

Fate and transport of POPs in the aquatic environment

- with focus on contaminated sediments

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Sammanfattning (Summary in Swedish)

Persistenta organiska föroreningar (POPs på engelska) är långlivade ämnen som ackumuleras i levande organismer. De är hydrofoba, dvs. binder till organiskt material i t.ex. partiklar och kolloider istället för att vara fritt lösta i vatten. Bindningen påverkar föroreningarnas biotillgänglighet och transport i miljön. De föroreningar som har studerats i avhandlingen är polyklorerade dibenso-*p*-dioxiner och dibensofuraner (PCDD/F), polyklorerade bifenyler (PCB), polybromerade difenyletrar (PBDE), hexaklorbensen (HCB) och oktaklorstyren (OCS). Fokus i avhandlingen ligger på sedimentets roll som sekundär källa till föroreningar. På grund av sin hydrofobicitet ansamlas POPs i sedimenten på havs- och sjöbottnar. När utsläppen från den ursprungliga (primära) föroreningskällan upphör finns det i sedimenten kvar stora mängder föroreningar som kan läcka ut till vattnet och sprida sig till organismer. Utläcket kan ökas genom bioturbation, dvs. omrörning av sedimentpartiklar och porvatten av bottenlevande organismer.

Om föroreningarna som kommer ner till sedimentet täcks med rent sediment blir de begravda och är då inte längre i kontakt med vattnet. För många POPs har utsläppen från primärkällor minskat kraftigt under de senaste decennierna, och därför är koncentrationerna i regel högre längre ner i sedimentet än vid ytan. Experiment i den här avhandlingen visade att en invaderande grupp av maskarter, *Marenzelleria* spp., som upptäcktes i Östersjön på 1980-talet, kan remobilisera begravda föroreningar från sedimentet eftersom de gräver djupare än tidigare förekommande arter. Föroreningar som har betraktats som begravda på ett säkert djup kan således transporteras upp igen. Eftersom *Marenzelleria* har påträffats ner till 50 cm djup kan deras bioturbation omfatta föroreningar som har sedimenterat under det senaste århundradet i Östersjön.

Capping är en metod som används för att minska utflödet av föroreningar från sediment. Den innebär att ett skikt av rent material placeras som ett täcklager på sedimentet. Genom att använda aktiva material som binder de organiska föroreningarna kan tunna skikt användas, s.k. 'active capping' eller 'tunnskiktscapping'. I avhandlingen undersöktes hur tunnskiktscapping påverkar utläckage och bottenlevande djurs ackumulation av olika föroreningar, bl.a. dioxiner. Både utläckage och ackumulation minskade med ökad captjocklek, och tillsats av aktivt material (aktiverat kol eller kraftlignin) ökade cappingeffektiviteten ytterligare. Aktiverat kol var mest effektivt, och en 3 cm cap med 3.3% aktiverat kol minskade utläckage och ackumulation med ca. 90%. Resultaten från avhandlingen visar att tunnskiktscapping är en effektiv saneringsmetod.

List of papers

This thesis is based on the following papers, which are referred to in the text by their respective Roman numerals. It also includes additional unpublished results.

- I. **Josefsson S**, Karlsson OM, Malmaeus JM, Cornelissen G, Wiberg K. Structure-related distribution of PCDD/Fs, PCBs and HCB in a river – sea system. *Chemosphere*, 2011, 83:85-94.
- II. **Josefsson S**, Leonardsson K, Gunnarsson JG, Wiberg K. Bioturbation-driven release of buried PCBs and PBDEs from different depths in contaminated sediment. *Environmental Science & Technology*, 2010, 44: 7456-7464.
- III. **Josefsson S**, Leonardsson K, Gunnarsson JG, Wiberg K. Influence of contaminant burial depth on the bioaccumulation of PCBs and PBDEs by two benthic invertebrates (*Monoporeia affinis* and *Marenzelleria* spp.). *Submitted manuscript*.
- IV. **Josefsson S**, Schaanning M, Samuelsson G, Gunnarsson JG, Olofsson I, Eek E, Wiberg K. Capping efficiency of various carbonaceous and mineral materials for *in situ* remediation of marine sediments contaminated with PCDD/Fs, OCS and HCB. *Manuscript*.

Paper I and II are reprinted with permission from Elsevier and the American Chemical Society, respectively.

Contribution by the author of this thesis to the papers

Paper I: The author was involved in the planning of the experiment, performed all experimental work except sampling, and wrote the paper.

Paper II: The author was highly involved in the planning of the experiment, performed the experimental work, and wrote the paper.

Paper III: The author was highly involved in the planning of the experiment, performed the experimental work, and wrote the manuscript.

Paper IV: The author was involved in the planning of the experiment, contributed substantially to the experimental work, and wrote the manuscript.

Abbreviations and definitions

AC	activated carbon
AhR	aryl hydrocarbon receptor
BAF	bioaccumulation factor
BC	black carbon
BCF	bioconcentration factor
BDE	brominated diphenyl ether
BSAF	biota-sediment accumulation factor
CB	chlorinated biphenyl
CDD	chlorinated dibenzo- <i>p</i> -dioxin
CDF	chlorinated dibenzofuran
DL-PCB	dioxin-like PCB
DOC	dissolved organic carbon
dw	dry weight
<i>ex situ</i>	not in (original) place (often with the meaning 'off-site')
GC	gas chromatography
HCB	hexachlorobenzene
HRMS	high resolution mass spectrometry
<i>in situ</i>	in place
<i>K_{ow}</i>	octanol-water partition coefficient
LDPE	low density polyethylene
LG	lignin
LLE	liquid-liquid extraction
<i>Mo</i>	<i>Monoporeia affinis</i>
MTC	mass transfer coefficient
MW	molecular weight
<i>Mz</i>	<i>Marenzelleria</i> spp.
NDL-PCB	non-dioxin-like PCB
OCS	octachlorostyrene
PAH	polycyclic aromatic hydrocarbon
PBDEs	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, toxic
PCBs	polychlorinated biphenyls
PCDD	polychlorinated dibenzo- <i>p</i> -dioxin
PCDD/Fs	polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans
PCDF	polychlorinated dibenzofuran
POC	particulate organic carbon
POM	polyoxymethylene
POP	persistent organic pollutant
PUF	polyurethane foam

SC	Stockholm Convention
SPM	suspended particulate matter
SPMD	semipermeable membrane device
spp.	species
TEF	toxic equivalency factor
TEQ	toxic equivalent
TOC	total organic carbon
WHO-TEF	the TEF scale of the World Health Organization
WHO-TEQ	TEQs according to the WHO-TEF scale
ww	wet weight

Congener	Substances with the same backbone structure but different numbers and placements of the halogen atoms
Homologue	Congeners with the same number of halogen atoms but different placements

Words for numerals

non	0
mono	1
di	2
tri	3
tetra (T)	4
penta (Pe)	5
hexa (Hx)	6
hepta (Hp)	7
octa (O)	8
nona	9
deca	10

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1. Introduction

During the 20th century, a rapid technical development led to increased welfare in many parts of the world. Diverse chemical substances were developed and put to use in numerous applications, such as polychlorinated biphenyls (PCBs) as insulating fluids in electrical equipment, hexachlorobenzene (HCB) to protect crops and wood from fungi, and polybrominated diphenyl ethers (PBDEs) to reduce the risk of fires. After having been produced, used, and distributed in the environment worldwide for decades, some of these substances turned out to be toxic for living organisms. As evidence on their toxicity mounted, the production of these substances was gradually phased out and the unintentional release was decreased by changing the industrial processes and installing more cleaning equipment. This led to substantial reductions of the primary sources of many of the so-called persistent organic pollutants (POPs) (1-3).

Due to their slow degradation, POPs persist in the environment for long time periods even after a total cessation of production and use, and continue to pose a risk to biota. The persistence also allows them to be transported in the environment, far from their original sources. Water covers around 70% of the Earth's surface, and the aquatic environment is a large sink for POPs from the terrestrial environment (4). Since the POPs are hydrophobic, they prefer to sorb to organic matter in particles instead of being dissolved in water, and an important process for removing the POPs from the water column is their sorption to particles and subsequent sedimentation to the sediment surface.

Large amounts of POPs have accumulated in sediments, especially close to former point sources (e.g. 5-8). When the emissions of POPs from primary sources decrease, the contaminated sediment can become the main source of contaminants to the aquatic environment. From the sediment, the POPs are continuously dispersed to animals living in the sediment and in the water column. This contamination can continue for long time periods, and it is believed that the secondary sources, such as contaminated sites, can become the main source of POPs as the releases from primary sources decrease (9,10).

If the sediment, on the other hand, is covered with new layers of cleaner sediment, the contaminants will become buried in the sediment, and the sediment will act as a sink for the pollutants, removing them from the aquatic environment. However, different processes in the sediment can

counteract the burial process. One important factor is bioturbation, the mixing of sediment particles and pore-water by benthic organisms, which can increase the release of sediment contaminants. The influence of bioturbation on contaminant remobilization became a concern in the Baltic Sea region when the species *Marenzelleria* spp. entered the area in the mid-1980s. *Marenzelleria* spp. burrow deeper in the sediment than the native Baltic Sea species (11-13), and have the potential to remobilize contaminants previously considered to be buried at a safe depth.

