
p,p'-DDT	$C_{14}H_9Cl_5$	354.5	1.11×10^{-4} *a*	6.19	5.66
PCB 28†	$C_{12}H_7Cl_3$	257.5	1.281 *a*	5.67	5.68
PCB 52†	$C_{12}H_6Cl_4$	292.0	0.418 *a*	5.84	5.65
PCB 77*	$C_{12}H_6Cl_4$	292.0	0.114 *a*	6.36	6.05
PCB 81	$C_{12}H_6Cl_4$	292.0	0.360 *b*	6.36	6.05
PCB 101†	$C_{12}H_5Cl_5$	326.4	0.102 *a*	6.38	5.90
PCB 105	$C_{12}H_5Cl_5$	326.4	0.110 *b*	6.65	6.38
PCB 114	$C_{12}H_5Cl_5$	326.4	0.110 *b*	6.65	6.32
PCB 118†	$C_{12}H_5Cl_5$	326.4	0.110 *b*	6.74	6.28
PCB 123	$C_{12}H_5Cl_5$	326.4	0.110 *b*	6.74	6.35
PCB 126*	$C_{12}H_5Cl_5$	360.9	0.034 *b*	6.89	6.47
PCB 138†	$C_{12}H_4Cl_6$	360.9	0.034 *b*	6.83	6.35
PCB 153†	$C_{12}H_4Cl_6$	360.9	0.016 *a*	6.92	6.50
PCB 156	$C_{12}H_4Cl_6$	360.9	0.034 *b*	7.18	6.64
PCB 157	$C_{12}H_4Cl_6$	360.9	0.034 *b*	7.18	6.59
PCB 167& PCB128	$C_{12}H_4Cl_6$	360.9	0.034 *b* 0.029 *a*	6.74**	6.70**
PCB 169*	$C_{12}H_4Cl_6$	360.9	0.034 *b*	7.42	6.89
PCB 170	$C_{12}H_3Cl_7$	395.3	0.010 *b*	7.27	6.54
PCB 180†	$C_{12}H_3Cl_7$	395.3	0.010 *b*	7.36	6.67
PCB 189	$C_{12}H_3Cl_7$	395.3	0.010 *b*	7.71	7.12
PCB 209	$C_{12}Cl_{10}$	498.7	0.012 *a*	8.18	7.49

**Non-ortho-substituted PCBs (co-planar congeners, i.e. dioxin-like);*

***Coeluting compounds PCB 167 and PCB 128 can only be analyzed combined. Log K_{ow} and log K_{POM} values of PCB 128 were used.*

†PCB_7

a. Mackay et al. (2006)

b. Calculated based on Schenker et al. (2005)

c. Log K_{ow} for HCB & DDX from Mackay et al. (2006); log K_{ow} for PCBs from Hawker and Connell (1988)

d. Log K_{POM} forHCB & DDX from Endo et al. (2011); log K_{POM} for PCBs from Hawthorne et al. (2009)

3.1.2 Standards and calibration solutions

For HCB and all the PCB congeners corresponding mass labeled (^{13}C) compounds were used as internal standards (IS) for analysis. Mass labelled p,p'-DDE was used as IS for p,p'-DDE, o,p'-DDE and o,p'-DDD, and p,p'-DDT was used as IS for p,p'-DDT, o,p'-DDT and p,p'-DDD. Both IS mixtures used (HCB/PCB and DDX) had a concentration of 25 pg μL^{-1}, and 40 µL were added to each sample and calibration solution, resulting in an addition of 1 ng absolute.

A mixture of ^{13}C-PCB 97 and ^{13}C-PCB 188 was used as recovery standard (RS), and 1 ng absolute was added to each sample and calibration solution prior to the instrumental analysis.

For the calibration curve, seven calibration concentrations were used for most compounds: 0.005, 0.05, 0.25, 1, 2.5, 30 and 120 ng absolute of native compounds in 100 µL tetradecane. Due to non-linearity, the two highest concentrations were removed for HCB, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and o,p'-DDT. Additionally, for o,p'-DDT and p,p'-DDT the lowest calibration level (0.005 ng/sample) did not exceed the limit of detection (LOD) (For further information see Chapter 3.5). Consequently, for these two compounds the lowest calibration level was 0.05 ng/sample. Due to the fact that PCB 118 was present in two native standard mixes used for the calibration solutions, the calibration curve for these compounds ranged from 0.01 to 240 ng/sample.

Native and mass labeled standards were purchased from Wellington Laboratories, Cambridge Isotope Laboratories, and Sigma-Aldrich.

3.1.3 Other chemicals and equipment

Acetone (SupraSolv), *n*-hexane (SupraSolv), diethyl ether (SupraSolv), hydrochloric acid 30% (Suprapur) and silica gel 60 (0,063 – 0,200 mm) were purchased from Merck KGaA, Darmstadt (Germany). Tetradecane and copper (ACS reagent, granular, 10-40 mesh, ≥99,90%) were from Sigma-Aldrich (Steinheim, Germany and St. Louis, USA). Sulphuric acid 96%, sodium sulphate anhydrous (AnalaR NORMAPUR) as well as extraction thimbles (501, cellulose) were purchased from VWR France.

For evaporation of solvents from the samples a rotary evaporator (Buechi, Switzerland: Rotavapor R-210 in combination with Vacuum Pump V-700, Vacuum

Controller V-855 and Heating Bath B-491) as well as a nitrogen evaporator (Organomation Associates, Inc., Berlin (MA, USA): N-EVAP™112) were used.

All the glassware, Soxhlet equipment, mortar and other equipment used was burned at 400°C over night and rinsed at least three times with acetone:*n*-hexane (1:1, v/v) before use. Silica, Na_2SO_4 and glass wool were burned at 400°C overnight. The silica was stored at 130°C. The Soxhlet and extraction thimbles were cleaned by extracting with acetone:*n*-hexane (1:1, v/v) over night, after which the thimbles were dried in a vacuum desiccator.

3.2 Study area and sampling

Samples were taken in July 2014 in three of the fiber bank areas that had been mapped within the *Fiberbank project* (see section 2.1). The three fiber bank areas in the Bothnian Bay are located near Kramfors, Sandviken and Väja (Figure 4) in the Kramfors estuary, at the outlet of the Ångerman river. The three pulp and paper factories associated with the fiber bank formation had different production processes. Kramfors was a sulfite pulp mill active between 1907 and 1977, Sandviken and Väja were sulfate pulp mills (Apler *et al.*, 2014). Sandviken was in production between 1929 and 1979 and got demolished and deposited on site afterwards. Väja was started 1914-1915 and is still active (Apler *et al.*, 2014). The fiber bank near Kramfors has a total area of 135000 m^2, and the thickness of the fiber bank has been identified to be 6 m or more in all three fiber bank areas (Apler *et al.*, 2014). The fibers consist of cellulose fibers in Väja and Kramfors, while depositions outside Sandviken mainly consist of wood fibers and wood shavings (Apler *et al.*, 2014).

The sampling areas and precise sampling locations (Appendix Table A1, Figure A1, Figure A2) were chosen based on existing knowledge about on-land pollution sources and results from earlier studies about the level of contamination in the sediments and the distribution of fiber banks, fiber-rich sediments and less affected sediments (Apler *et al.*, 2014). In each of the three fiber bank areas, five different sampling points were chosen in a gradient from fiber bank (FB), to fiber rich sediment (FRS), and to less affected sediment (SED). Throughout this thesis work, these abbreviations are used for naming of sites, indicating the sediment type of the sample. Additionally, letters P, Q and R indicate sample origins: fiber bank area near Kramfors (P), fiber bank area near Sandviken (Q) and fiber bank area near Väja (R).

Two additional replicates of sediment were sampled for one of the sampling points in each area. At every location sediment and biota was sampled, but at some sites (mostly fiber bank sites), no biota could be found. Biota samples of two different

Figure 4: Location of the 3 fiber bank areas studied (indicated with red triangles) near Väja (R), Sandviken (Q) and Kramfors (P) in Västernorrland, Sweden.

species could be taken at 8 of 15 sampling points (Details in Table 5, Chapter 4.6). Sampling was performed prior to the start of this master thesis.

Sampling was done from the SGU sampling ship Ocean Surveyor. Sediment was sampled using a gemini core sampler (Gemax) (Figure 5). The top 0-4 cm was sliced off, placed in an ethanol-rinsed glass jar, and stored cold (+4°C) until pore water extractions (approx. 14 days). After the pore water extractions, the sediment was frozen (-18°C) until analysis of total sediment concentrations. Some fiber bank sediments were too soft to allow the Gemax sampler to close and retain the sediment (e.g. site R-FB1), or there were timber logs that could damage the sampler (site R-FB2). An Orange Peel Bucket (OPB) sampler (Figure 6) was used, and surface samples (approx. 0-40 cm) were taken at these sites (R-FB1, R-FB2, Q-FB and P-FB2). However, for site R-FB1 the OPB sampler also did not close, and instead the material was sampled from the surfaces of the sampler.

Figure 5: Gemini core sampler (Gemax) used for sediment sampling.

Figure 6: OPB sampler used for sediment sampling in soft sediment.

Biota was sampled using Ekman box core samplers with the dimensions 32 × 32 cm (for sites R-FRS2 and R-SED, two samples for each site), or 20 × 20 cm (remaining sites, five samples each site), i.e. corresponding to 0.2 m^2 surface area for all sites. The sediment was placed in plastic boxes and immediately sieved (1 mm sieve) using sea water to retrieve animals. The animals were placed cold (+4 °C) in ethanol-rinsed glass jars with sea water for 24 h for purging, blotted dry with filter paper and frozen in ethanol-rinsed glass jars until analysis.

3.3 Sample extraction and clean-up

3.3.1 Sediment

The sediment samples were extracted using Soxhlet. In total, 24 samples were analyzed: 15 sediment samples, three of which in triplicates, and 3 solvent blanks. In order to bind water and homogenize the samples before extraction, approx. 5 g of the sediment sample was mixed in a mortar with 50 g of sodium sulfate (Na_2SO_4). However, due to their high fiber and water content of samples R-FB1, R-FRS1, and P-FB2, 10 g of sample was instead taken and mixed with 100 g of Na_2SO_4. After transferring the powder to a pre-cleaned cellulose extraction thimble, the sample was spiked with 40 µL of each internal standard and covered with glass wool. Soxhlet extraction was performed for 20-24 hours using 225 mL of acetone:*n*-hexane (1:1, v/v).

After the extraction, the extract was evaporated to around 1 mL using a vacuum rotavapor. After adding activated copper (activated with hydrochloric acid and rinsed with millipore water, acetone and *n*-hexane) to the sample in order to remove sulfur, the extracts were put through a multilayer clean-up column. From bottom to top, this was filled with glass wool, 3 g activated silica, 6 g sulfuric acid silica (40% H_2SO_4-silica) and 3 g Na_2SO_4. The column was rinsed with *n*-hexane, corresponding to a volume two times the column height before the samples were put on, using a Pasteur pipette. The extract flask was rinsed three times with 1 mL of *n*-hexane which was also transferred to the clean-up column. The sample was then eluted with 60 mL of *n*-hexane into a pear shaped flask. 40 µL of recovery standards (RS) and 100 µL of tetradecane as a keeper were added to samples. Finally, the samples were evaporated down to 100 µL using rotavapor before being transferred to GC-vials. If necessary, nitrogen evaporation was done to decrease volume after the transfer.

For nine samples (R-FB1, R-FB2, R-FRS1, R-FRS2, R-SEDr1, R-SEDr2, R-SEDr3, P-FB2, P-FRS1), a second clean up step was necessary. This was conducted in the same way as the first, except that no more copper was added. One blank (SB1) was also included. For R-FRS1 and R-SEDr3, the observations of crystals or fibers in the samples during or after evaporation made even more clean-up steps necessary, which was conducted in a miniaturized clean-up column, inside a Pasteur pipette. From bottom to top it was filled with glass wool, 0.1 g of activated silica, 0.2 g of sulfuric acid silica (40% H_2SO_4-silica) and 0.1 g of Na_2SO_4. The column was rinsed with *n*-hexane two times the column height. The sample was applied and the vial rinsed four times with 200 µL of *n*-hexane. Elution was done using 8 mL *n*-hexane.

The water content of the sediment was determined as the weight loss after heating to 105°C for 24 h, and the loss on ignition (LOI) as the weight loss after heating to 550°C for 4 h. Both parameters were determined before the start of this thesis work, and the organic carbon content was determined by the laboratory at the Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU).

3.3.2 Pore water

Polyoxymethylene (POM) strips were used to determine the concentration of POPs in sediment pore water. In total 24 samples, including three solvent blanks, were analyzed (corresponding to the samples for determination of total concentrations in sediment).

POM sheets (76 µm thick, CS Hyde, Lake Villa, IL, USA) were cut into 2 * 3 cm strips and cleaned by immersing in acetone/*n*-hexane (1/1, v/v) for 2*24 hours (solvent exchange after 24 h), followed by methanol 2 * 24 h (solvent exchange after 24 h). They were then rinsed with Millipore water, dried in a vacuum desiccator, and stored in a sealed glass scintillation vial until use.

Sediment (20-30 g wet weight (ww), corresponding to 1-10 g dry weight (dw) was placed in a 40 mL amber glass jar with Teflon-lined cap. A POM strip was added to each jar, and Millipore water with 0.001 M $CaCl_2$ and 0.015 M NaN_3 was added to fill the vials, leaving a small head space. The water volume added was 10-22 mL for the different samples. The samples were shaken for 28 days in the dark using an end-over-end shaker. The pore water extractions was then terminated, and the POM strips were retrieved, wiped clean using Millipore water and tissue paper, and stored in scintillation vials at -18°C until extraction for POPs.

For extraction, 20 mL of acetone:*n*-hexane (1:1, v/v) and 40 µL of each IS were added to the vial containing the POM sample. The samples were shaken for 24 h in the end-over-end shaker at a speed of 30 rounds/min. The first aliquot of each sample was collected in a pear shaped flask. Another 20 mL of the solvent mixture was added to the vials and shaken at the same speed over the same time again. The second aliquot was collected into the same pear shaped flask. After addition of 40 µL RS and 100 µL tetradecane, the samples were evaporated to 100 µL using the rotavapor and transferred to GC vials. If necessary, samples were further evaporated using N_2. The POM strips were dried and weighed.

One of the POM samples (P-FB2) turned milky in the GC vial after the nitrogen evaporation step. Therefore, a miniaturized clean up in a Pasteur pipette (the same as for some of the sediment samples) was used for this extract as well as on one of the blanks (PB1). Apart from this, no cleanup was performed.