In order to stop the continuous remobilization of old contaminants from sediment, the sediment can be remediated. If the natural sedimentation and burial is not sufficient for decreasing the remobilization of contaminants on an acceptable time scale, different remediation methods can be used. One method is dredging, when the sediment is removed from the site, or capping, when the sediment is covered with a layer of clean material to stop the remobilization. A development of capping is to mix in active sorbents in the cap. These active sorbents, for instance activated carbon (AC), are good sorbents for the POPs, and by enhancing the sequestering of the POPs, their mobility and bioavailability can be decreased.

1.1 Objectives

The overall aim of this thesis was to investigate the fate and transport of different POPs in the aquatic environment. The focus is on marine environments, and particularly on the role of contaminated sediment as secondary sources of POPs. The thesis is based on four papers (I-IV; Figure 1), and the objectives of the papers were to increase the understanding on:

- how POPs are distributed in the water phase in a river – sea system in a Baltic Sea coastal area (Paper I)
- to what extent POPs buried in sediment are remobilized to the water phase as a result of bioturbation by benthic species (Paper II)
- to what extent POPs buried in sediment are accumulated in benthic species (Paper III)
- how capping of contaminated sediment, using different cap thicknesses and materials, can decrease the POP sediment-to-water flux and bioaccumulation by benthic species (Paper IV).

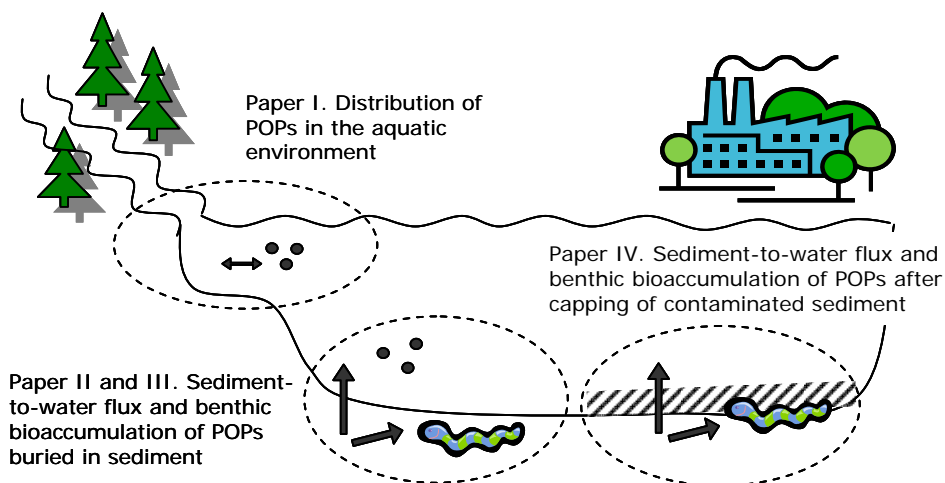


Figure 1. The research areas investigated in this thesis.

1.2 Brief summary of Papers I-IV

In paper I, *Structure-related distribution of PCDD/Fs, PCBs and HCB in a river – sea system*, the POP concentration in water was sampled in two rivers, an estuary, and the adjacent sea. The incentive for the study was the problematically high levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in fish in the study area (the Bothnian Sea basin of the Baltic Sea). The objective was to increase knowledge on PCDD/F levels, distribution and seasonal dynamics in a coastal background area (i.e. an area without significant point sources), and to investigate if the POP levels were related to parameters such as amount of organic carbon or particles.

The driving environmental issue for paper II, *Bioturbation-driven release of buried PCBs and PBDEs from different depths in contaminated sediments*, was the invasion of *Marenzelleria* spp. in the Baltic Sea in the 1980s. *Marenzelleria* spp. can burrow to a substantial depth (50 cm; 14) in sediment, and the objective of the study was to examine to what extent POPs buried at different depths in the sediment was remobilized to the water column due to different types of bioturbation (by *Marenzelleria* spp. and the native species *Monoporeia affinis*).

Paper III, *Influence of contaminant burial depth on the bioaccumulation of PCBs and PBDEs by two benthic invertebrates (Monoporeia affinis and Marenzelleria spp.)* is based on the same experiment as Paper II, but the objective was to investigate the uptake of buried contaminants in benthic organisms, a

second potential transfer route (trophic transfer) of sediment contaminants to pelagic biota.

In the final work of the thesis (Paper IV), *Capping efficiency of various carbonaceous and mineral materials for in situ remediation of marine sediments contaminated with PCDD/Fs, OCS and HCB*, a remediation method for contaminated sediments was investigated. The objective was to explore the effect of *in situ* active capping on the sediment-to-water release and benthic bioaccumulation of POPs. The results are, together with toxicity studies and field experiments, a basis for planned remediation actions in the heavily contaminated Grenlandsfjord area in Norway.

2. Persistent organic pollutants (POPs)

2.1 General properties of POPs

'Persistent organic pollutants' (POPs) is a generic term for a wide range of substances that are resistant to degradation in the environment and poorly soluble in water (hydrophobic). The POPs are often halogenated substances, having a carbon backbone with e.g. chlorine or bromine atoms as substituents. Substances with the same backbone structure but varying numbers and placement of halogen atoms are called congeners. The congeners differ in their physicochemical properties, which affects their environmental fate and transport.

In the environment, the POPs tend to partition to organic phases such as organic matter in soil and sediment and lipids in biota. The hydrophobicity is described by the octanol-water partition coefficient (K_{ow}), which expresses the ratio between the POP concentration in 1-octanol and water at equilibrium. POPs have relatively similar solubilities in lipids, but exhibit a large variation in their solubility in water, and differences in K_{ow} thus primarily express differences in hydrophobicity rather than in lipophilicity (15). Most POPs are semi-volatile, with vapour pressures enabling them to undergo long-range atmospheric transport through repeated cycles of evaporation and deposition (16). They can also be transported in air or water while attached to particles. Due to their potential for long range environmental transport, POPs have become widely distributed in the environment, and can be found in remote locations where they have been neither produced nor used in extensive amounts (17). Overall, increased halogenation tends to increase the hydrophobicity and the K_{ow} , while decreasing the vapour pressure (18-20).

POPs is a concept associated with the Stockholm Convention (SC) on POPs, a global treaty under the United Nation Environmental Program (UNEP) (21). The SC lists POPs whose intentional or unintentional production, use, and emissions should be eliminated or reduced. Three properties define the POPs: persistency, bioaccumulating potential, and toxicity (PBT). The POPs selected in the SC should fulfil different criteria for PBT¹ and have potential for long range environmental transport. The initial set of POPs listed by the

¹The PBT criteria for the POPs, as defined in Annex D of the SC, are that the half-lives should be >6 months in soil or sediment, or >2 months in water; the BCF or BAF in aquatic species >5000 or log K_{ow} >5; and that there should be evidence of adverse effects to human health or to the environment or data indicating the potential for damage to human health or the environment.

SC, the so-called “dirty dozen”, consisted of twelve chlorinated substances. In 2009, nine additional substances were added to the list, including the polybrominated diphenyl ethers (PBDEs). A closely related abbreviation to POPs is HOCs (hydrophobic organic contaminants), although this is a more general concept than POPs.

The persistence of the POP depends on the chemical as well as the conditions in the environment, for instance the concentration of hydroxyl radicals in the atmosphere and the type of microbial community in sediments (15). Although PCBs and PCDD/Fs can degrade in sediment by anaerobic dehalogenation (22,23), their half-lives are long. For instance, the half-lives of different PCDD/Fs in sediment have been estimated to several decades or even centuries (24). The persistence of the POPs, combined with their hydrophobicity, enables the POPs to reach high concentrations in biota, bioaccumulate. There are two similar concepts: bioconcentration and bioaccumulation. The bioconcentration and bioaccumulation factors (BCF, BAF) express the ratio between the concentration in the organism and the concentration in the surrounding medium (e.g. water) (25). Organisms can accumulate POPs through different uptake routes, such as via the respiratory system, dermally (via the skin), or via the gastrointestinal system after ingestion, and they can also metabolize and eliminate the POPs. For bioconcentration, only the passive uptake from the surrounding environment is considered (e.g. by ventilation through fish gills), but for bioaccumulation, all uptake routes are included (25). For benthic species, the bioaccumulation can be expressed as biota-sediment bioaccumulation factors (BSAFs), which is the ratio between the lipid-normalized concentration in biota and the organic-carbon normalized concentration in sediment (25). The normalization to lipid and organic carbon is performed as these compartments are considered as the main sorbing compartments for the POPs in biota and sediment, respectively. A closely related concept to bioaccumulation is biomagnification. If a compound is biomagnified, its concentration successively increases upwards in a trophic chain, leading to higher POP concentrations in top predators.

It is frequently in the top predators that the toxic effects of POPs have been observed, particularly in fish-eating but air-breathing animals like seals and piscivorous birds (26). It is the chronic toxicity associated with long-term exposure to POPs that is most problematic. Since the POPs are a diverse group of substances with varying structures, the toxicity can be caused by different mechanisms and lead to different effects. Observed adverse effects

in vertebrates include e.g. disturbances on the neurobehavioural, immunological and reproductive systems, and the development of cancer (27-31).

2.2 POPs investigated in this thesis

The sources and history of the POPs investigated in this thesis (Figure 2) are described briefly below, with selected physicochemical properties compared in Table 1.

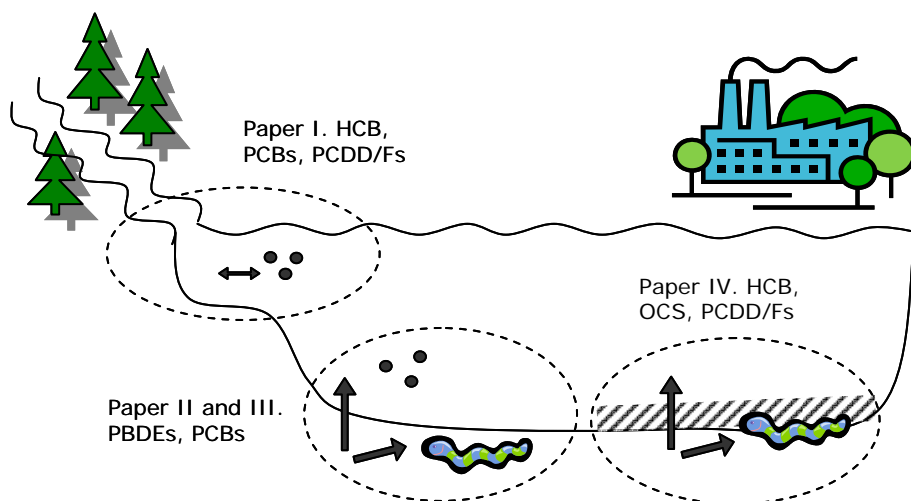


Figure 2. The different POPs investigated in Papers I-IV.

Table 1. Physicochemical property data (octanol-water partition coefficient ($\log K_{ow}$), vapour pressure (V_P) and water solubility (S_w)) at 20-25°C for the POPs investigated in this thesis.

	$\log K_{ow}$	V_P (Pa)	S_w (mol/m ³)
HCB ^a	5.6	9.4×10^{-2}	1.4×10^{-3}
OCS ^b	6.3	1.5×10^{-2}	4.9×10^{-4}
PBDEs (3-7 Br) ^c	5.7 – 8.3	1.6×10^{-3} – 1.1×10^{-6}	8.2×10^{-4} – 8.7×10^{-6}
PCBs (3-10 Cl) ^d	5.0 – 8.2	2.2×10^{-1} – 3.0×10^{-5}	2.4×10^{-3} – 1.4×10^{-6}
PCDDs (4-8 Cl) ^e	6.9 – 8.3	8.8×10^{-4} – 3.6×10^{-6}	1.0×10^{-4} – 2.8×10^{-6}
PCDFs (4-8 Cl) ^e	6.2 – 8.0	3.3×10^{-4} – 2.1×10^{-7}	1.9×10^{-4} – 1.5×10^{-7}

^a All values from Shen and Wania (32).

^b $\log K_{ow}$ from Mackay et al. (33); V_P and S_w calculated using EPI Suite™ v. 4.10 (US EPA, www.epa.gov).

^c $\log K_{ow}$ from Braekveit et al. (20); V_P and S_w from Wania & Dugani (34); values are for *tri- to hepta*-BDEs.

^d $\log K_{ow}$ from Hawker & Connell (19), V_P and S_w from Mackay et al. (33); values are for *tri- to deca*-CBs.

^e All values from Åberg et al. (18), for *tetra- to octa*-CDD/Fs.

2.2.1 PCDD/Fs

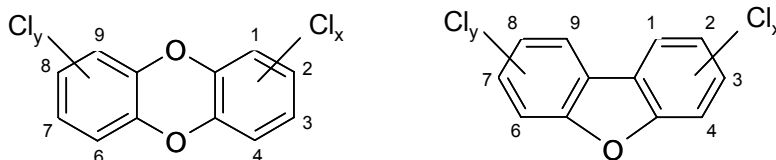


Figure 3. General chemical structure of PCDDs (left) and PCDFs (right).

The polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly referred to collectively as 'dioxins', are planar compounds that can have 1-8 chlorine substituents (Figure 3). They thus constitute groups of 75 and 135 congeners, respectively, or in total 210 congeners. PCDD/Fs have never been commercially produced. Instead, they are formed unintentionally in various combustion processes such as waste incineration and biomass burning, in the production of ferrous and non-ferrous metals, in the bleaching of pulp with chlorine gas, and in the production of chlorinated chemicals, for instance PCBs and pentachlorophenol (1,6,10,35). Due to process changes and improvements in the cleaning technology, the industrial emissions of PCDD/Fs have been reduced (1), and the importance of sources such as open burning of waste (35) or secondary sources such as the release of contaminants from contaminated sites (10) has increased.

The toxicity of the PCDD/Fs is highly dependent on the position of the chlorine substituents, and the PCDD/Fs which are fully chlorinated in the 2, 3, 7, and 8 positions (Figure 3) are most toxic, i.e. 7 PCDDs and 10 PCDFs. These are also the 17 congeners which lack adjacent hydrogen atoms and have the lowest metabolism in biota, with half-lives of 2-7 years in humans (36). The toxic action of the 2,3,7,8-substituted congeners is mediated through binding to the aryl hydrocarbon receptor (AhR), which is present in most vertebrate tissue (37). Since the congeners differ in their affinity to the AhR, they differ in their toxicity. In order to facilitate risk assessments, the concept of toxic equivalency factors (TEFs) was therefore developed. This relates the toxicity of the different congeners to the toxicity of 2,3,7,8-TCDD, considered to be the most toxic congener. 2,3,7,8-TCDD has a TEF of 1, while remaining congeners have values ≤ 1 . Several different TEF-systems have been used (for instance the Nordic-TEF and the I-TEF), but the WHO-TEF is the most common system today. The latest re-evaluation of the TEF-values occurred in 2005, and the WHO 2005 TEF values range from 1 for 2,3,7,8-

TCDD and 1,2,3,7,8-PeCDD to 0.0003 for OCDD and OCDF (37). In order to get a single value of the PCDD/F toxicity, the concentration of the individual congeners is multiplied by their respective TEF value, before being summed as a toxic equivalent (TEQ) value.

The TEF/TEQ concept is intended for risk assessment via dietary intake, as most studies that have been used to determine the TEFs are based on oral ingestion (37). However, the use of the TEF/TEQ concept has also been extended to abiotic matrices such as soils and sediments. As pointed out by van den Berg et al. (37), the TEQs calculated for soils and sediments are not directly relevant for a risk assessment of the toxicity to humans, as the bioavailability of the contaminants has not been taken into account. Some congeners are tightly bound to the abiotic matrix, and the sorption can also increase with time (so-called aging), which decreases the bioavailability. Even so, the TEQ is widely used also for abiotic compartments due to the ease of comparisons.

2.2.2 PCBs

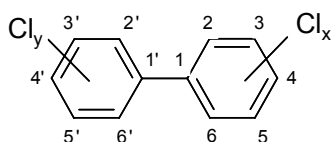


Figure 4. General chemical structure of PCBs.

Polychlorinated biphenyls (PCBs; Figure 4) were, unlike the PCDD/Fs, intentionally produced to be used for a wide range of industrial applications due to their chemical and thermal stability. The main use was in electric equipment such as transformers and capacitors, but also as hydraulic fluids and as additives in plastics and paints (38,39). PCBs were produced between 1929 and 1993, when production ceased in Russia (40), and the total global production has been estimated to >1.3 million tons (3), of which about one third is believed to have been released into the environment (4). PCBs were sold as technical products constituting complex mixtures of congeners with different degrees of chlorination (41). Almost half of the global production of PCBs was by Monsanto, USA, under the tradename Aroclors; other trade names include Chlophens, Sovol, and Kanechlors (3).