3.3.3 Biota

The biota analyzed for POPs was the isopod crustacean S*aduria entomon* and the polychaete worms *Marenzelleria* spp. These were the only species found at the sampling locations. Biota samples could not be found for all of the sampling locations. For sites R-FB1, R-FRS1, R-FB2, P-FB2, P-FRS3 and Q-FB, no biota was found. Only at the sampling spots P-FRS1, Q-FRS1 and Q-FRS2, both of the species were found. However, only *Marenzelleria* samples were found at R-FRS2 (not analysed due to too low amounts of tissue), R-SED, Q-SED1, Q-SED2, P-FB1 and P-FRS2.

The samples were weighed, and a known amount was taken for dry weight and lipid weight determination. The remaining sample was mixed and mortared with Na_2SO_4. For the *Marenzelleria* samples, 30 g of Na_2SO_4 were used, whereas *Saduria* was mortared with only 5 g, due to the difference in weight. The samples were left for an hour, mortared again and packed into solvent-rinsed glass columns containing glass wool at the bottom. Internal standards were added on top, and the samples were extracted into a round bottom flask using cold-column extraction with 75 mL acetone:*n*-hexane (5:2, v/v) and 75 mL *n*-hexane:diethylether (9:1, v/v). Extracts were evaporated to 1 mL, followed by a clean-up step. This was conducted in the same way as the clean-up of the sediment samples; however, an additional layer of 3 g 20% H_2SO_4-silica was placed between the 40% H_2SO_4-silica and the Na_2SO_4. After clean-up, recovery standard and 100 µL tetradecane was added. The samples were concentrated using rotary evaporation, transferred into GC-vials, and if necessary further concentrated using nitrogen evaporation.

The dry weight of the *Marenzelleria* samples was determined by drying an aliquot of the biota sample (0.13-0.64 g) at 60°C for 24 hours. The lipid content was then determined by mortaring the sample (re-wetted with a few drops of Millipore water) with 4 g of Na_2SO_4, placing the mixture in pasteur pipettes with glass wool in the bottom and eluting with 6 mL acetone:*n*-hexane (5:2, v/v) and 6 mL *n*-hexane:diethylether (9:1, v/v). For *Saduria entomon* samples, it was not possible to take an aliquot of the original samples since they consisted of very few animals. Instead, an aliqout of the extract obtained after cold-column extraction for POPs was taken. Both *Marenzelleria* and *S. entomon* extracts were evaporated in a rota-

vapor until approx. 0.5 mL and placed on pre-weighed, warm aluminum cups for the solvent to evaporate. The lipid weight was then determined by re-weighing the aluminum cups.

3.4 Instrumental analysis

The instrumental analysis was conducted using a gas chromatograph (Agilent Technologies 7890 A GC System) combined with a triple quadrupole mass spectrometer (Agilent Technologies, 7010 GC/MS Triple Quad), thus GC-MS/MS. The GC was equipped with a DB5 capillary column (60 m × 250 µm × 0.25 µm, Agilent Technologies) and helium was used as a carrier gas (2 mL min^{-1}). Extract aliquots of 2 µL was injected in splitless mode at an injector temperature of 275°C. The oven temperature program started at 190°C for 2 min, increased with 3°C/min to 250°C, and then with 6°C/min to 310°C, which was held for 1 min, resulting in a total run time of 33 min. For the MS/MS, electron impact ionization was used. N_2 was used as collision gas and He as quench gas in the collision cell. The MS/MS was operated in MRM mode, and two transitions were monitored for each compound. For data evaluation the software Agilent MassHunter Quantitative Analysis (for QQQ) was used.

3.5 Quality assurance

For each batch of samples of every sampling area, a solvent blank was run and treated the same way as the other samples. For the biota samples an additional blank was run consisting of only the solvents used in the biota extraction method.

At the start of the extraction, isotopically labelled compounds were added to each sample as internal standard in order to be able to correct for losses during the process of sample analysis.

The performance of the method was checked by calculating the recovery of the internal standard with the help of a recovery standard which was added before GC-MS/MS analysis. The recovery was calculated as the fraction of the ratios between the peak area of internal standard in the sample to the one in the calibration solution and the peak areas of recovery standard in the sample to the one in the calibration solution (Equation 1). The areas for the IS and RS in the calibration

solution were the average value of the 1 ng calibration solution that was run nine times during instrumental analysis.

$$R\ (\%) = \frac{A_{IS(sample)}}{A_{IS(calibr\ sol)}} \times \frac{A_{RS(calibr\ sol)}}{A_{RS(sample)}} \times 100$$

Equation 1: Calculation of method recovery.

In order to measure the target analyte, it must be present in a concentration that exceeds the method's limit of detection (LOD). This is necessary in order to distinguish reliably between analytical signal and noise. In the chromatographic method applied, the LOD used was a signal-to-noise ratio of 3. Compounds were considered detected if their respective peak was 3 times higher than the background noise of the instrument. However, the analyte could only be quantified if its concentration exceeds the method's limit of quantification (LOQ), which was the lowest of the calibration solution concentrations which could still be detected reliably by the GC-MS/MS. For all compounds analyzed, the LOQ was 0.005 ng absolute with the exception of o,p'-DDT and p,p'-DDT. These two compounds could only be quantified if the amount in the vial exceeded 0.05 ng absolute. On average, the 0.005 ng absolute limit of quantification correspond to 0.0036 ng/g sediment dw, 0.073 ng/g POM, 0.0015 ng/g ww *Marenzelleria* and 0.014 ng/g ww *Saduria entomon*. For any concentration lower than LOQ, the compound was not quantified and the concentration of that compound was set to zero.

Average values were taken of all compound concentrations in the blanks for each matrix. Sample concentration values were corrected for any contamination found in the blanks of the corresponding matrix. Concentrations found in blanks compared to sample concentrations were generally low. However, in a few samples contaminant concentrations did not exceed two times the value found in the blank. This was the case for PCB 28 in one sediment sample and for HCB, PCB 28, 52, 77 and 101 in a total of six biota samples. Among the analytes, these compounds have high volatility and water solubility and are therefore more likely to be found in blanks. The data is included in the study but are related to some uncertainties.

3.6 Data analysis and calculations

The biota-sediment-accumulation factor (BSAF) was calculated by dividing the contaminant level in the biota per lipid weight by the contaminant level in the sediment per organic carbon weight. This ratio shows to which extent a certain compound bioaccumulates.

$$BSAF = \frac{C_b}{f_l} / \frac{C_s}{f_{oc}}$$

Equation 2: Calculation of biota-sediment-accumulation factor (BSAF). C_b is the concentration of the contaminant in the organism, while C_S is the concentration in the sediment. f_l expressed the lipid fraction of the tissue while f_{OC} is the fraction of organic carbon in the sediment (National Research Council of the National Academies, 2003).

The concentration in the pore water (C_{pw}) was calculated by dividing the concentration in the passive sampler (C_{POM}) by the passive sampler-water partition coefficient (K_{POM}) assuming that equilibrium between the phases had been reached. Compound specific K_{POM} values were taken from or calculated based on Endo *et al.* (2011) for DDX and HCB and Hawthorne *et al.* (2009) for PCBs. For detailed values see Table 1.

$$C_{\mathrm{pw}} = \frac{C_{\mathrm{POM}}}{K_{\mathrm{POM}}}$$

Equation 3: Calculation of pore water concentration [unit: ng/L_{pw}]. (Based on Lydy *et al.* (2014)).

Besides the equilibrium requirement, non-depletive conditions are a requisite for passive sampling with POM. In order to check for depletion, the amount of contaminant found in the POM extract was divided by the amount of contaminant in the sediment it was exposed to. Non-depletive conditions are ensured if that ratio is smaller than 0.05.

Compound sorption was expressed as empirical K_d value which was calculated dividing sediment concentration at equilibrium ($C_{sed(eq)}$), on a dry weight (dw) basis, by the concentration in pore water (C_{pw}).

$$K_{\mathrm{d}} = \frac{C_{\mathrm{sed(eq)}}}{C_{\mathrm{pw}}}$$

Equation 4: Calculation of the K_d values [unit: L_{pw}/kg_{dw}].

The sediment concentration at equilibrium was calculated by dividing contaminant mass in the sediment at equilibrium ($M_{sed(eq)}$) with the sediment dry weight (M_{sed}). The contaminant mass in the sediment at equilibrium was calculated by subtracting the contaminant mass in the POM and in the water at equilibrium from the initial contaminant mass in the sediment (before equilibrium).

$$C_{sed(eq)} = \frac{M_{sed(eq)}}{M_{sed}} = \frac{\left(M_{sed(init)} - M_{POM(eq)} - M_{water\ (eq)}\right)}{M_{sed}}$$

Equation 5: Calculation of sediment concentration at equilibrium.

For the statistical analysis of the results, Pearson's r was used to measure linear relationship between K_d values and hydrophobicity of contaminants as well as relationships between BSAFs and hydrophobicity. It was used again to test for correlations between concentrations in biota and concentrations in sediment and pore water. Regressions were calculated using the data analysis tool of Excel.

One-way ANOVA was applied to check for significant differences between the three different sediment categories regarding their K_d values and BSAFs. In one case, the ANOVA was significant. Therefore two-tailed z-tests (with alpha 0.05) were used as a post-hoc test to check for significant differences between the sediment types fiber bank, fiber rich sediment and less affected sediment. ANOVA and z-test were calculated using the data analysis tool of Excel.

4 Results

4.1 Method recovery

The analysis methods applied showed overall high recovery. Average recoveries per compound group and sample type are presented in Table 2.

Table 2: Method recoveries (average recovery ± standard deviation)

	HCB	**DDX**	**PCBs**
Sediment	84 ± 11%	99 ± 14%	83 ± 23%
POM	98 ± 2%	112 ± 22%	106 ± 5%
Biota	98 ± 5%	93 ± 20%	96 ± 12%

4.2 POP concentrations and organic carbon content in sediment

Detailed results of the contaminants found in each of the sediment samples show that concentrations differ substantially between the different samples (Figure 7). Besides HCB as a single compound, the concentrations of all DDX compounds have been summed up as well as all for the group of PCBs (∑PCBs). PCB_7 being a commonly used indicator parameter, is presented additionally. The error bars in Figure 7 indicate the standard deviations where triplicates were taken. Two of the PCB compounds were not detected in any of the sediment samples taken (PCB 126 and 169), nor in the other sample matrices (POM and biota samples).

For all the compound groups, fiber banks had much higher concentrations than other types of sediment in the same sampling area. Levels exceeded 0.5 ng/g dw for HCB and 1.2 ng/g dw for DDX in the fiber bank locations. Regarding ∑PCBs in the fiber banks, levels were above 22 ng/g dw and more than four times higher

than the highest value of the other types of sediment. However, P-FB1 forms clearly an exception from the other fiber banks, in that concentrations are lower and similar to concentrations in fiber rich sediment. In fact, the fiber rich sediment in sampling site P-FRS3 had higher concentrations than P-FB1 for all three contaminant groups. Furthermore, it can be seen that even in the less affected sediments the targeted compounds can be found. Concentrations in fiber rich sediments and less affected sediments were not that different from each other. Differences in contaminant concentrations between the two sediment types were more obvious in fiber bank R; all contaminant groups had higher concentrations in FRS than SED. In fiber bank area Q, differences in concentrations for different sediment types were less obvious. Nevertheless, the fiber rich sediments seem to generally have slightly more elevated levels, especially for the PCBs.

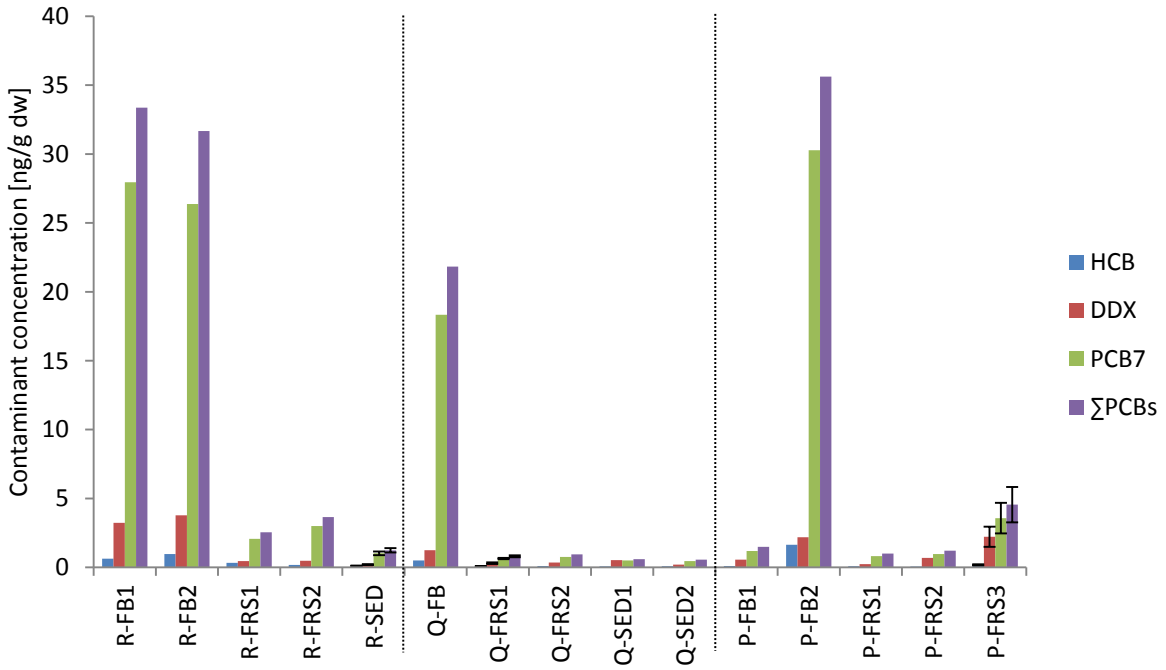


Figure 7: Contamination levels [ng/g dw] of the different compound groups in sediment samples.