Since PCBs can contain 1-10 chlorine substituents, there are in total 209 possible congeners, although not all of these are common in the technical products (41). In environmental monitoring, it is common to analyze only six or seven congeners, the so-called indicator-PCBs (Σ PCB₆ or Σ PCB₇: 28, 52, 101, 138, 153, 180, sometimes including also 118). The toxicity of the PCBs is dependent on their substitution pattern, and the PCBs that lack or have no more than one chlorine atom in the *ortho*-positions (2,2',6 or 6'; Figure 4) can rotate around the biphenyl bond and assume a planar conformation. Twelve PCBs have a chlorine substitution pattern that allows them to assume a planar structure similar to the PCDD/Fs and bind to the AhR, and they have been assigned WHO-TEF values (37). These twelve co-planar PCBs are known as the WHO-PCBs, or 'dioxin-like' (DL) PCBs. Four of them are congeners that lack chlorines in the *ortho*-position, the non-*ortho* PCBs (77, 81, 126, 169), and eight have one chlorine substituent in the *ortho* position, the mono-*ortho* PCBs (105, 114, 118, 123, 156, 157, 167, 189). The non- and mono-*ortho* PCBs overall have lower TEFs than the PCDD/Fs (0.1-0.00003; 37), but since the concentration of PCBs in environmental samples often exceeds the concentration of PCDD/Fs, their contribution to the total TEQ can be significant (42). The *ortho*-substitution also affects the physico-chemical properties, for instance, PCB hydrophobicities and log *K*_{ow} values tend to decrease with increased number of *ortho*-chlorines (19,43).

2.2.3 PBDEs

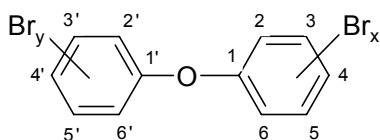


Figure 5. General chemical structure of PBDEs.

The polybrominated diphenyl ethers (PBDEs; Figure 5) are used as flame retardants in various textiles and plastic materials. There are three major technical products of PBDEs: pentabromodiphenyl ether (PeBDE), octabromodiphenyl ether (OcBDE) and decabromodiphenyl ether (DeBDE), which are mixtures of congeners with differing degree of bromination, similar to the commercial technical product of PCBs. Towards the end of the 20th century, concerns over PBDEs grew due to observations of bioaccumulating and toxic properties, and of rapidly rising concentrations in environmental and human samples world-wide (31,44). Restrictions or voluntary

cessations of the production and use of PeBDE and OcBDE were introduced in the European Union and North America in 2004-2005 (45), and in 2009 the *tetra-* to *hepta-*brominated congeners (corresponding to the technical products PeBDE and OcBDE) were listed as POPs under the Stockholm Convention (21). A ban on the DeBDE technical product, which consists almost entirely of the fully brominated congener BDE 209, is more debated since the large size of the BDE 209 molecule can hinder its transport over biological membranes, and thus decrease its bioavailability and bioaccumulation. However, it can debrominate to lower brominated PBDEs, which are more bioaccumulating (31). Regulations on DeBDE in products are in force in the European Union, but most countries world-wide have no restrictions on its production or use (45). Recent data show that PBDE levels tend to decrease in biota in Europe (46), while the concentrations of *tetra-* to *hepta-*BDEs in the Arctic region are increasing or possibly stagnating during the last 2-5 years, and BDE 209 concentrations are still increasing in Arctic air (45).

2.2.4 HCB

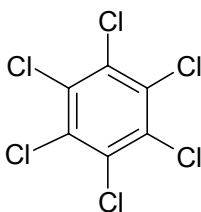


Figure 6. The chemical structure of HCB.

The production of hexachlorobenzene (HCB; Figure 6) started in 1933, and it was used in both agriculture and industry, for instance as a fungicide and a wood-preserving agent, and as an intermediate in the production of other chlorinated substances such as pentachlorophenol (2,47). HCB is also formed unintentionally during e.g. waste incineration and chlorination processes in the manufacturing of chemicals and metals (2,48). The total global production of HCB has been estimated to >100 000 tonnes, but the annual production decreased from around ~1980 onwards as a result of bans in many countries in the 1980s (2). However, HCB was manufactured in China until 2004 (47). The current emissions are mainly from unintentional production, and have been estimated to be 70-95% lower than in 1970 (2,48). HCB is relatively volatile (Table 1), which facilitates its atmospheric trans-

port. A large part of the current HCB in the atmosphere is believed to be the result of volatilization of HCB from reservoirs of past contamination in *inter alia* soil and vegetation, i.e. secondary sources (48).

2.2.5 OCS

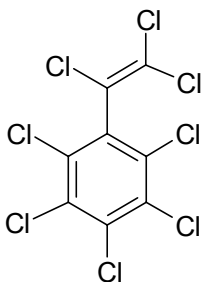


Figure 7. The chemical structure of OCS.

Octachlorostyrene (OCS; Figure 7) is the only of the POPs investigated in this thesis that is not on the SC list, and its emissions, distribution, and toxicity are also less well-investigated. OCS has, similarly to the PCDD/Fs, never been manufactured commercially, but has formed unintentionally in *inter alia* electrolytic processes with chlorine and graphite electrodes (49). Other sources are believed to be the manufacturing of chlorinated solvents and incineration of waste (50). It has been pointed out that OCS probably forms in the same processes as HCB and PCDD/Fs, as these compounds co-occur (50), for instance as the case is in the Grenlandsfjord in Norway where the source is a magnesium production plant (Paper IV).

3. Sampling and chemical analysis of POPs

3.1 Sampling of POPs in water

For accurate measurements of POPs in environmental media, both the sampling and the chemical analysis are important steps. The POPs can be present in water in different phases: associated with larger particles, with colloids (e.g. dissolved organic carbon (DOC) such as humic matter), or freely dissolved in the water. Since the POPs are hydrophobic, their levels in water are low. The PCDD/Fs, which are very hydrophobic and present in the environment at low levels, are especially challenging to sample. Since their total concentration in water can be $\sim 100\text{--}1000\text{ pg m}^{-3}$ (Paper I; $1\text{ pg} = 10^{-12}\text{ g}$, and 1 m^3 of water weighs $\sim 1000\text{ kg}$; thus 1 pg per m^3 is equivalent to 0.0000000000000001%), several hundred litres of water have to be sampled in order to detect the PCDD/Fs in the following chemical analysis. The freely dissolved concentration is even more demanding to sample, as this concentration can be as low as $\sim 10\text{ pg m}^{-3}$ (Paper I). However, the freely dissolved fraction is important to determine, because particle-associated contaminants are less available for biological uptake and the freely dissolved fraction is therefore considered to be more bioavailable (51-53).

If POPs are present at higher concentrations in the water, it is feasible to sample a minor volume (e.g. $<10\text{ L}$) and transport it to the laboratory for *ex situ* extraction, such as liquid-liquid extraction (LLE) or solid phase extraction (SPE) (54). For compounds at low concentrations, however, the sampling step must in effect be combined *in situ* with a concentration step for sufficient detection, especially when sampling is performed in an area without significant point sources such as in Paper I. The sampling can be divided into active water sampling, where the water is pumped through filters and sorbents, and passive water sampling, where the analytes diffuse passively into the sorbent. Since only the freely dissolved analytes are available for diffusion, the passive samplers capture the freely dissolved phase, while the active sampling captures both particulate and dissolved phases. Active water sampling was employed in Paper I and II, and passive water sampling with different samplers in Paper I and IV (Figure 8).

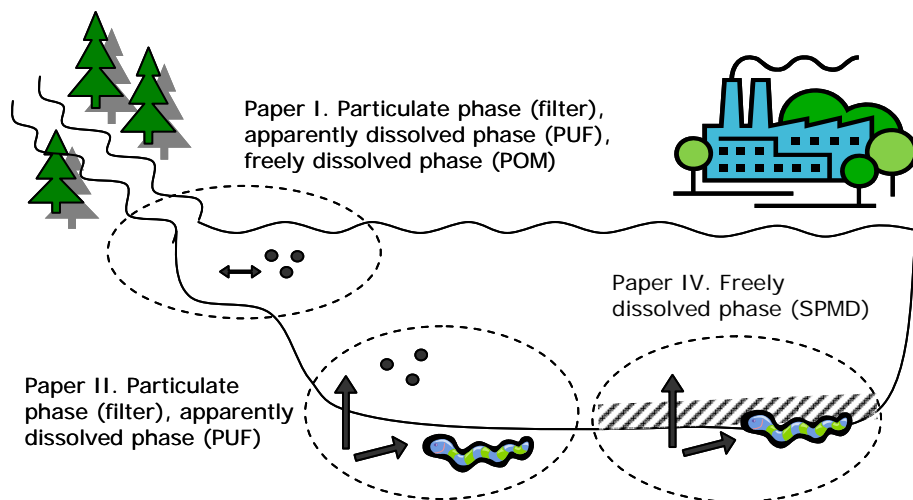


Figure 8. Sampling of POPs in different phases in the water column.

3.1.1 Active water sampling

Active water sampling is performed by pumping water through a filter, which samples particles, and a sorbent, which samples the dissolved phase. The filter used for POP sampling throughout the thesis is a borosilicate glass fibre filter with a pore size of $0.7\ \mu\text{m}$ (Whatman GF/F filters). Hence, the cut-off size of the particulate fraction is operationally defined as $0.7\ \mu\text{m}$, while smaller particles pass through the filter to the sorbent. The sorbent used in large-volume water sampling of POPs is usually polyurethane foam, known as PUF (55-58), or XAD-2 resin, a styrene-divinylbenzene polymer (59-61). In the thesis, PUF was used throughout. Another option is on-line LLE, where the water interacts with a non-polar organic solvent in a multi-step extraction unit, but the flow rates at which water can pass through the sampler is lower than when PUF or XAD-2 is used (62). The use of LLE, PUF and XAD-2 for the sampling of *inter alia* PCBs in sea water was compared by Gómez-Belinchón et al. (62), who found that the highest concentrations were measured with LLE, but that PUF was easier to use and gave quantitative results close to LLE. Both PUF and XAD have also been used as sorbents in air sampling (63).

It is well-known that POPs sorbed to colloidal particles in the water can lead to erroneously high estimations of the dissolved fraction (64), and it has been recognized that PUFs sample not only the dissolved fraction, but also filter-passing colloidal material (e.g. 55,56, Paper I and II). Consequently, the fraction sampled by the PUFs in Paper I and II have been termed the

“apparently dissolved fraction” in this thesis to differentiate it from the freely dissolved concentrations measured by the passive sampling. A comparison between the dissolved concentrations of POPs measured with passive sampling (“freely dissolved”) and with active sampling using PUF (“apparently dissolved”) clearly demonstrates that PUFs sample also colloidal particles, since the discrepancy between freely dissolved concentrations and PUF-measured concentrations was largest for the more hydrophobic, and thus more colloid-associated, POPs (Figure 9).

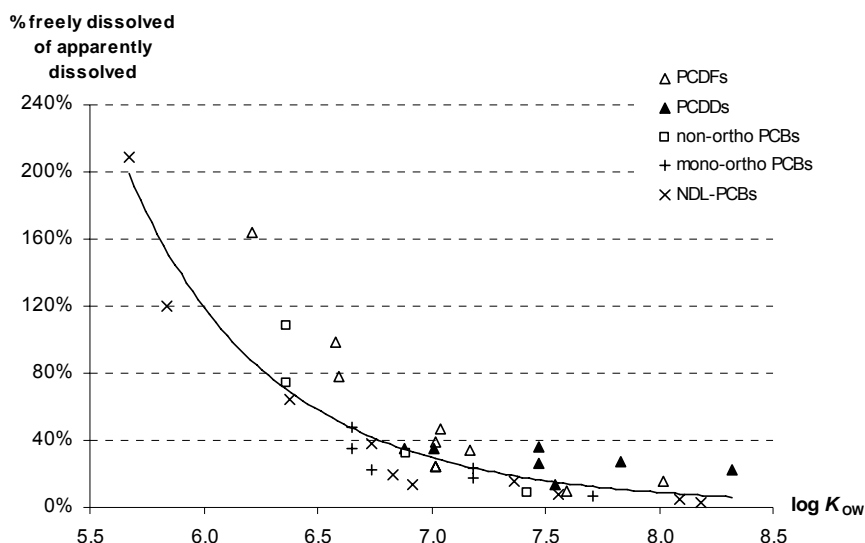


Figure 9. The ratio (expressed as %) between freely dissolved concentrations of PCDD/Fs and PCBs and apparently dissolved concentrations measured with PUF, as a regression on the hydrophobicity of the congeners ($\log K_{ow}$). Figure from Supplementary material to Paper I. The partition coefficients used to determine the freely dissolved concentration may be underestimated, leading to an overestimation of the freely dissolved concentration, see Paper I.

In order to avoid the artefact caused by including the colloidal fraction in the dissolved concentrations, the dissolved POP concentration sampled by the PUFs can be corrected for the colloidal (DOC bound) fraction by using the measured DOC concentration and dissolved organic carbon-water partition coefficients (K_{DOC}) (55,56,64). However, the environmental variation in the quality (structure and composition) of DOC, and thus also in its sorptive properties for POPs, is high and determined K_{DOC} consequently display a large variation, with 95% confidence intervals ranging a factor of 20 (65). In the field study of POP water concentrations described in Paper I, we instead opted for using the freely dissolved concentrations measured with passive

samplers, and correcting the amounts measured in filters and PUFs with this to achieve a total particle + colloidal fraction.

In the comparison of different sampling sorbents, including PUFs, by Gómez-Belinchón et al. (62), a tendency to lower measured concentrations (i.e. analyte breakthrough) was observed at sample volumes exceeding 400 L, particularly for less hydrophobic compounds. For more hydrophobic substances such as PCBs, it was considered to be of minor importance (62), and the risk for breakthrough when sampling POPs such as dissolved PCBs or PCDD/Fs is generally considered to be low (55,56). In Paper I, the breakthrough of PCDD/Fs, PCBs and HCB when sampling ~0.8 m³ of water was evaluated, and determined to be on average 10%. The breakthrough was interpreted to be due to inefficient retention of colloids in the PUFs, rather than inefficient sampling of dissolved contaminants. This conclusion was based on a study by Choi et al. (66), and on experiments in Paper II. Choi et al. (66) found that PUFs were efficient in retaining dissolved POPs in drinking water, as 99.7% of 2,3,7,8-TCDD were found in the first two PUFs (of four). This study has drawbacks, as distilled water was used, i.e. with particle and colloid levels lower than environmental levels, but it still indicates that dissolved compounds are efficiently retained in the PUFs. In Paper II, due to high levels of SPM and frequently clogging filters in the experimental systems, filters could not be used throughout the experiment. When the filter was present, the second PUF contained 3% of the total amount of *tri*-CBs found in the first and second PUFs, while the fraction increased to 19% for the more hydrophobic *hepta*-CBs. When filters are not used, the PUFs will contain higher levels, i.e. they sample also POPs bound to particles >0.7 µm, but the total amount in the sampling system will be lower than if also a filter is used. The loss of analyte in the absence of filters was positively correlated to the hydrophobicity of the analytes (PCBs, PBDEs). These observations support the conclusion that PUFs also sample colloid- and particle-associated POPs, but that the sampling is less efficient than for dissolved POPs.

The drawbacks with active sampling using filter + PUF is that it requires electricity and is labour intensive, since the sampling has to be monitored in order to change clogging filters. The sampling reflects the concentration in the water when it was taken, instead of a time-integrative sample. The major benefits with active sampling are that it is faster than passive sampling, and samples also the particulate phase.

3.1.2 Passive water sampling

In order to determine the freely dissolved (also called the “truly dissolved”) concentration of POPs in water, passive sampling was used. Passive sampling is based on the diffusive movement of a substance from the sampled medium (e.g. water) into the sampler due to a difference in chemical potential of the substance between the two media (67). The sampler is deployed in the environment and accumulates the substance over a certain time period. It therefore provides a time-integrated sample (or pseudo time-integrated for the equilibrium sampler). Since the first passive samplers for hydrophobic organic trace contaminants in water were introduced in the 1980s, various sampling devices have been put to use (67). The samplers used in this thesis were polyoxymethylene samplers (POM; Paper I) and semi-permeable membrane devices (SPMDs; Paper IV).

SPMDs filled with triolein were introduced in 1990 by Huckins et al. (68), and it is now one of the most widely used passive samplers for POPs (67). The SPMDs usually consist of a non-porous low density polyethylene (LDPE) membrane filled with triolein, a neutral triglyceride lipid. Since the membrane has cavities (transient holes) with a size up to 1 nm, only freely dissolved phase contaminants can traverse the membrane, while larger molecules (MW > 600), e.g. colloids, are excluded and triolein is kept within the membrane (69). The size of the LDPE cavities is similar to the cut-off size suggested for POP transport through biomembranes, e.g. a width of 0.95 nm in fish gills (70). POM samplers were introduced in 2001 by Jonker and Koelmans (71), and consist of strips of a polyacetal plastic. It has been used as an environmental sampler of POPs, including PCDD/Fs (58,72).

The passive samplers can be divided into equilibrium and kinetic (or integrative) samplers, depending on whether equilibrium between the sampler and the surrounding medium has been reached (Figure 10). POM is used as an equilibrium sampler, while SPMDs are generally used as kinetic samplers.

The difficulty in passive sampling is to determine the concentration in water from the concentration in the sampler. In the equilibrium approach, this is done by sampler-water partition coefficients (K_{sw}), which have been determined in the laboratory: $C_w = C_s / K_{sw}$, where C_w is the freely dissolved concentration in water and C_s the concentration in the sampler. In the time-integrative approach, the water concentration is determined by using sampling rates: $N_s = C_w \times R_s \times t$ (69), where N_s is the amount of analyte in the sampler, R_s the sampling rate (e.g. in L day⁻¹) and t the time. Since the real

sampling rates in the environment can differ from the laboratory-determined sampling rates (increased temperature and water flow rate can increase the sampling rates in SPMD, while biofouling on the membrane surface can decrease rates; 67), the dissipation rates of performance reference compounds (PRCs) added to the sampler before deployment can be related to changes in the uptake rate of the analytes. The time required for PCDD/Fs to reach the equilibrium phase in an SPMD has been estimated to several years or even decades (73), and thus the SPMD measurements are time-integrative. In paper IV, SPMDs were used as an “infinite sink”, similar to e.g. Eek et al. (74). The SPMDs sample the dissolved POPs from the water column and thus maintain a high concentration gradient between the sediment pore-water and the overlying water in the experimental boxes.