Analysis of the organic carbon (OC) content of the sediment samples showed, that the fiber bank samples not only have high contaminant concentrations, but also high organic carbon content (Table 3). Fiber impact and organic carbon content are related to each other, as the fiber accumulations consist of organic material, i.e. cellulose and wood fibers or wood shavings, originating from polluted discharge water from the paper, pulp and saw mills. All fiber bank sites had the highest organic carbon content within their sampling area. In area R there is a clear gradient in organic carbon content increasing from less affected sediment to fiber rich sediment to fiber banks. In area Q fiber rich sediments had only slightly higher organic carbon content than the less affected sediment in Q-SED2. The other less affected sediment site (Q-SED1), however, differed and had higher organic carbon content than the other sediment sample in the same area. In area P, only two types of sediment were sampled.

Fiber bank P-FB2 had the overall highest content of organic carbon. However, also within the organic carbon analysis the second fiber bank site in that area (P-FB1) was an exception from all other fiber banks. It showed similar organic carbon content to most of the fiber rich sediment sites. The classification into the different types of sediments was based on maps from the *Fiberbank project* of SGU. Site P-FB1 was located further out from the shoreline along which the other fiber banks were located. P-FB1 was classified by SGU as a fiber bank, based on the assumption that this area resulted from dredging activities of fiber banks (see section 2.1). However, P-FB1 may have been misclassified. Based on the organic carbon analysis, this site might be fiber rich sediment instead. P-FRS3 in return had 2.5 times higher organic carbon content than the other fiber rich sediment samples. The deviations in organic carbon content at site P-FRS3 may be explained by its location in the inner part of the bay. It therefore might be more influenced by releases from other industries.

Table 3: Percentage of total carbon content and the organic carbon content in each of the sediment samples.

	Tot-C %	Org-C %
R-FB1	34.8	34.7
R-FB2	12.0	12.0
R-FRS1	4.8	4.7
R-FRS2	4.5	4.5
R-SED	2.9	2.9
Q-FB	8.6	8.6
Q-FRS1	2.1	2.0
Q-FRS2	2.0	2.0
Q-SED1	2.1	2.1
Q-SED2	2.0	2.0
P-FB1	2.6	2.5
P-FB2	36.6	36.6
P-FRS1	2.4	2.4
P-FRS2	2.6	2.6
P-FRS3	6.5	6.5

The highest values of organic carbon were found in P-FB2 (37%) and R-FB1 (35%). These were the samples that showed the highest ∑PCBs concentrations based on a dry weight basis, and HCB and DDX concentrations were also high. Contaminant concentrations (ng/g dw) (Figure 7) were normalized with their respective organic carbon content and are presented in Figure 8, where error bars indicate the standard deviation for samples taken as triplicates. The results show more even concentrations (ng/g OC) between sites. This is due to the fact that the fiber bank sites are not only high in pollution, but also high in organic carbon content. Therefore these concentrations are preferable when comparing between different sites or for calculations of other indicators like for example BSAFs.

Figure 8 shows that, when normalized to OC, the sites Q-FB (380 ng/g OC) and R-FB2 (250 ng/ OC) are the most polluted ones concerning ∑PCBs and differ much in comparison to all other sites. In relation to their organic carbon content, the fiber bank at R-FB1 had relatively low ∑PCBs contamination in comparison to all other fiber banks and even compared to most other less fiber impacted sites. Site P-FB1, that showed low POP concentrations on a dry weight basis, when compared to other fiber banks, had the third highest ∑PCBs contamination on an organic carbon basis. For ∑PCBs, a clear trend of increasing concentrations with increasing fiber impact can only be seen in sampling area Q.

Regarding the DDX compounds on an organic carbon basis, fiber banks R-FB1 and P-FB2 had the lowest concentrations. The highest pollution of DDX was found in the fiber rich sediment at site P-FRS2. The relation between concentrations and fiber impact are not obvious for the DDX. In contrast to the PCB results, it seemed that in site Q, DDX concentrations on OC basis instead increased with decreasing fiber impact, with the exception of Q-SED2. Regarding HCB, concentrations normalized to OC content did not vary widely. Only results for R-FB1 and P-FRS3 were notably lower than HCB concentrations at all other sites.

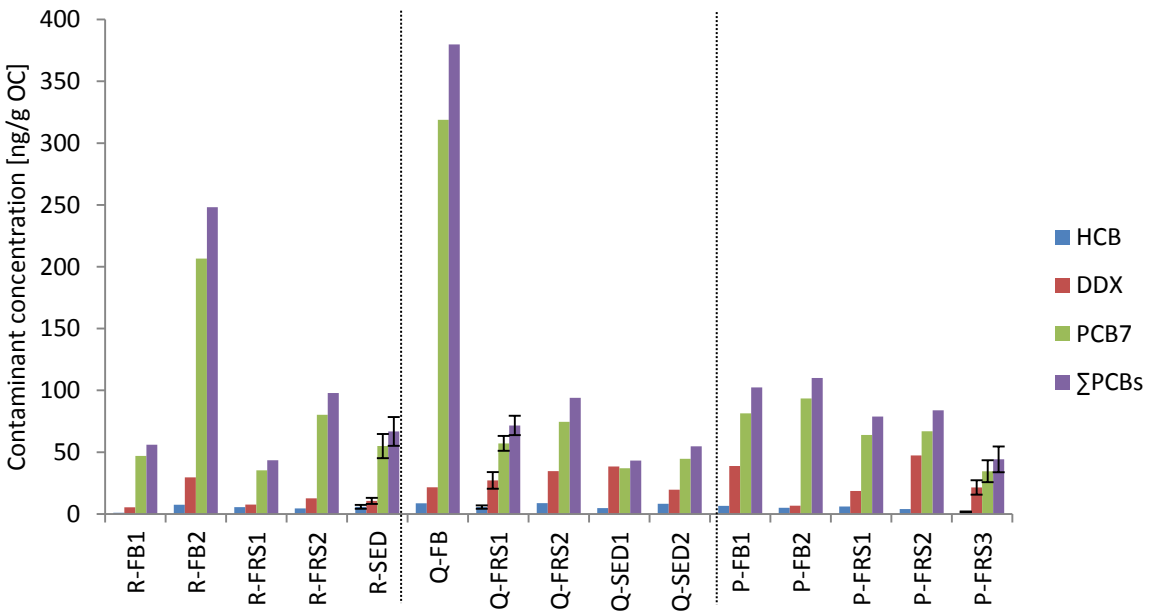


Figure 8: Contamination levels (ng/g OC) of the different compound groups in sediment samples.

4.3 Classification of sediments

Based on the POP concentrations on a dry weight basis, the sediments were classified according to the Swedish assessment criteria for organic pollutants in sediment along the Swedish coast (Naturvårdsverket, 1999). The concentrations of HCB, the sum of the p,p'-DDX (p,p'-DDT, p,p'DDD, p,p'-DDE) and the PCB_7 (PCBs 28, 52, 101, 118, 138, 153, 180) in each sediment sample are presented in Table 4. Relating the results to the above mentioned assessment criteria allows distinguishing between no detectable (class 1), low (class 2), mid (class 3), high (class 4) and very high (class 5) levels. Triplicates were taken for R-SED, Q-FRS1 and P-FRS3. For these sites the values are presented as average values of the triplicates with standard deviations.

All compound groups were found at elevated levels at all sites. For HCB, all sites sampled were classified with at least mid-level. Very high HCB levels (class 5) were found at one of the fiber bank sites (P-FB2). All other fiber bank samples were classified as high level (class 4), with the exception of fiber bank P-FB1 (class 3).

For the sum of the p,p'-DDX, none of the sites had very high levels. Two of the three less impacted sediment sites showed low levels; however, one was more impacted by pollution (mid-level). All fiber bank sites were highly polluted with DDX. Interestingly, the P-FB1 was the exception again for this compound group, being classified one level below the other fiber bank sites.

For PCB_7, fiber bank sites exhibited very high levels, except for P-FB1 (low). All less affected sediment sites showed low levels as well. Fiber rich sediments were classified with mid-levels in area R and with low levels in area Q. Area P exhibited both classes for this type of sediment.

Table 4: Level of contamination in sediment samples in ng/g dw classified based on the Swedish assessment criteria for organic pollutants in sediments along the Swedish coast (Naturvårdsverket, 1999).

Site	HCB	∑ p,p'-DDX	PCB_7
R-FB1	0.63	1.6	28
R-FB2	0.96	1.5	26
R-FRS1	0.33	0.35	2.1
R-FRS2	0.17	0.36	3.0
R-SED *	0.11 ± 0.02	0.18 ± 0.03	1.0 ± 0.1
Q-FB	0.50	1.1	18
Q-FRS1 *	0.063 ± 0.015	0.26 ± 0.05	0.64 ± 0.05
Q-FRS2	0.089	0.30	0.75
Q-SED1	0.066	0.45	0.51
Q-SED2	0.084	0.17	0.45
P-FB1	0.096	0.44	1.2
P-FB2	1.6	1.7	30
P-FRS1	0.077	0.21	0.81
P-FRS2	0.058	0.53	0.97
P-FRS3 *	0.17 ± 0.05	1.0 ± 0.1	3.6 ± 1.1

* = Average value of the triplicate samples and standard deviation

Class 1	Class 2	Class 3	Class 4	Class 5
No level	Low level	Mid-level	High level	Very high level

4.4 POP relative distributions in sediments

The relative distributions of the contaminants detected, calculated as the concentration of that compound divided by the total concentration of all compounds, vary between different sampling points (Figure 9). The variation in contaminant composition between the sites could indicate that usage and release of contaminants differs at the local sources where the pollution comes from. However, as the compounds investigated were applied as mixtures, the differences in sample composition could instead be due to different degradation rates.

The three triplicates (R-SED-r1 – R-SED-r3; Q-FRS-r1 – Q-FRS-r3; P-FRS-r1 – P-FRS-r3) were similar in their pollutant distribution patterns per site. However, the triplicates in site P (P-FRS3-r1 – P-FRS3-r3) exhibited some deviations between the three samples. This is mostly due to different shares of o,p'-DDD and PCB 156. While o,p'-DDD was found in a higher proportion at P-FRS3-r3, PCB 156 was found in much higher proportion at P-FRS3-r1 than at any other site. These deviations in the contaminant distribution of the triplicate may be due to different degradation processes in the field at different spots or during the instrumental analysis (see 5.4), or be explained by how the triplicate sampling was done. To not sample at exactly the same spot, the boat moved about 1 m between the three replicates. Moreover, sediment concentrations on a dry weight basis at site P-FRS3 were slightly higher than at the other fiber rich sediment sites in this fiber bank area. This could indicate that the P-FRS3 may be located closer to the source of pollution or may be influenced by several sources and consequently show a patchier contaminant distribution than other samples more distant from the pollutant source.

The highest PCB levels detected were the PCB_7 congeners. Moreover, other PCBs that were detected in relatively high amounts were PCB 105, 156, 170 and 167+128. Site Q-FB had the highest proportion of ∑PCBs followed by P-FB2.

Most of the differences in composition between different samples seem to occur for DDX. For DDX, the most frequent detected compounds were o,p'-DDD and all of the p,p'-configured DDX (i.e. DDT, DDD and DDE). The p,p'-DDT share had a higher relative distribution in less affected sediment and in fiber rich sediment than in fiber bank samples. For o,p'-DDD the patterns in the graph suggested the same assumption. However, at site R it was the opposite, and o,p'-DDD was more common in fiber banks than in sediment with less fiber impact. The proportion o,p'-DDD was highest at site P-FRS3, for triplicate P-FRS3-r3.

Finally, the results indicate that the fiber bank samples differ in their pollutant distribution pattern from the less fiber impacted samples within the same fiber bank area. However fiber bank P-FB1 was an exception and resembled more the fiber rich sediment of that sampling area.

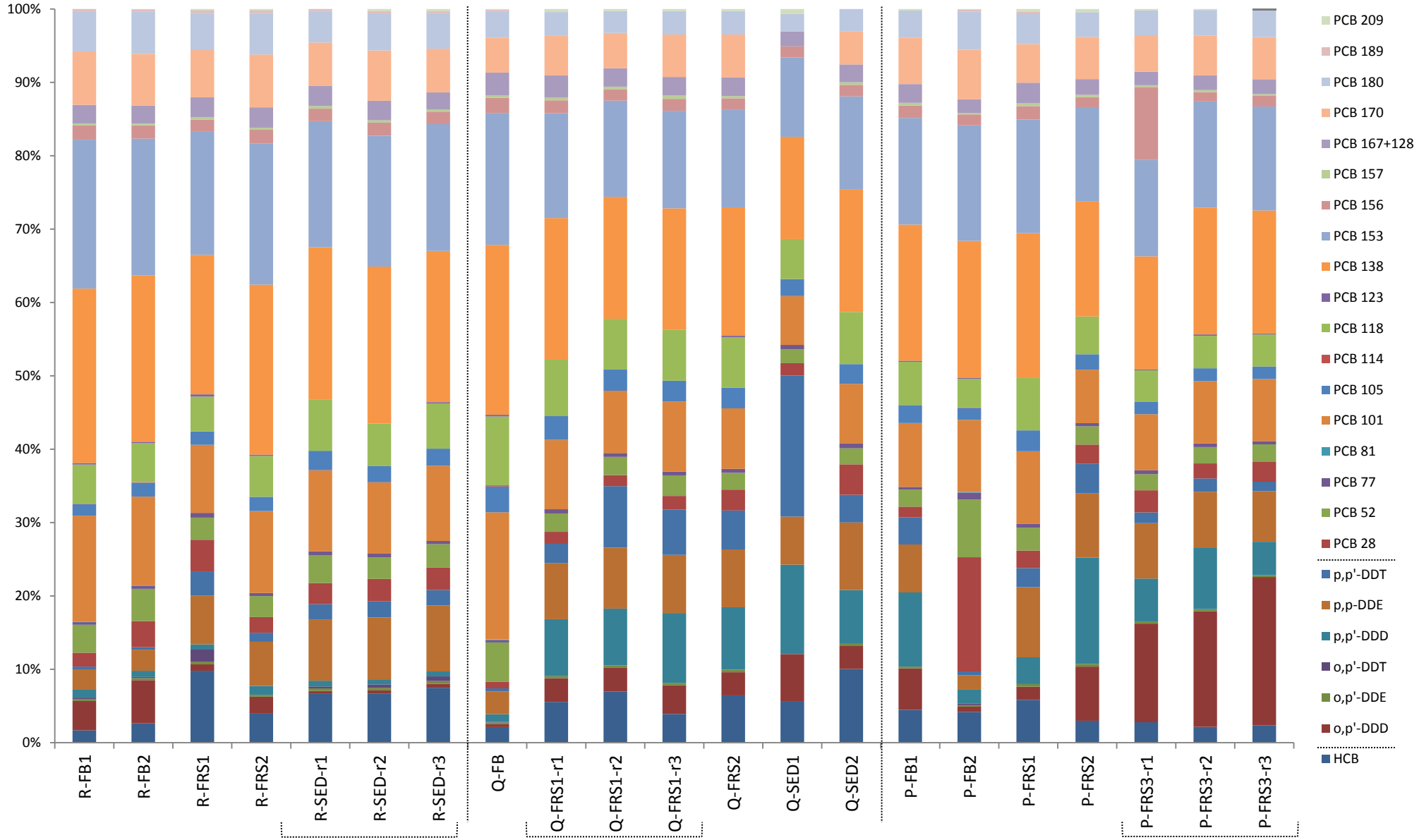


Figure 9: Distribution of analyzed compounds in each sediment sample.