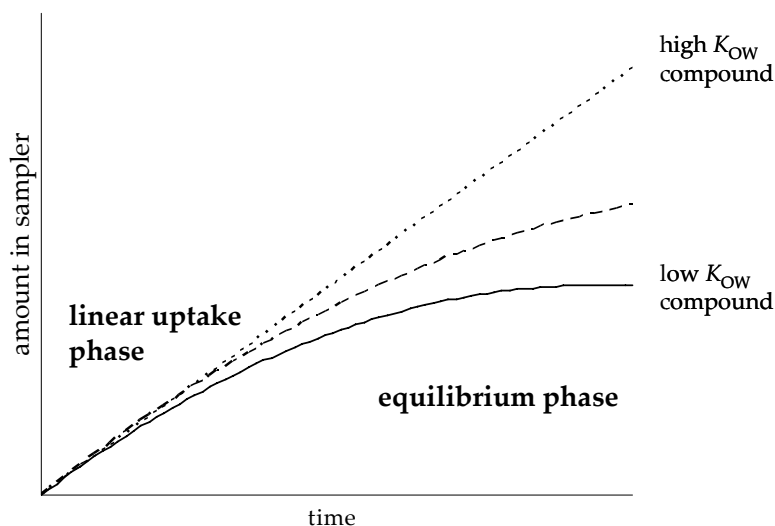


Figure 10. Uptake in passive sampler over time for compounds of differing hydrophobicity. Figure modified from Booij et al. (75).

For equilibrium samplers, one drawback is that the deployment time required to reach equilibrium may be extended, especially for very hydrophobic compounds as the highly chlorinated PCDD/Fs which have slower uptake kinetics (72). In Paper I, a deployment time of 3 months was normally used, and analysis of congener patterns in POMs displayed for 3 months compared to 6 months did not indicate that the deployment time was too short. Cornelissen et al. (72) found that *penta*- and *hexa*-chlorinated PCBs reached equilibrium in POM-17 (17 μm thick) after 10-40 days in

marine water, but based on measurements using a thicker POM (55 μm), it was estimated that highly chlorinated PCDD/Fs could be 10-20% short of equilibrium even after a deployment time of 154-192 days (72). The extended time required for these passive equilibrium samplers thus rules out the possibility of using them for more detailed seasonal studies of dissolved PCDD/Fs.

3.2 Chemical analysis

3.2.1 Extraction

After possible pre-treatment of the sample, for instance drying, the first step in the chemical analysis is extraction of the sample. In this work, the analytes were extracted using different techniques. The sediments, filters and PUFs were Soxhlet extracted, with a Dean-Stark water trap to remove water, and the extraction solvent was toluene, which forms an azeotrope with water. For the passive samplers, extraction was performed by shaking the sampler with organic solvent (*n*-hexane) for 48 hours, under which the analytes diffuse out from the sampler to the solvent. The biological samples were mixed with a desiccant (sodium sulphate) and liquid-extracted with combinations of organic solvents on cold columns.

3.2.2 Clean-up and fractionation

Since not only the desired analytes are extracted, but also unwanted substances that can disturb the detection, the next step is clean-up of the sample extract to remove lipids and other interferences. Multi-layer open columns with acid and basic silica were used. Samples were often also fractionated in order to remove interferences between analytes in the detection step. For instance, PCBs are present in environmental samples at higher levels than PCDD/Fs, and since they can interfere with each other in the detection step, they need to be fractionated into different samples. For separation of PCDD/Fs from PCBs, activated carbon columns were used. PCBs with one or more *ortho*-chlorines were eluted using dichloromethane/*n*-hexane, while the planar PCDD/Fs and non-*ortho* PCBs, which sorb strongly to the carbon, were back-eluted using toluene. The clean-up and fractionation were based on methods by Smith and co-workers (76,77). Finally, in order to improve the detector response, the samples were concentrated to a small volume (30-40 μL) of a low-volatile solvent (keeper).

3.2.3 Detection and quantification

The detection was performed with gas chromatography coupled with high resolution mass spectrometry (GC-HRMS). Quantification was based on the isotope dilution method, in which peak areas for analytes and isotopically (^{13}C) labelled internal standards were used. For many of the PCB and PBDE congeners analysed in Papers II and III, corresponding isotopically labelled congeners were not available and instead an isotopically labelled standard for each homologue group was used (e.g. ^{13}C -CB 28 was used for ^{12}C -CB 28 and ^{12}C -CB 30).

3.3 Quality control

Different measures were undertaken to ensure that the analysis was of high quality. Blank samples (field, analytical, material and instrumental) were run to detect possible contamination. Replicate samples were performed for information on precision. ^{13}C -labelled standards, which behave similarly as the analytes during the clean-up and detection steps, were used both as internal standards (added to the samples prior to extraction) and as recovery standards (added to the samples prior to analysis on GC-HRMS). The use of internal standards corrected for losses during clean-up and for short-term variations in the instrument performance, while recovery standards were used to monitor the recovery of the internal standards (i.e. the extent of losses during clean-up).

4. POPs in the aquatic environment

POPs can enter the aquatic environment from the atmosphere, through groundwater transport and run-off from land, and in direct discharges from point sources. In the water column, several processes will influence the fate and transport of the POP (Figure 11). The POPs distribute between particles, colloids, and the water phase, and the POPs sorbed to settling particles will be deposited to the bottom sediment, where burial with sediment particles can constitute a permanent removal process. Other loss processes of POPs from the aquatic environment are degradation and volatilization to the atmosphere of dissolved POPs.

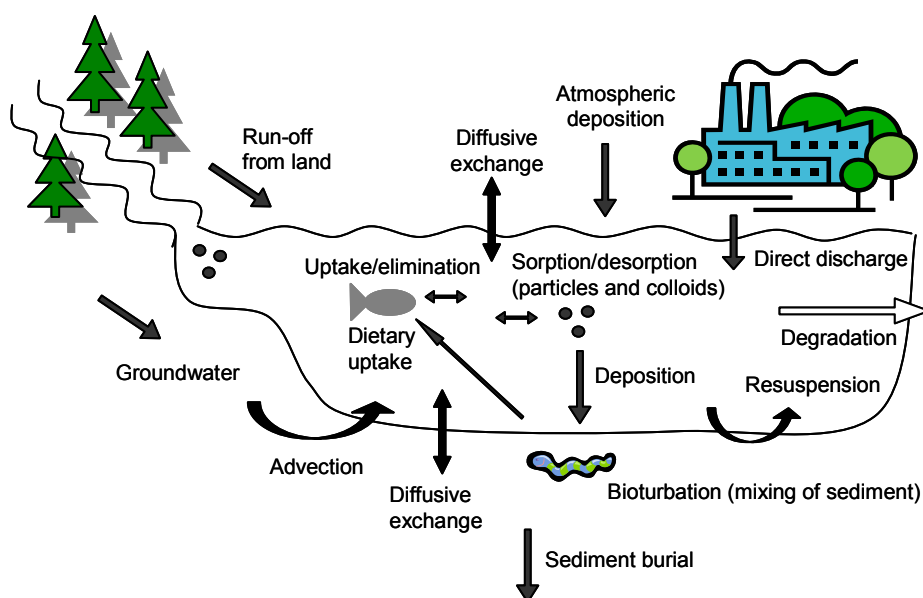


Figure 11. Processes involved in the fate and transport of POPs in the aquatic environment.

When the POPs sorb to particles and colloids, the freely dissolved concentrations decrease and thus also the bioavailability of the organic contaminants to organisms (51,78). On the other hand, the sorption of POPs to colloids can enhance the transport, due to the higher mobility of small colloids compared to larger particles. For instance, the groundwater transport of PCDD/Fs from a contaminated soil site was found to be mediated by colloid-facilitated transport (79), and colloids can also facilitate the transport of POPs over the thin stagnant aqueous films (diffusive boundary layers)

that are present at the interface between *inter alia* water and sediment or passive samplers (80,81). The extent of sorption to particles/colloids and the distribution between different phases in the aquatic environment thus has a large impact on POP fate and transport, for instance their sedimentation, bioavailability, and degradation (25).

4.1 Distinctions between particulate, colloidal and dissolved phases

Colloids are microparticles or macromolecules of such small size that they can move by Brownian diffusion instead of settling under the influence of gravity, as opposed to particles (25). The size distinction between particles and colloids is not precise, but colloids can be defined as having a diameter of 1-1000 nm, i.e. smaller than 1 μm (82). In practise, however, the border between particles and colloids is operationally defined and a commonly set limit between the particulate fractions (e.g. particulate organic carbon, POC) and colloidal fractions (e.g. DOC) is 0.45 μm . In the present work (Paper I, II), the distinction between the particulate and the colloidal fraction of POPs is set to 0.7 μm , as this was the smallest filter pore size available that was feasible for high-volume water sampling. There is also no clear distinction between colloidal and dissolved substances, but to function as a sorbent for POPs, the organic macromolecule has to be large enough to accommodate the POPs, as pointed out by *inter alia* 25,83. The sorption of POPs to particles (POC) is generally higher than to colloids (DOC) on equal organic carbon basis (84). However, since the content of DOC in the aquatic environment tend to exceed the content of POC substantially, for instance around ≥ 10 times in Paper I, the sorption to colloids can be quantitatively important.