4.5 POP concentrations in pore water

The results of the pore water analysis based on the passive sampling are shown in Appendix Figure A3. POM results were used to calculate sorption coefficients, K_d, in order to provide answers to the hypotheses stated in the beginning. Non-depletive conditions were not given for all compounds. In the calculation of the K_d values, corrections for depletion are included. Regarding results of the POM analysis, it should also be noted that for the sites where triplicates were taken (R-SED and Q-FRS1), results are presented as average values. For site P-FRS3, triplicates were taken. However, P-FRS3r3 exhibited an extremely high concentration in the POM for o,p'-DDD, which deviated substantially from the other replicates and also exceeded the highest calibration standard by far (P-FRS3r1: 13 ng/g POM; P-FRS3r2: 15 ng/g POM; P-FRS3r3: 1068 ng/g POM). Therefore, this POM replicate (P-FRS3-r3) was excluded from calculations and results. However, in the sediment sample taken at this site, o,p'-DDD was a common contaminant. In fact P-FRS3 was the sample with the highest proportion of o,p'-DDD.

In all three fiber bank areas investigated, the highest ∑PCBs concentrations in the pore water were found in the fiber bank sites. The only exception was for area P, where one of the fiber rich sediment sites (P-FRS3) had higher ∑PCBs concentrations than one of the fiber bank sites (P-FB1). That site, in turn, was more similar in its levels to the other fiber rich sediment sites. This supports previous suggestions (see section 4.2) that the classification of sediment type at site P-FB1, based on previous mapping, may be incorrect, as shown by the organic carbon content.

The highest contamination levels in pore water were due to DDX contamination (R-FB2: 160 pg/L_{pw}). In contrast to the pore water concentrations, the highest concentrations in biota and sediment samples were due to ∑PCB contamination. One interesting finding about pore water concentration results was that in all but one sampling site, DDX concentrations were higher than ∑PCB concentrations. The exception was R-SED where the highest contaminant concentrations were in fact HCB concentrations. HCB pore water concentrations were generally higher than ∑PCB concentrations. However, exceptions were all fiber bank sites and one fiber rich sediment site (P-FRS2). At these sites, the highest contaminations were due to DDX followed by ∑PCBs, PCB_7 and HCB concentrations being lowest.

4.6 POP concentrations in biota

Results for the characterization of the biota samples are summarized in Table 5. Details on POP concentrations in biota are shown in Appendix Figure A4-5. The POP concentrations in biota were used to calculate biota-sediment-accumulation factors (BSAFs) as described in 3.6. In the fiber bank area R, biota could only be sampled in one of the spots (R-SED). Moreover, only in one of the fiber bank sites (P-FB1), biota could be found (*Marenzelleria*). However, due to low organic carbon content, this site might rather be fiber rich sediment, as mentioned previously in chapter 4. While *Marenzelleria* was sometimes the only biota type sampled, *Saduria entomon* was always found together with *Marenzelleria*. All sites that provided habitat to both biota types were classified as fiber rich sediment. The amount of specimen found corresponded to animal densities ranging from 3.7 to 27 g/m^2 for *Marenzelleria* and from 0.5 to 3.0 g/m^2 for *Saduria entomon*.

Table 5: Properties of biota samples found at different sampling sites

Site	Biota type	Dry matter Content (%)	Lipid content (% of dw)	Lipid content (% of ww)	Animal density [g/m^2]
R-FB1	NA	NA	NA	NA	NA
R-FB2	NA	NA	NA	NA	NA
R-FRS1	NA	NA	NA	NA	NA
R-FRS2	NA	NA	NA	NA	NA
R-SED	*Marenzelleria*	8.7	12.4	1.1	22.54
Q-FB	NA	NA	NA	NA	NA
Q-FRS1	*Marenzelleria*	14.0	9.9	1.4	23.05
	Saduria entomon (3)	43.1*	**	1.4	1.85
Q-FRS2	*Marenzelleria*	10.7	10.9	1.2	20.67
	Saduria entomon (1)	43.1*	**	0.8	0.53
Q-SED1	*Marenzelleria*	7.6	11.8	0.9	11.23
Q-SED2	*Marenzelleria*	19.0	9.6	1.8	23.81
P-FB1	*Marenzelleria*	13.4	9.9	1.3	16.67
P-FB2	NA	NA	NA	NA	NA
P-FRS1	*Marenzelleria*	8.7	18.0	1.6	3.69
	Saduria entomon (2)	43.1*	**	1.9	2.96
P-FRS2	*Marenzelleria*	9.3	11.8	1.1	27.17
P-FRS3	NA	NA	NA	NA	NA

() = Number in brackets after biota type indicates number of animals of the species *Saduria entomon*

* for *Saduria entomon* the average value of two samples was taken due to lack of the third value

** due to small sample amount only wet weight was used to determine lipid content for *Saduria entomon*

In all biota samples, ∑PCBs concentrations on a dry weight basis were much higher than concentrations of the other contaminant groups, and ranged between 8.8 and 31 ng/g dw (Appendix Figure A4a). On a dry weight basis, DDX, PCB_7 and ∑PCBs concentrations in *Marenzelleria* were slighty higher than in the *Saduria entomon* samples found at the same site (Appendix Figure A5a). However, for concentrations normalized to biota lipid weight, all *Saduria entomon* samples showed noticeably higher values of PCB_7, ∑PCBs and HCB than the *Marenzelleria* samples found at the same site (Appendix Figure A5b). For DDX, the differences between the two biota types were not that clear.

4.7 Relation between sorption or bioaccumulation and hydrophobicity (hypothesis 1)

4.7.1 Sorption

To provide answers to hypothesis 1, the sorption expressed as log K_d for each contaminant was investigated in relation to contaminant hydrophobicity. Figure 10 shows the sorption of each contaminant as an average for all sampling sites and error bars indicate the standard deviation. Contaminant log K_{ow} values, as an indicator of their hydrophobicity, ranged from 5.5 to 7.7. Values of log K_d ranged between 3.7 (p,p'-DDD) and 7.0 (PCB 189). Sorption could not be calculated for compounds PCB 81, 126, 169 and 209, as these contaminants were not detected in one or both of the sample matrices (sediment or POM) the calculation is based on. A linear trendline has been fitted through the data points to check for correlation. The graph shows that sorption increases with increasing hydrophobicity. The statistical analysis showed that that the sorption of a certain compound could be explained significantly ($p<0.001$) by its log K_{ow} value with 83%.

4.7.2 Bioaccumulation

Furthermore, the bioaccumulation expressed as *Marenzelleria* BSAF values was compared to the hydrophobicity of the contaminants. Average values (for all sites with *Marenzelleria*) and their standard deviations are presented in Figure 11. Contaminant log K_{ow} values ranged from 5.5 to 8.2. BSAF values ranged from 0.01 (o,p'-DDD) to 3.64 (PCB 180). BSAFs could not be calculated for o,p'-DDT, PCB 81, 114, 126 and 169 because these contaminants were not detected in one or both of the sample matrices (sediment or biota). A polynomial trendline was fitted through the data points in order to check for the presumed relationship between bioaccumulation and contaminant properties (see chapter 1.2). The R^2 value indicated that the variance in the *Marenzelleria* BSAFs of a certain contaminant could

be explained by its hydrophobicity with 22%. However, with a p-value of 0.079 these results were slightly above the threshold (p=0.05) in order to be considered significant.

Similarly as for *Marenzelleria*, BSAF values of the other type of biota sampled, *Saduria entomon*, were plotted against contaminant hydrophobicity. Figure 12 shows a slightly different picture to *Marenzelleria* BSAFs, but in turn consists of fewer data points, as *Saduria entomon* was only found at three sampling sites. Contaminant log K_{ow} values ranged from 5.5 to 7.7. BSAF values ranged between 0.3 (p,p'-DDD) and 8.7 (PCB 153). For *Saduria entomon* BSAFs, a linear trend-line was the better fit to the data. The graph showed a significant ($p<0.001$) trend of increasing BSAF values with increasing hydrophobicity which had a R^2 value of 0.53.

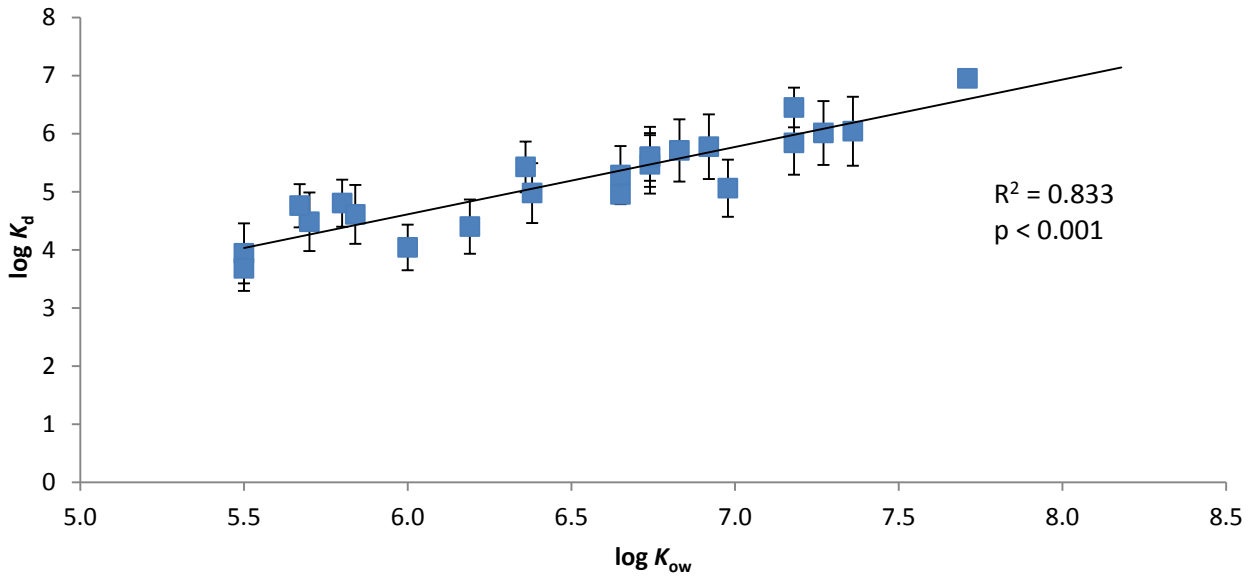


Figure 10: Relationship between average sorption of contaminants (expressed as log K_d) and contaminant hydrophobicity. Error bars represent standard deviation.

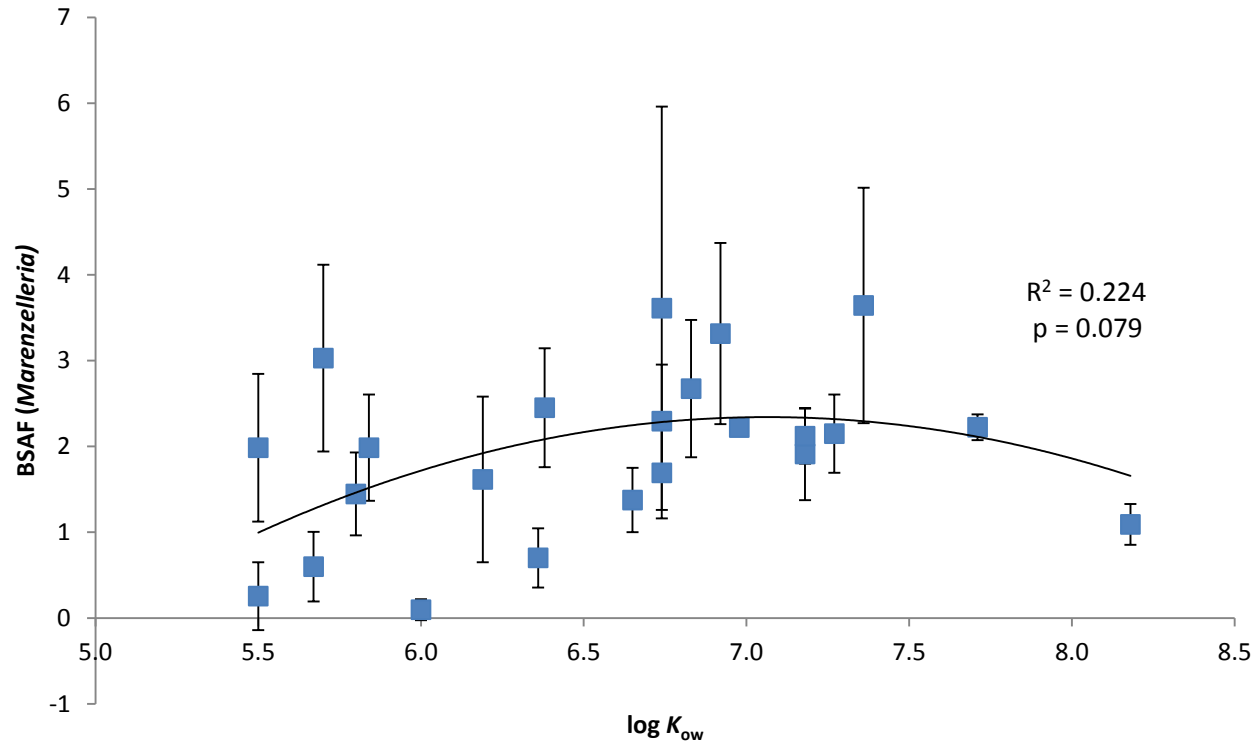


Figure 11: Relationship between average *Marenzelleria* biota-sediment-accumulation factors of contaminants and contaminant hydrophobicity. Error bars represent standard deviation.

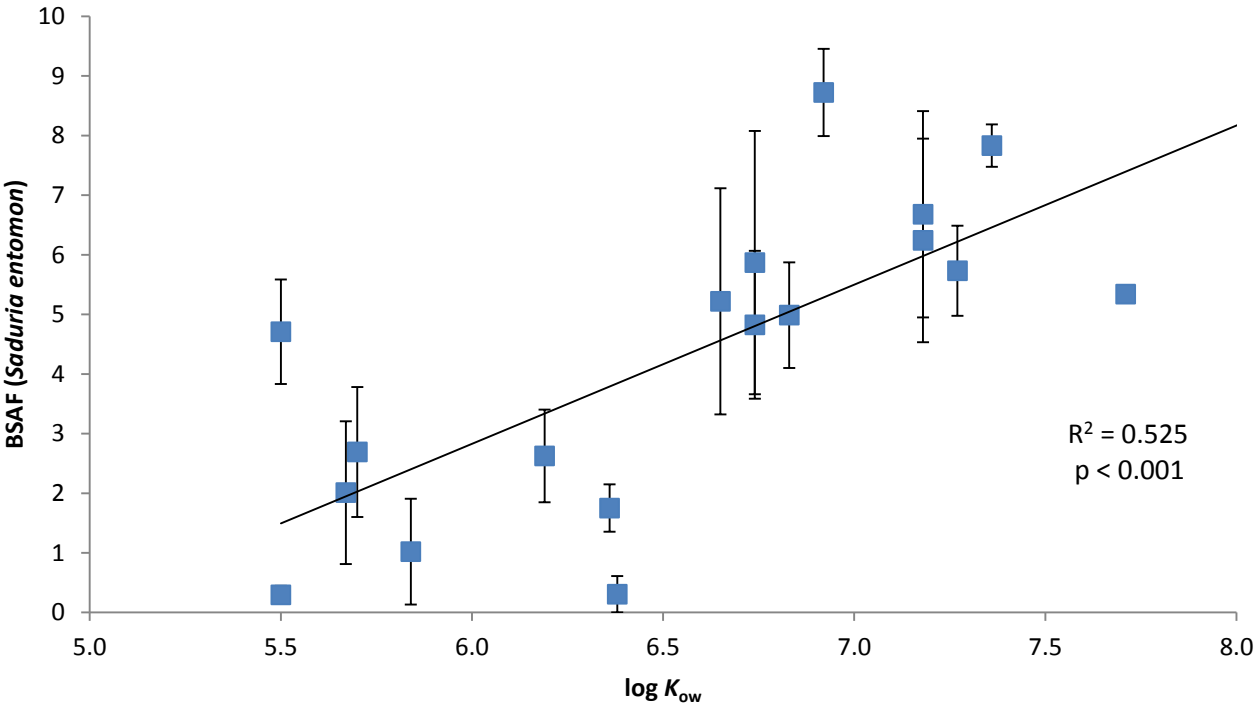


Figure 12: Relationship between average *Saduria entomon* biota-sediment-accumulation factors of contaminants and contaminant hydrophobicity. Error bars represent standard deviation.

4.8 Relation between sorption or bioaccumulation and sediment composition (hypothesis 2)

4.8.1 Sorption

In order to find out if there was a correlation between the type of sediment and the sorption of contaminants, the sites were grouped by their fiber impact. The average values of the sorption in each of the three groups of sediment type (FB = fiber bank, FRS = fiber rich sediment, SED = less affected sediment) and their standard deviations are presented in Figure 13. It needs to be noted that due to the sampling set up, the sediment type groups did not exhibit the same amount of log K_d values, because more samples were taken in fiber banks and fiber rich sediment than in less affected sediment. The data included five sampling points of fiber bank sites, seven of fiber rich sediment but only three of less affected sediment.

Sorption was lowest in the less affected sediment (log K_d=4.6) and highest in the fiber banks (log K_d=5.5). The graph indicated an increase in sorption with increasing fiber impact. Significant ($p<0.001$) differences in sorption between the three sediment types with varying fiber impact were proved using single-factor ANOVA. Therefore, two-tailed z-tests were used as a post-hoc test to check for differences between the groups. The test was significant for the combinations fiber bank and fiber rich sediment ($p<0.001$) as well as for fiber bank and sediment ($p<0.001$). In conclusion, contaminants in fiber banks had significantly higher average sorption than fiber rich sediment and less affected sediment. The experiment however could not prove that average sorption is different between fiber rich sediment and less affected sediment ($p=0.068$).

4.8.2 Bioaccumulation

The same investigation was conducted for sediment type and BSAF values. *Marenzelleria* was found at three less affected sediment sites and at four fiber rich sediment sites and but only at one fiber bank sediment site (P-FB1). Considering the organic carbon content, this site might not be a fiber bank but rather also fiber rich sediment, as mentioned previously. The average BSAF values ranged between 1.6 and 2.4, and the fiber bank sediment appears to have the highest BSAF values (Figure 14). However, there was no relationship observed for BSAF values along the gradient of fiber impact. Likewise the single-factor ANOVA could not prove significant differences between the means of *Marenzelleria* BSAFs in different sediment types ($p=0.994$).

Specimen of the second biota type sampled (*Saduria entomon*) were only found at three sampling sites. As all of them were in fiber rich sediment, the relation between *Saduria entomon* BSAF values and sediment composition could therefore not be investigated.

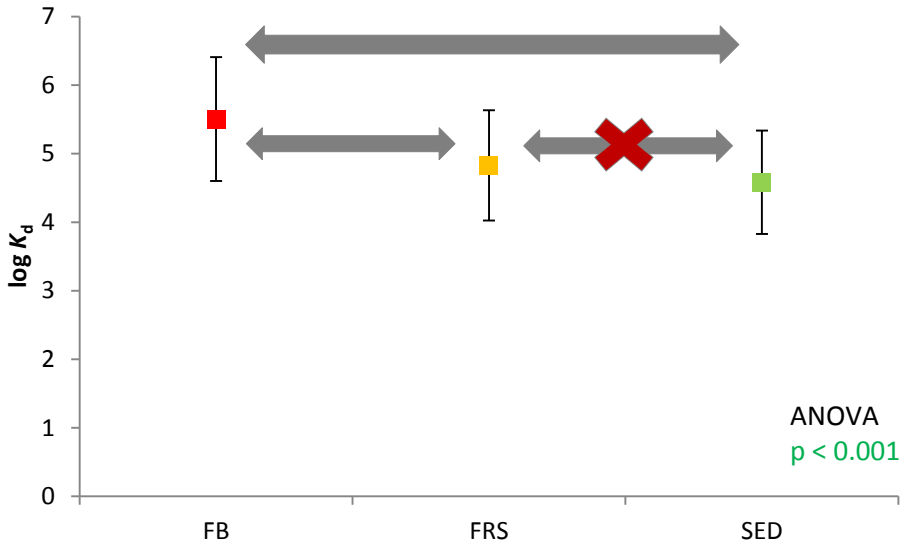


Figure 13: Average sorption expressed in log K_d values in different sediment types. Error bard represent standard deviation.

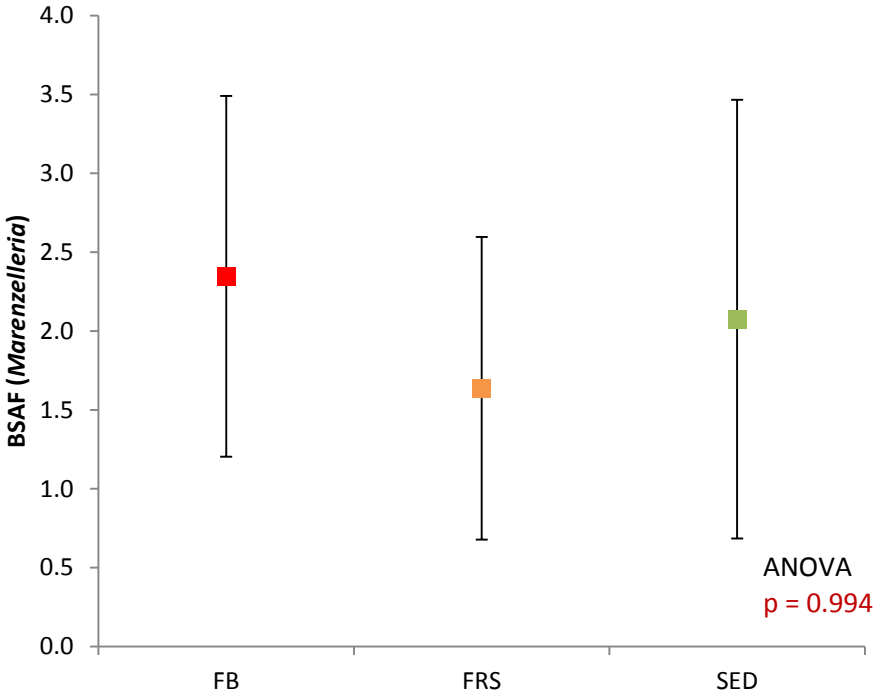


Figure 14: *Marenzelleria* biota-sediment-accumulation factors in different sediment types, shown as an average BSAF of all compounds at one (FB) or more sites (FRS and SED). Error bars represent standard deviation.

4.9 Relations between POP concentration in biota and concentration in pore water or total concentration (hypothesis 3)

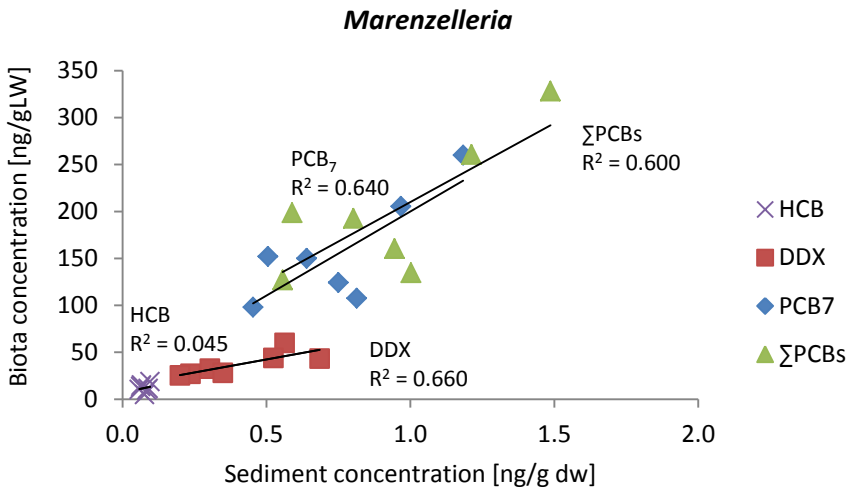
The POP concentrations in biota (based on lipid weight) were analyzed for correlations with the concentrations found in pore water and in sediment (based on dry weight as well as on organic carbon content). The data and trendlines are shown in Figure 15 a-c - Figure 16 a-c. R^2 values indicate how well the parameters in each of the combination pairs correlate. For better overview these are summarized in Table 6. The analysis was conducted for the two biota types separately. The only statistically significant correlation between biota concentrations and sediment or pore water concentrations was found between concentrations in *Marenzelleria* and total sediment concentrations based on sediment dry weight for DDX, PCB_7 and ∑PCBs.

For levels in *Saduria entomon*, the highest R^2 was found for concentrations in the sediment on an organic carbon basis for HCB and DDX, and for pore water concentrations for PCB_7 and ∑PCBs. However, none of the correlations tested with concentrations in *Saduria entomon* was significant. Closest to the significant threshold was the correlation between biota concentrations and concentrations in sediment based on organic carbon for DDX (p=0.069). Negative correlations were observes for PCB_7 and ∑PCBs concentrations between biota and sediment (on organic carbon basis), as well as for all contaminant groups between biota (*Saduria entomon*) and pore water concentrations. These findings were unexpected, as generally for high contamination in sediment or pore water, more elevated contaminant levels are to be expected in biota.

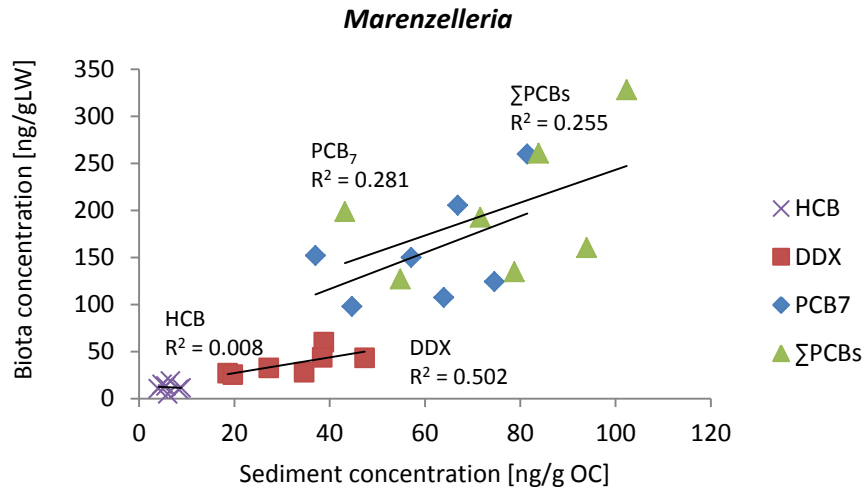
Table 6: Results of the correlations between the concentrations in the two biota types and the concentrations in sediment and pore water. Highest R^2-values for each contaminant group and significant p-values (below 0.05) are stressed in bold.