4.2 POP distribution coefficients and models

The partitioning of the POP between the water phase and particles or other sorbing phases can be expressed as a solid-water partition coefficient (K_D), which is the ratio between the concentrations in the solid phase (C_s) and the water phase (C_w) at equilibrium: $K_D = C_s/C_w$. Since organic matter is considered the main sorbing phase for POPs (25,53,85), partitioning can be estimated from the organic carbon content of the phase (f_{oc}), and the partition coefficient between organic carbon and water (K_{oc}) for the compound: $K_D = f_{oc} \times K_{oc}$. The organic carbon-water partition coefficient (K_{oc}) can in turn be predicted from the hydrophobicity of the POP in the form of the octanol-water coefficient (K_{ow}), for instance from the relationship $K_{oc} = 0.35 K_{ow}$ suggested by Seth et al. (86) for soil and sediment organic matter or the

relationship $K_{\text{DOC}} = 0.08 K_{\text{OW}}$ suggested by Burkhard (65) for dissolved organic matter. However, the degree of uncertainty is large in both suggested regressions, partly due to analytical differences but also due to the large variability in the organic matter in soils, sediment, and water (65). The variability in the organic matter quality affects the sorption of POPs. For instance, terrigenous material generally sorbs POPs better than planktonic material (83,87), which may be due to the better sorption to the more aromatic structure in the terrestrial colloids (83), and humic acids tend to display higher sorption of POPs than fulvic acids (65,84).

Observations of more enhanced sorption of POPs to soil and sediment than could be explained with the organic matter partitioning model led to the development of a model with dual-phase sorption domains, where the sorption can be explained with both (linear) absorption into amorphous organic matter, and (nonlinear) adsorption onto black carbon (BC) and other carbonaceous georesidues such as coke (88,89). The BC sorption is more favourable for compounds with a planar structure (89,90). The dual-mode sorption has been connected to the observation of a rapid and a slow phase in kinetic studies on sorption/desorption of organic compounds to natural particles. In the rapid phase (hours or days), the hydrophobic compounds sorb/desorb in the outer regions of the particle, but by time (months), they can migrate to/from the inner regions. The slow desorption can be caused by the energy required to break bonds between the compound and the natural particle, or the resistance to mass transfer when the compounds are diffusing through the matrix (91). Sorption to amorphous OC would correspond to the rapidly desorbing phase, while sorption to BC equals the slowly desorbing phase (89). A related concept of relevance for the POP bioavailability is aging, the phenomenon that the bioavailability of POPs in soils and sediments can decrease with time (92). However, as demonstrated by Birdwell and Thibodeaux (93), if the labile fraction (rapid release fraction) is removed, it will be replenished from the nonlabile (slow release fraction) fraction.

4.3 Distribution of POPs in the water in a river-sea system (Paper I)

Due to the low water solubility of PCDD/Fs, there are few studies on PCDD/F levels in water, particularly in background areas with low contamination levels (72,94). The study in Paper I, *Structure-related distribution of PCDD/Fs, PCBs and HCB in a river – sea system*, therefore focused on the run-off from land and the distribution of PCDD/Fs between particles, colloids and dissolved phases. The objective was to increase the

knowledge on the levels, distribution and seasonal dynamics of POPs such as PCDD/Fs in the water phase of a Baltic Sea coastal area without significant point sources. The water concentrations of the seventeen 2,3,7,8-substituted PCDD/F congeners, twenty-two PCB congeners (NDL and DL), and HCB were determined in two rivers, an estuary, and the adjacent Baltic Sea. The sampling took place four times during the year, and both the particulate, apparently dissolved (using PUF), and freely dissolved concentrations (using POM) were determined (active sampling displayed in Figure 12). Parameters such as total organic carbon (TOC) and the amount of suspended particulate matter (SPM) were also measured, and the relationships between these parameters and the POP levels were studied.

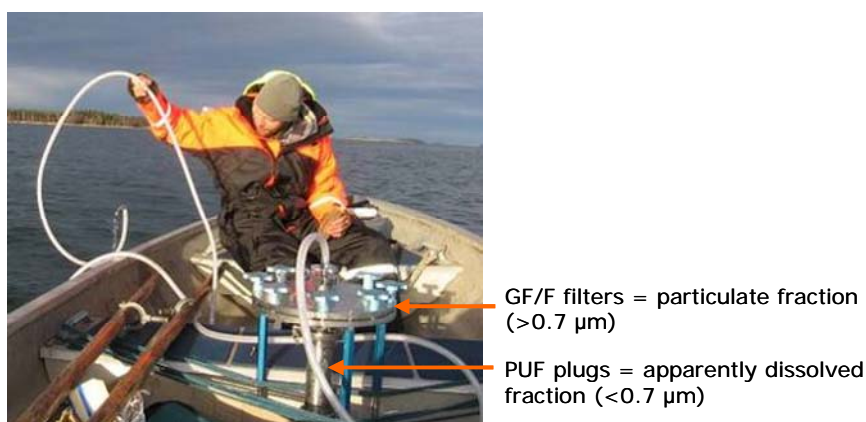
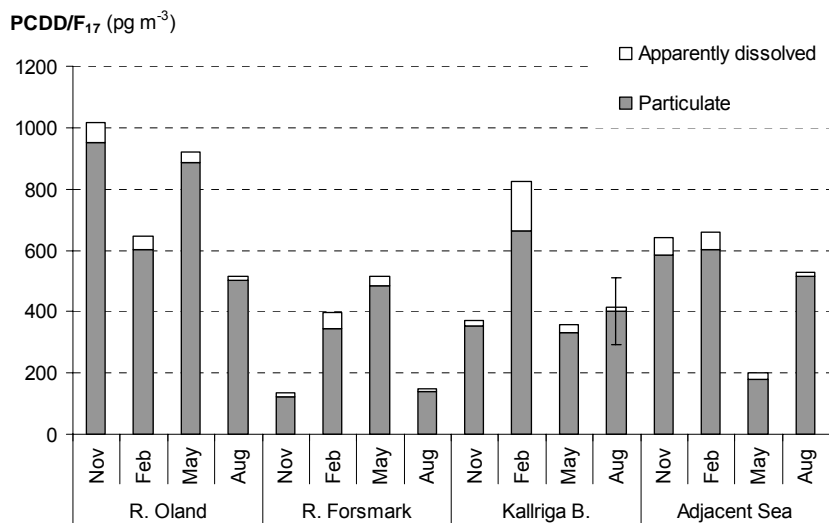


Figure 12. Active water sampling in the Kallrigafjärden area (Paper I). Photo by O.M. Karlsson.

4.3.1 Concentrations of PCDD/Fs

The concentrations of particulate and apparently dissolved fractions of the seventeen 2,3,7,8-substituted PCDD/Fs (PCDD/F₁₇) are displayed in Figure 13a, and the freely dissolved concentrations are displayed in Figure 13b. The bulk (particulate+apparently dissolved) levels were high (140-1000 pg m⁻³) compared to the freely dissolved concentrations (2.5-22 pg m⁻³). The bulk levels fluctuated more in the rivers (R. Oland and R. Forsmark) than in the estuary (Kallriga B.) and the sea, and levels were higher in R. Oland, which had higher SPM concentrations, than in R. Forsmark. The PCDD/F concentrations were generally more spatially and temporally variable than PCB₇ or HCB concentrations.

a)



b)

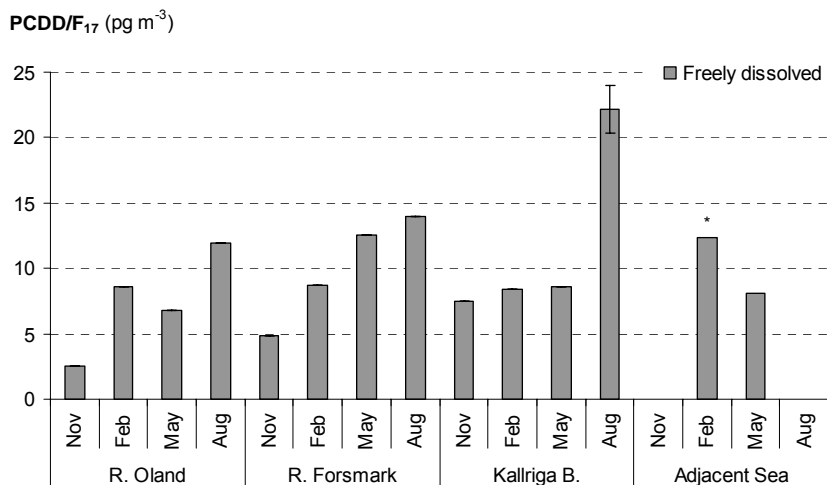


Figure 13. PCDD/F concentrations in the a) particulate and apparently dissolved phases and b) the freely dissolved phase, at the four sampling sites over the year. Error bars for triplicate sample denote ± 1 SD. The passive sampler for the Adjacent Sea in February (marked with *) could not be retrieved in November, and the deployment period was therefore 6 instead of 3 months. Figure from Paper I.