			HCB	DDX	PCB_7	∑PCBs
Marenzelleria	Sed dw	R^2	**0.045**	**0.660**	**0.640**	**0.600**
		p-value	(0.649)	**(0.026)**	**(0.031)**	**(0.041)**
	Sed OC	R^2	0.008	0.502	0.281	0.255
		p-value	(0.847)	(0.075)	(0.221)	(0.247)
	PW	R^2	0.022	0.279	0.413	0.382
		p-value	(0.750)	(0.223)	(0.120)	(0.139)
Saduria entomon	Sed dw	R^2	0.558	0.969	0.429	0.242
		p-value	(0.463)	(0.112)	(0.546)	(0.673)
	Sed OC	R^2	**0.919**	**0.988**	0.090	0.225
		p-value	(0.184)	(0.069)	(0.807)	(0.685)
	PW	R^2	0.299	0.683	**0.939**	**0.981**
		p-value	(0.632)	(0.381)	(0.159)	(0.088)

a)



b)



c)

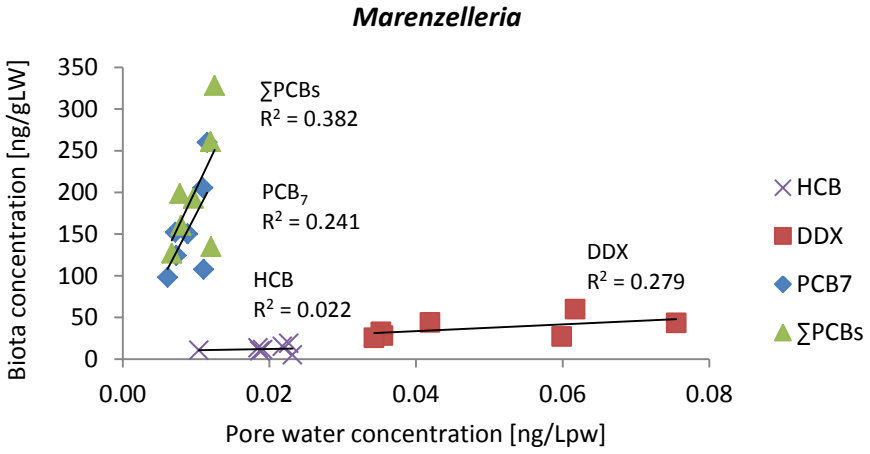
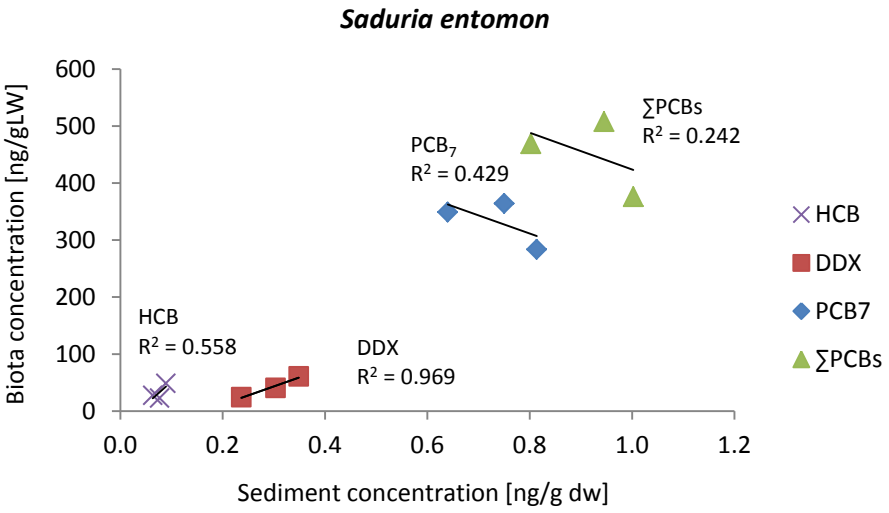
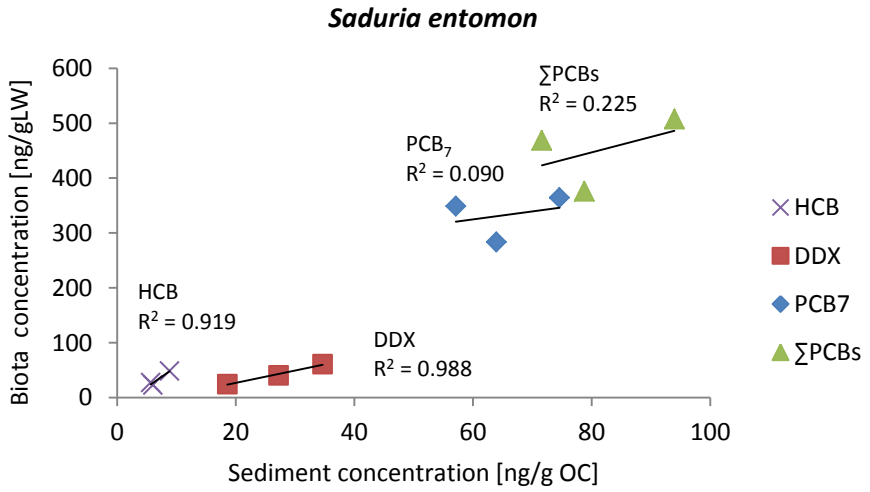


Figure 15: Correlation between contaminant concentrations in *Marenzelleria* and a) sediment based on sediment dry weight, b) sediment based on organic carbon and c) pore water.

a)



b)



c)

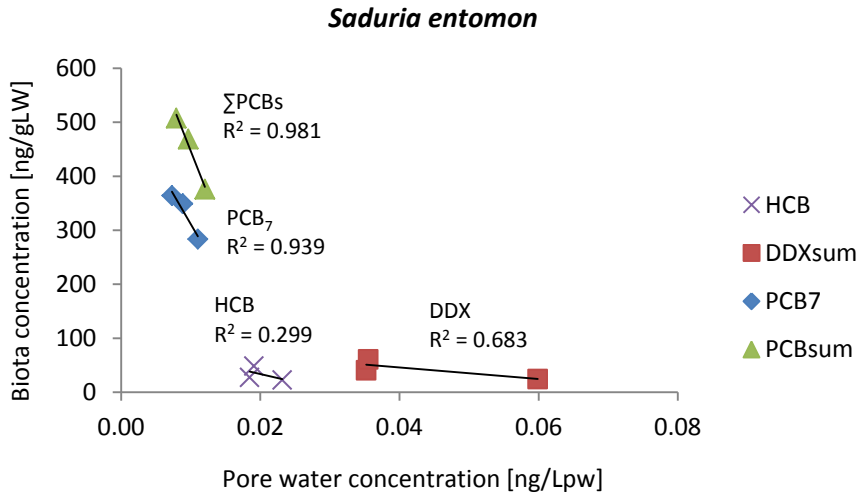


Figure 16: Correlation between contaminant concentrations in *Saduria entomon* and a) sediment based on sediment dry weight, b) sediment based on organic carbon and c) pore water.

5 Discussion

5.1 General findings

In general, method recoveries of all sample types were on average within a tolerable range of 100±20%. In sediment samples 8 contaminants had average recoveries below 80%: PCB 52 (70±18%), PCB 114 (78±10%), PCB 126 (78±15%), PCB 157 (78±16%), PCB 169 (60±25%), PCB 170 (60±25%), PCB 189 (45±29%), PCB 209 (62±25%). The lowest recoveries exhibited four out of the five latest eluting compounds which could be related to their large molecular size and high hydrophobicity. An evaluation of the method regarding these compounds could improve future results.

Some contaminants could only be detected in low concentrations or in only a few of the samples, and two of the target analytes (PCBs 126 and 169) were not detected in any of the sediment, POM or biota samples. As these compounds are non-ortho PCBs, their absence can be considered a positive result due to their coplanar molecular structure and corresponding dioxin-like toxicity (see section 2.2.1). However, in sediment samples the recovery of PCB 126 and PCB 169 was considerably lower. Instead of indicating absence of these contaminants this could also point out that the method should be validated to ensure its suitability for these compounds.

5.2 POP concentrations and organic carbon content in sediment

Fiber banks exhibited the highest sediment contamination for all three contaminant groups analyzed (Figure 7). This is only apparent when concentrations are based on sediment dry weight. However, due to their hydrophobic properties the contaminants partition into the organic matter fraction in sediments. Consequently, for sediments with high organic carbon content, higher contaminant concentrations are expected. The organic carbon contents in the fiber banks are considerably

higher than in the other sediment types (Table 3), as a result of deposition of mainly cellulose (fiber bank area R & P) as well as wood fibers and wood shavings (fiber bank area Q). Therefore, the results normalized to sediment organic carbon content (Figure 8) allow an alternative way for comparison between sites. Concentrations normalized with organic carbon show less extreme differences between the different sediment types. However, after normalization, two sites (Q-FB and R-FB2) differed substantially from the other sites for PCB_7 and ∑PCBs concentrations (Figure 8). This clearly indicates influence of a nearby local source. For site Q-FB, this is most likely the Sandviken sulfate pulp mill, judging by its location just outside the factory (Appendix Figure A2). R-FB2 is one of the two fiber banks in the proximity of the Väja sulfate pulp mill. The two fiber bank sites there are separated by an erosion channel. The fiber bank site (R-FB1), which according to the map seems to be located closer to the actual factory area (Appendix Figure A1), had considerably lower PCB concentrations on an organic carbon basis than R-FB2, but the organic carbon content is higher. The two fiber banks may both have been part of the same fiber bank before. The formation of the erosion channel might be the reason why they have been mapped as two independent fiber banks, but in fact belong together with R-FB2 being the peripheral area of R-FB1. For R-FB2, the larger distance from the mill could explain the lower organic carbon content, as more of the fibers in the discharge water may have accumulated already close to the effluent inlet of the mill (forming R-FB1). The influence of the nearby source together with comparably lower organic carbon content can explain the high concentrations (on OC basis) at R-FB2 and the differences observed (Figure 8) compared to the neighboring fiber bank site (R-FB1).

As mentioned in Chapter 4, the fiber bank site P-FB1 often showed exceptional behavior compared to the other fiber bank sites. As suspected previously, the classification of sediment types made by SGU in the *Fiberbank project* may be incorrect for P-FB1. This can be explained by the fact that it differs in many site-specific attributes from the other fiber bank sites. Compared with the other fiber bank sediment samples, P-FB1 had low organic carbon content (2.55%) and was the only site in this type of sediment where biota could be found. The sample could be taken with the Gemax sampler unlike the others (OPB sampler). Also the sampling depth was much deeper and the location differs: P-FB1 lies offshore, while the remaining fiber banks are all located with connection to the shore. While the other FB sites were formed around the discharge areas of the mills, P-FB1 most likely developed from dredging and depositing activities (Apler *et al.*, 2014). Due to these disparities one could argue that a further division into subcategories would have been reasonable or rather, that the classification of fiber impacted sediment types should be based on organic carbon contents. However, then the question needs to be answered which specific organic carbon contents may be the thresholds between the different fiber sediment types, i.e. FB, FRS, SED.

5.3 Classification of sediments

The results showed that the sediments in the whole study area around Kramfors, Sandviken and Väja are relatively high polluted with persistent organic pollutants. At a few sites, low levels could be found for p,p'-DDX and PCB_7. However, for HCB, all of the sediment samples were classified with mid, high or even very high (P-FB2) levels (Table 4). For PCB_7 four sites were classified in the very high pollution category (class 5). For ∑p,p'-DDX, however, none of the sites exhibited class 5 contamination levels, nevertheless five sites were classified with high levels (class 4). The highest classified level per compound group was always found at fiber bank sites (with the exception of P-FB1). This suggests that the pollution is connected with the fibers and consequently arouse from the sources of the fibers, namely the pulp and saw mills in the area. Nevertheless, the existence of other sources cannot be excluded.

The contaminants summed up as PCB_7 are the seven most common PCBs, which are also included in most studies. It is therefore applied as a standard indicator parameter which facilitates comparison across different studies, which may not target the same PCB congeners. Even though it is a helpful tool, it may lead to an underestimation of the actual PCB burden by not taking into account the 14 other PCB congeners analyzed in this master thesis study. Correspondingly, only the p,p'-DDX were summed up as parameter leaving out the three o,p'-DDX. Nevertheless, it was found that for DDX, all sites were classified with the same level when applying the same classification thresholds (Appendix Table A2) to the total sum of DDX. However, for DDX this underestimation might not be as relevant as for the PCBs, due to the fact that in nature, o,p'-DDX are generally present at substantially lower concentrations than p,p'-DDX.

5.4 POP relative distributions in sediments

The compound distribution patterns in each of the sediment samples showed that the samples had different contaminant compositions. The most apparent differences were noticeable in the proportion and composition of DDX. Differences in the composition of DDX in sediments could indicate that usage and release of the DDX compounds vary at the various local sources in different areas. However, as these compounds are commonly applied as mixtures, the differences in the composition of DDX in different samples could also be due to problems during instrumental analysis. In the injector of the gas chromatograph, DDT can breakdown to DDD and/or DDE (Foreman & Gates, 1997). This has been observed for p,p'-DDT but o,p'-DDT is suspected to undergo similar breakdown. The breakdown of this thermolabile contaminant in the GC is often of relevance in sediment

samples (Foreman & Gates, 1997). Therefore, analysis of relationships between the different DDX compounds should be interpreted with caution. Monitoring of a performance evaluation standard (PES), after or several times during the field samples injection in the GC would improve data quality and interpretations (Foreman & Gates, 1997). Additionally, differences in the progress of the degradation process of DDT in the field could play a role as well.

5.5 POP concentrations in pore water

In biota and sediment samples, PCB concentrations were generally the highest; this was not the case for pore water concentrations. The highest concentrations in pore water were due to DDX contamination (Appendix Figure A3). HCB and ∑PCBs concentrations were rather similar. But at some sites HCB concentrations even exceeded the ∑PCBs concentration, even though HCB is only a single compound. The reason might be that HCB and the DDX have lower log K_{ow} values, and are therefore less hydrophobic than the majority of the PCB contaminants included in this master thesis study (Table 1). Less hydrophobic contaminants are more likely to be found in the aqueous phase than the more hydrophobic ones.

5.6 POP concentrations in biota

Site P FB1 was the only fiber bank sediment where biota could be sampled (Table 5). However, this site might be misclassified and instead be fiber rich sediment. In that case, it was not possible to sample biota at any of the fiber bank sites. This could indicate that fiber banks might not be suitable as habitat for biota, at least for the two species investigated in this master thesis, due to the influences of the fibers. A possible reason could be the anoxic conditions in the fiber bank, due to the consumption of oxygen during microbial degradation of organic material. Furthermore, the microbial degradation may lead to the presence of toxic products, e.g. sulfide and ammonium, from microbial decomposition processes of organic material (Forbes et al., 1998), which evidently is present in fiber banks in large amounts. This will be discussed in more detail in 5.9.

5.7 Relation between sorption or bioaccumulation and hydrophobicity (hypothesis 1)

The results showed a significant relationship between the sorption of a contaminant and its hydrophobicity (Figure 10). The variation in the sorption could be significantly explained by the log K_{ow} value of the contaminant with 83%. This is coherent with the general understanding of how organic compounds partition between different phases. The log K_d value gives insight on the sorption behavior of contaminants. Sorption increases with increasing log K_d value. This means that contaminants sorb stronger the more hydrophobic they are. At the same time, this also gives insight about bioavailability. Contaminants with lower sorption will have higher concentrations in the pore water. This explains why pore water concentrations of HCB and DDX exceed the concentration of the ∑PCBs (compare 4.5). Except for PCB 28 and 52, all other PCBs had higher log K_{ow} values than the HCB and DDX. In consequence, these less hydrophobic compounds will be more readily available for uptake in biota. However, the real amount of the bioavailable part that is actually taken up, depends on parameters such as feeding type of the organisms (Kaag *et al.*, 1997) and uptake paths (Forbes *et al.*, 1998).

To what extent contaminants were taken up into biota is reflected by the BSAF values. When related to corresponding log K_{ow} values the polynomial trendline had a rather poor (R^2=0.224) and insignificant (p<0.079) fit for *Marenzelleria*. The presumed bell-shaped distribution of the compounds implying low bioaccumulation for compounds of both low and high hydrophobicity was observed for example by Tracey and Hansen (1996). Their study compiled BSAF values of numerous other studies and found a log K_{ow} dependent bell shaped distribution for PCBs, with lower bioaccumulation outside the log K_{ow} range of 6.0-7.3. Reasons for this behavior may be associated with lower accumulation efficiency, due to molecular size for contaminants with high log K_{ow}, and metabolization for compounds with low log K_{ow} (Tracey & Hansen, 1996). The data of this master thesis project could not reliably confirm the observation by Tracey and Hansen (1996). In this master thesis study, only two PCB compounds were analyzed that were below the log K_{ow} range identified by Tracey and Hansen (1996) as having high bioaccumulation, and only 3 compounds had higher log K_{ow} values. This might be too few data points outside that range to be able to see a statistically significant bell-shaped distribution. It needs to be mentioned that the study from 1996 observed the bell shaped distribution for PCBs only and did not include DDX and HCB, unlike this master thesis study. When only the PCBs were taken into account the R^2 improved (R^2=0.327) but results were still not significant (p=0.077).

Regarding BSAF values of *Saduria entomon*, the results showed a significant linear relationship (R^2=0.525, p<0.001) between average BSAF values of a compound

and its hydrophobicity. As mentioned above, underrepresentation of compounds outside the log K_{ow} range may be a reason why a bell shaped distribution could not be observed. Even though both biota species investigated are sediment-dwelling organisms, they differ from each other regarding several characteristics, e.g. feeding type and trophic level. These differences may possibly explain why for *Saduria entomon* and *Marenzelleria* not the same BSAF distributions were observed with increasing contaminant hydrophobicity. However, *Saduria entomon* could only be sampled at three spots, resulting in a generally low total number of data points. Even though the statistical analysis resulted in a significant relationship, the total amount of samples collected has influence on precision and uncertainty of retrieved BSAF values (Burkhard, 2003). A higher amount of *Saduria entomon* samples would be preferable for more representative results. Finally, the log K_{ow} range of contaminants detected in the two biota species differed. The high hydrophobic compounds that were related with the slight downward trend of the BSAF distribution in *Marenzelleria*, were not detected in *Saduria entomon* samples. The distributions of BSAF values between the two biota types may be more similar if analyzed for the same log K_{ow} range.

The average BSAF value per species showed that *Saduria entomon* (average of all datapoints: 4.3) had a generally higher BSAF than *Marenzelleria* (average of all datapoints: 1.9). While *Marenzelleria* is a surface deposit-feeder (Dauer *et al.*, 1981), *Saduria entomon* is a predator, feeding on other benthic fauna (Haahtela, 1990). Therefore, the higher average BSAF in *Saduria entomon* could be due to biomagnification, as this species is on a higher trophic level in the food chain. Other possible reasons might be differences in metabolism, lipid content or lipid quality leading to different BSAF and BSAF distributions across different species.

To conclude, regarding sorption, hypothesis 1 could be accepted. Sorption proved to be significantly correlated with contaminant properties showing low sorption for compounds with low hydrophobicity (low log K_{ow}). Regarding bioaccumulation, hypothesis 1 had to be rejected. For *Marenzelleria*, the correlation between bioaccumulation and hydrophobicity resembled the presumed bell-shaped distribution, but the relationship was not significant. For *Saduria entomon* the relationship between the two parameters was significant, but with a linear relationship instead of the expected bell-shaped distribution.

5.8 Relation between sorption or bioaccumulation and sediment composition (hypothesis 2)

Hypothesis 2 could partly be accepted. There is a relationship between sorption and sediment composition regarding fiber banks and other sediment types. Sorption proved to be higher in fiber banks. Differences of sorption between fiber rich sediments and less affected sediments, however, could not be confirmed. Regarding bioaccumulation, no relationship between BSAFs and fiber impact on sediment could be found, so hypothesis 2 was rejected.

The suspended material in the discharged water, coming from pulp and paper mills, led to the formation of the fiber banks. Sedimentation of cellulose fibers and even wood fibers and wood shaving in the fiber banks introduced large amounts of organic material. The increase of organic carbon enhances the opportunities for pollutants to sorb and therefore increased sorption can be observed in the fiber banks compared to other type of sediment. One could argue that the increased sorption reduces availability of the contaminants. However, the organic material may be degraded over time. In that case, the reduction of organic content could lead to decreasing sorption. In consequence, contaminants could become even more bioavailable in the future. Additionally, it needs to be considered that landslides or other movements arising from the land uplift (see section 2.1) can impact the fiber banks and make large amounts of pollutants available in a short time.

Bioaccumulation did not differ in the different sediment types. This could indicate that bioaccumulation is independent of the fiber impact on the sediment. However, the organic carbon content, which is the major difference between the sediment types, was already accounted for in the BSAF calculation (see section 3.6) unlike in the K_d calculation. This could explain why along the fiber impact gradient differences only could be observed for sorption. Nevertheless, it may be possible that there actually exist differences for bioaccumulation as well, but the study and experimental setup could not manage to reveal these. If the differences between the different sediment types only exist between fiber banks and other sediments, it may be difficult to reveal these, when no biota could be found at any of the fiber banks, except for P-FB1, which most likely was a fiber rich sediment site.

5.9 Relations between POP concentration in biota and concentration in pore water or total concentration (hypothesis 3)

Hypothesis 3 was formulated based on the assumption that contaminants are more bioavailable if present in the pore water. It was presumed that the pollutants are more readily available for uptake into biota when not being bound to the sediment but occurring in the aqueous phase. Therefore, it was suspected that the pore water concentrations reflect the concentrations found in biota best. However, results did not prove the expected hypothesis. Only for PCB_7 and ∑PCBs in *Saduria entomon* contamination levels correlated best with pore water concentrations (Table 6; Figure 16). Surprisingly, the direction of correlation opposed the expected one: PCB levels in biota decreased with increasing pore water concentrations. Nevertheless, results were not significant and with only three sampling sites the results should be interpreted with caution. HCB and DDX in *Saduria entomon* had best correlations with levels in sediment normalized to organic carbon, but these were also not significant.

For *Marenzelleria* significant correlations could be found. Increasing contaminant concentrations were best reflected by increasing sediment concentrations normalized to its dry weight. These findings were against expectations and therefore hypothesis 3 had to be rejected.

For the calculation of the pore water concentration, data from the POM sampling was used. As mentioned in 3.6, equilibrium and non-depletive conditions are required for the application of this method. Hawthorne *et al.* (2009) found the duration of 28 days sufficiently long in order to reach equilibrium. The check for depletion, however, revealed that several POM samples exceeded the depletion threshold of 5%. The sorption capacity of the passive sampling material should be negligible (Lydy *et al.*, 2014) in order to reflect pore water concentrations reliably. The exceedance of the threshold indicates that inadvertently a higher amount of the contaminant, originating from the sediment, is found in the POM sampler. Due to depletion, the pore water concentrations might be distorted. This could in turn influence which sample matrice reflects concentrations in biota best. In the present study, the amount of sediment used for POM sampling may have been insufficient. Its high water content could have played a role. In order to overcome this issue in the future, the amount of sediment taken for POM analysis could be increased, or the POM sampler size decreased. This in turn could, however, affect its ability for reliable contaminant detection.

The contaminants investigated are characterized among others by differences in their hydrophobicity. Uptake routes of contaminants into biota differ in their im-

portance depending on their hydrophobicity. With increasing log K_{ow} the importance shifts from uptake via pore water (for low log K_{ow} compounds) to uptake via ingested sediment particles (Josefsson *et al.*, 2011). Most POPs in this master thesis study have relatively high log K_{ow}, therefore pore water as the source for contaminant uptake may not be as important as the uptake by ingestion of contaminated sediment particles. Due to differences in the food sources, the uptake pathway from sediment may not be as important to *Saduria entomon*, as it is feeding on other biota (Haahtela, 1990). However, *Marenzelleria* can take up feed from either pore water or sediment (Dauer *et al.*, 1981). For highly hydrophobic contaminants, like the ones in this thesis project, the contaminant uptake via sediment may be the dominant pathway in that case. This could therefore explain why biota concentrations correlate better to sediment concentrations than to pore water concentrations. Additionally, some sediment-dwelling animals actively avoid contact with pore water, as it is toxic to most of them (Forbes *et al.*, 1998). This is due to different products (e.g sulfide and ammonium) produced by microbes when decomposing organic matter. Due to the fiber accumulation, sediments in the study area have high organic matter contents. In combination with decomposition processes taking place, it could be suspected, that the pore water in the contaminated sediments might be toxic to biota as well as low in oxygen content. This could be an additional explanation why pore water concentrations do not reflect biota concentrations best. In consequence, the presence of toxic metabolic products might be higher and oxygen content lower in areas with more organic matter available for composition. This could therefore additionally give an explanation why no biota samples could be found at fiber bank sites.

6 Conclusions and outlook

Besides determining contaminant burdens in sediment, pore water and biota, this master thesis project gave insight into how physical-chemical properties of contaminants, as well as sediment composition (regarding fiber impact) are related to the contaminant sorption and bioaccumulation. Increased organic carbon content, due to the fiber accumulation, played a major role in sorbing pollutants. The presence of a wide range of POPs in high concentrations in fiber banks shows that environmental impacts of paper and pulp mills should be focused on. This is especially true in an area like the High Coast, which is undergoing changes, due to the uplift of land and its consequences for the seabed. More research is needed to fully understand processes and reasons for pollutant behavior and pollutant transport in sediments on the one hand and in fiber impacted sediments on the other hand. Moreover, an improved classification system for differentiation between different fiber type sediment could improve future research and the comparability between fiber bank areas in different locations. Additionally, it would be interesting for future studies to investigate the contamination patterns, to see if significant differences in the contaminant composition between the different fiber bank areas exist and which congeners may be more relevant. Multivariate statistics, e.g principal component analysis (PCA), may be a suitable tool for this kind of investigations. In particular, differences linked to the different type of pulp and paper production processes (e.g. sulfate or sulfite factory) may be worthwhile analyzing and could help to track pollution sources and consequently to counteract. The determination of fiber bank impacts on the environment and assessing related risks for society and the environment are important prospective steps. Subsequently, possibilities for remediation of polluted sediments should be explored. Finally, once identified and localized, pollutant sources can more easily be assigned to their polluter. This in turn can facilitate the process of allocating responsibilities for potential remediation activities and corresponding costs.

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Appendix

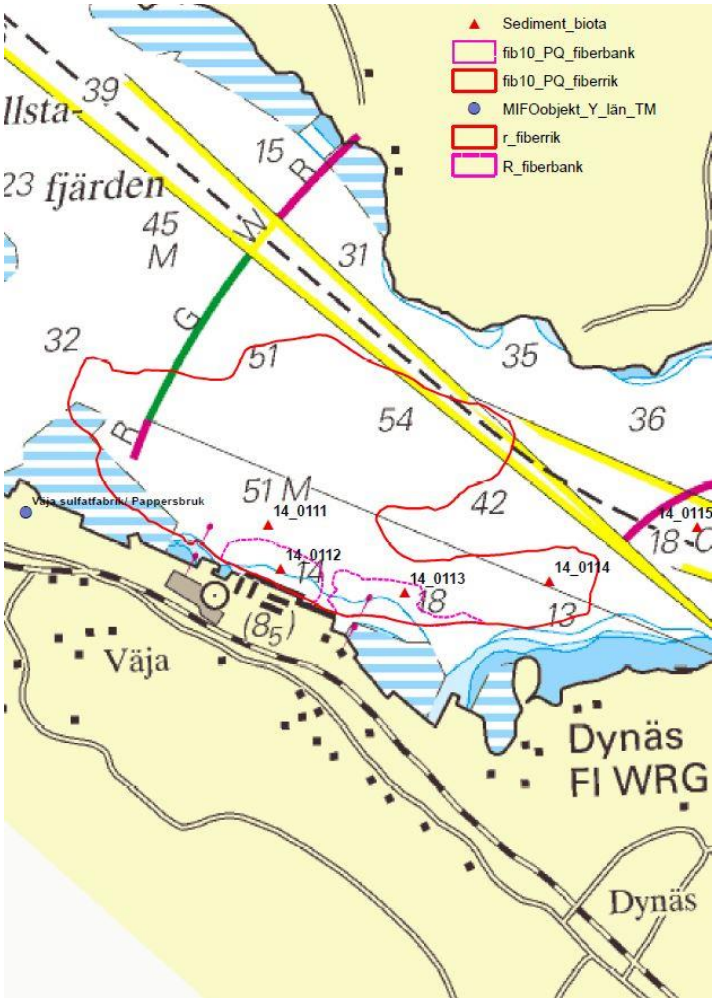


Figure A1: Map of the most northern sampling area, Väja (R), showing the exact locations of the sampling sites (red triangles) as well as the extent of the fiber banks (pink dashed line) and fiber rich sediment (red line). For interpretation of site names consult Table A1. Map provided by the Swedish Geological Survey.

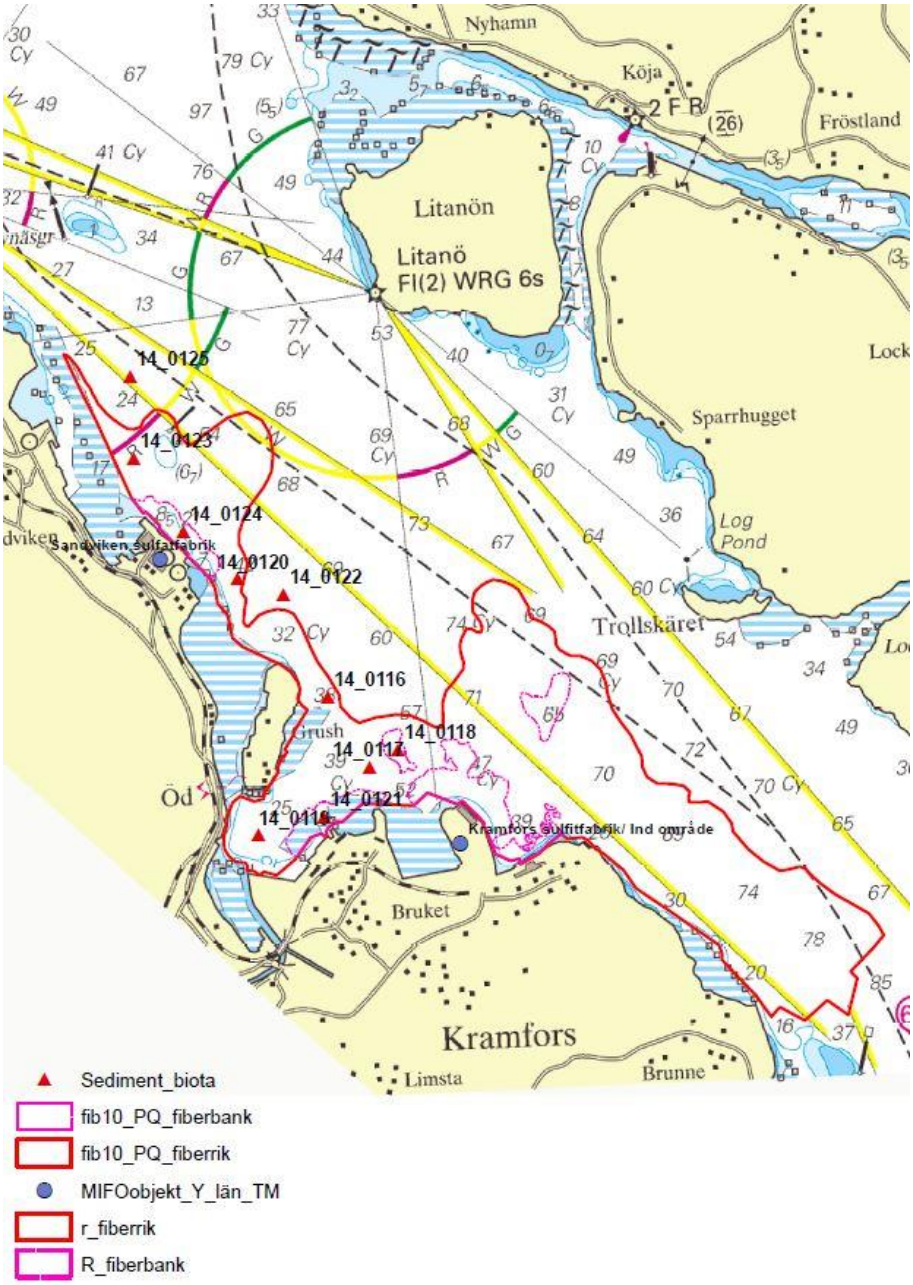


Figure A2: Map of the two southern sampling areas, Sandviken (Q) and Kramfors (P), showing the exact locations of the sampling sites (red triangles) as well as the extent of the fiber banks (pink dashed line) and fiber rich sediment (red line). For interpretation of site names consult Table A1. Map provided by the Swedish Geological Survey.

Table A1: Sampling details, including site names used in this thesis work, the corresponding sample name used during lab work, as well as details about date, exact location and depth of each sample taken.

Site name	Initial name	Method	Sampling date	X-coordinate	Y-coordinate	Depth [m]
R-FB1	112	OPB	2014-07-03	6985855.0	637852.8	15.3
R-FB2	113	OPB	2014-07-03	6985783.3	638231.3	20.3
R-FRS1	111	Gemax	2014-07-02	6985990.9	637814.0	36.9
R-FRS2	114	Gemax	2014-07-03	6985817.2	638673.3	16.2
R-SED	115	Gemax	2014-07-03	6985981.6	639125.2	29.0
Q-FB	124	OPB	2014-07-06	6983718.4	640768.7	13.9
Q-FRS1	120	Gemax	2014-07-05	6983476.2	641041.7	30.3
Q-FRS2	123	Gemax	2014-07-06	6984086.1	640515.2	19.3
Q-SED1	122	Gemax	2014-07-06	6983396.8	641275.4	45.6
Q-SED2	125	Gemax	2014-07-07	6984506.5	640498.2	22.3
P-FB1	118	Gemax	2014-07-04	6982610.3	641858.0	56.4
P-FB2	121	OPB	2014-07-05	6982270.9	641480.6	15.0
P-FRS1	116	Gemax	2014-07-04	6982880.3	641501.3	41.2
P-FRS2	117	Gemax	2014-07-04	6982518.4	641712.5	52.2
P-FRS3	119	Gemax	2014-07-05	6982175.8	641149.3	17.0

Table A2: Assessment criteria for statistical classification of organic pollutants in sediment along the Swedish coast (ng/g dw) according to Naturvårdsverket (1999).

	Class 1 No level	Class 2 Low level	Class 3 Mid level	Class 4 High level	Class 5 Very high level
HCB	0.00	0-0.04	0.04-0.2	0.2-1	>1
PCB_7	0.00	0-1.3	1.3-4	4.0-15	>15
∑ p,p' DDX	0.00	0-0.2	0.2-1	1.0-6	>6

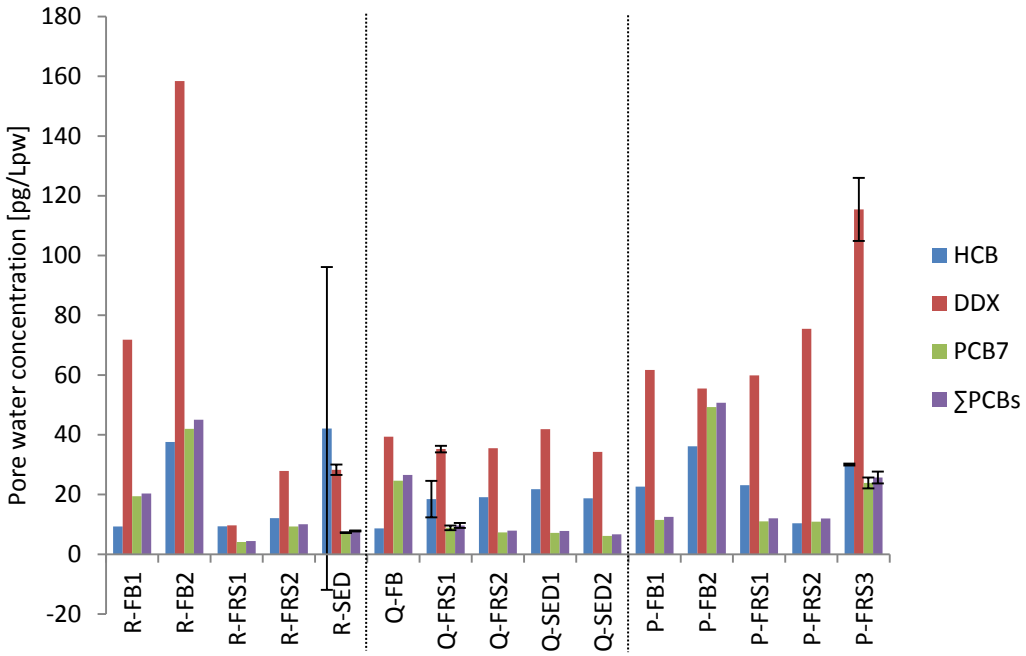
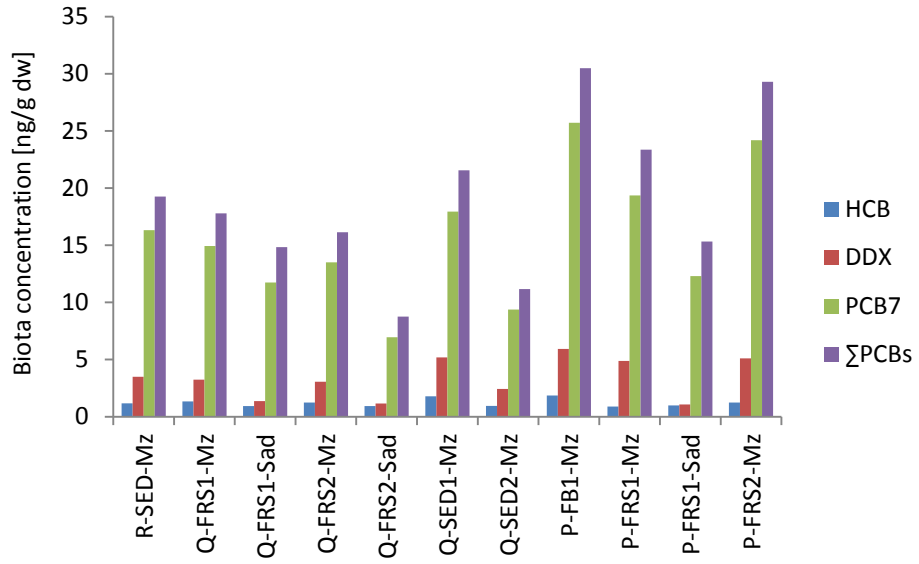


Figure A3: Pore water concentrations. Note that in contrast to other graphs these results are shown in pg/L_{pw}.

a)



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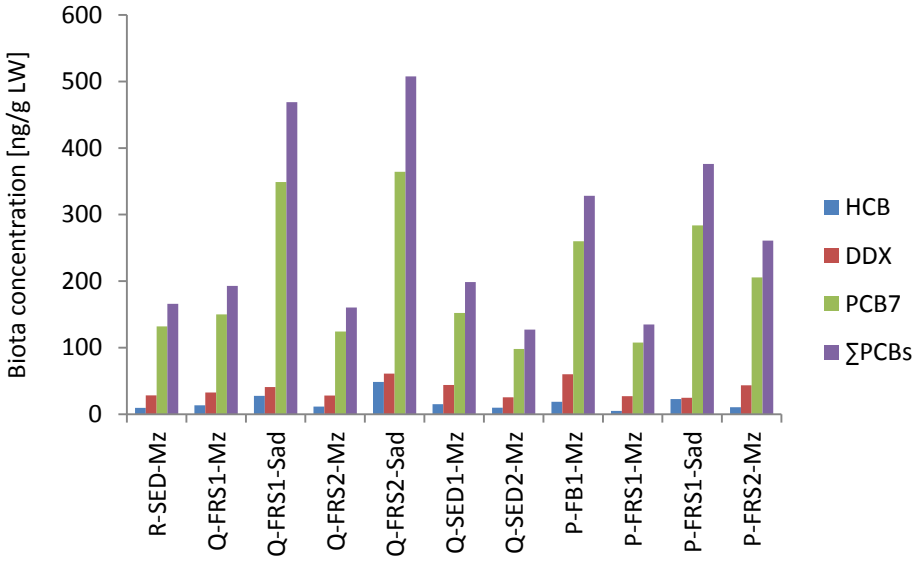
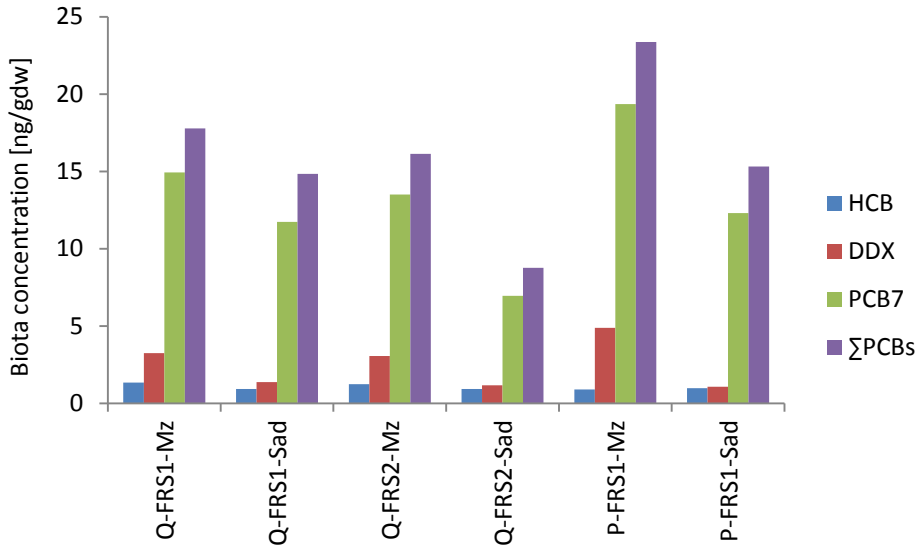


Figure A4: Biota contaminant concentrations normalized to biota **a)** dry weight and **b)** lipid weight. Biota types found were *Marenzelleria* (Mz) and *Saduria entomon* (Sad).

a)



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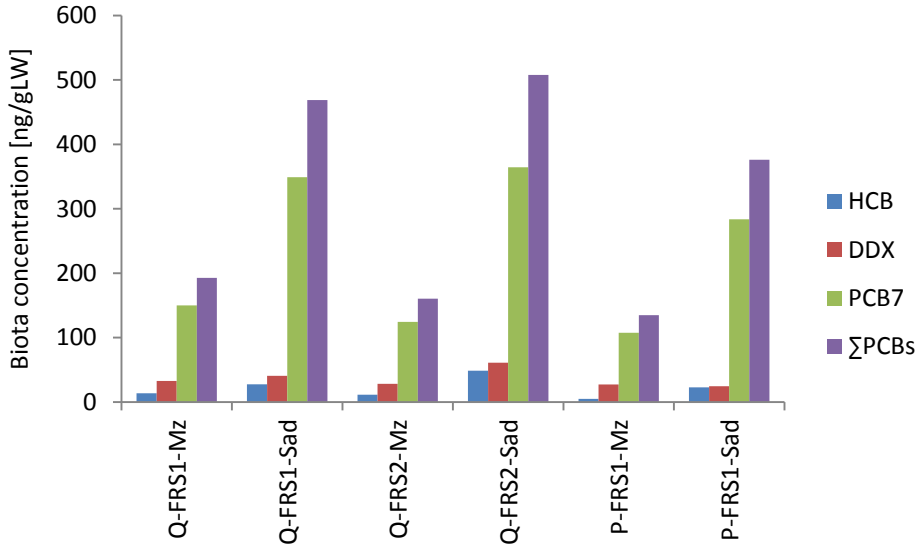

Figure A5: Biota contaminant concentrations normalized to biota **a)** dry weight and **b)** lipid weight, for sites where both biota types were found.