4.3.2 Distribution of POPs between phases

As apparent from the large differences between freely dissolved concentrations and bulk concentrations, the PCDD/Fs partitioned to particles to a large extent, with the particulate fraction constituting 92% of the bulk concentrations. In order to study the distribution between the particulate+colloidal and the dissolved fraction, TOC-normalized distribution ratios (K_{TOC} ; L kg⁻¹ OC) were calculated for the analyzed PCDD/Fs and PCBs:

$$K_{TOC} = \frac{C_{TOC}}{C_{Free}} = \frac{1}{f_{TOC}} \left(\frac{C_{Bulk}}{C_{Free}} - 1 \right)$$

C_{TOC} is the POP concentration in particles and filter-passing colloids, normalized to TOC (pg kg⁻¹ TOC), while C_{Free} is the freely dissolved concentration (pg L⁻¹), f_{TOC} is the concentration of organic carbon (kg L⁻¹), and C_{Bulk} is the particulate+apparently dissolved concentrations (pg L⁻¹). Plots of observed log K_{TOC} versus the log K_{OW} of the congener, as an average for the sites and seasons (Figure 3 in Paper I), showed that the slopes of the linear regression lines did not differ significantly from each other, indicating that the partitioning to particles+colloids was similar between the sites and seasons. There were no indications of enhanced sorption due to e.g. the presence of BC, unlike results from a study in the contaminated Frierfjord in Norway (56). Recently, Kuivikko et al. (84) studied the sorption of PBDEs and a polycyclic aromatic hydrocarbon (PAH) to DOC and POC along a salinity gradient, and found increases in the freely dissolved fraction with increased salinity, which was interpreted to be caused by changes in the structure of DOC and in the quality of POC. An increased salinity generally decreases the solubility of POPs in water ('salting out'), but as the structure of the dissolved organic matter also changes, leading to a decrease in the sorptive properties of the colloids, the overall result observed by Kuivikko et al. (84) was an increase of freely dissolved concentration with increased salinity. In the present experiment, there was no clear salinity trend in the sorption to particles and colloids, as apparent from the Adjacent Sea not having extreme values compared to the river samples. Salinity gradients were similar in both studies (0-4.5 in Paper I; 0-5.4 in Kuivikko et al.), but the distribution coefficients in Paper I included sorption to both particles and colloids, not specifically to colloids (DOC).

The homologue profile of the PCDD/Fs differed between different matrices sampled in the study area (Figure 14). In addition to the particulate, apparently dissolved and freely dissolved phases in the water column, sampling was also carried out for sediment, sediment pore-water (freely

dissolved phase, sampled with 55 μm POM) and perch (*Perca fluviatilis*). The homologue profile for sediment and particles in the water column were very similar, while the profiles for sediment pore-water, perch, the apparently dissolved and the freely dissolved phases in the water column revealed a higher proportion of the less hydrophobic homologue groups (primarily *tetra*- and *penta*-CDFs). The profile for the freely dissolved phase in sediment pore-water was similar as for the freely dissolved phase in the water column, while the apparently dissolved phase displayed a homologue profile in between the particulate and the freely dissolved phase, illustrating that colloids are included in the apparently dissolved phase. The profile for perch resembled the freely dissolved phase, but in addition, the contribution from *tetra*- and *penta*-CDDs was higher than for the other sampled matrices.

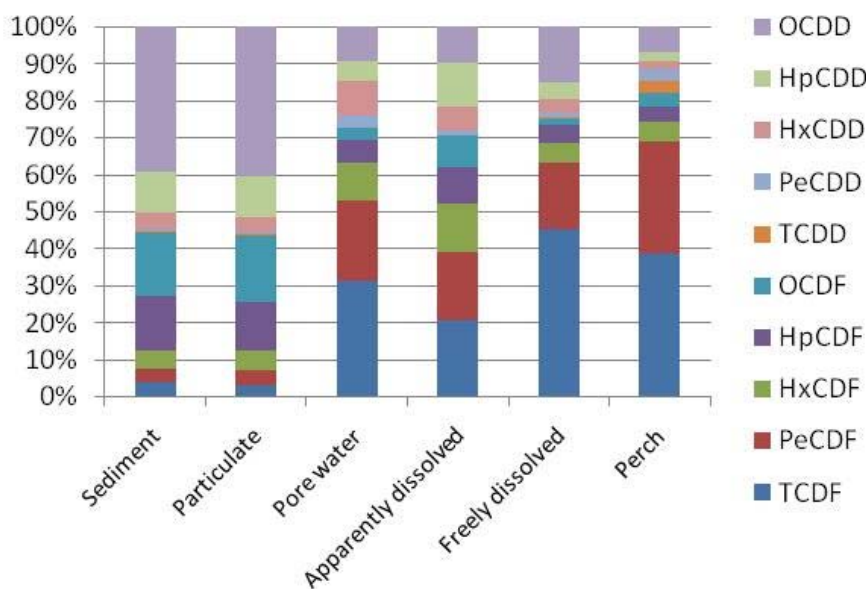


Figure 14. PCDD/F homologue profiles for different matrices sampled in the Kallrigafjärden area.

4.3.3 Relationship between POP concentrations and SPM/TOC

The relationship between POP concentrations and SPM or TOC was investigated to explore if these parameters could function as a proxy for the POP concentrations in this background area that was mainly affected by diffuse pollution. The PCB₇ concentrations displayed a positive correlation to TOC concentrations, but only for estuary and sea samples, while the PCDD/Fs

displayed a positive correlation to SPM concentrations (Figures 4 and 5 in Paper I). A principal component analysis (PCA) for the river samples showed a strong grouping of PCDD/Fs with SPM, while non-*ortho* PCBs and highly hydrophobic (*octa-deca*) NDL-PCBs formed a middle group, and remaining PCB congeners a group less related to SPM (Figure 6 in Paper I). Thus, there were differences between POPs with different structures, and if using a proxy for PCDD/F levels in rivers, SPM may be more appropriate than TOC.

4.3.4 Influence of spring bloom

The PCDD/F bulk levels were generally stable in the sea ($\sim 600 \text{ pg m}^{-3}$ in November, February and August), but dropped to one third ($\sim 200 \text{ pg m}^{-3}$) in May (Figure 13a). For PCBs, the bulk concentrations in the sea were also lowest in May, although the decrease was less pronounced than for the PCDD/Fs. The decrease seen in the POP concentrations is likely to be connected to the spring bloom, when the sedimentation rate is high. Several studies have found an increased vertical flux of PCBs with increased primary productivity (95-97). The decrease might also be driven by increased run-off of terrestrial particles during the spring flood. This illustrates the importance of particle sedimentation as a removal process for POPs from the water column, and the importance of sediments as a sink for POPs.

5. Sediment as a source of contaminants

Sediment can be a sink for POPs, but contaminated sediment is also a potentially important source of contaminants to the overlying water (5,98,99). Processes such as diffusion, advective pore-water transport and resuspension can re-introduce the POPs to the water column, and bioturbation can have a large influence on the sediment-water dynamics of POPs. The sediment-associated POPs can also be accumulated in benthic organisms and transferred along the benthic-pelagic trophic web.

If sedimentation of particles exceeds resuspension, as is the case in accumulation bottom areas, the contaminated layers of sediment are covered with layers of cleaner particles. The exchange with the water column decreases, and the POPs become buried. Due to the substantial decrease in primary emissions of many well-known POPs during the last decades, the levels may be elevated in deeper sediment layers as compared to the surface layer (7,100-103). The remobilization of buried contaminants from the sediment to the water column, and the uptake in biota, is therefore an increasingly important issue. Contaminants buried below the sediment depth bioturbated by organisms can be considered as unavailable. The average mixed depth of marine sediments world-wide has been estimated to ~10 cm (104), but the mixed depth is strongly dependent on the type of bioturbating fauna present. If new species with deeper bioturbation depth enter an area, contaminants previously considered buried may become available for sediment-to-water transport. In the Baltic Sea, the recent invasion of the deep-burrowing *Marenzelleria* spp. can lead to remobilization of contaminants previously considered to be buried at a safe depth. The impact of bioturbation by *Marenzelleria* spp. and the native species *Monoporeia affinis* on buried contaminants is investigated in Papers II and III.

5.1 Sediment-water abiotic transfer

5.1.1 Diffusion

Contaminants in the dissolved phase in the sediment pore-water can diffuse out from the sediment. The driving force for the diffusion is the concentration gradient between the pore-water and the overlying water. The dissolved contaminants in the sediment have to diffuse through both the sediment pore-water and the diffusive boundary layer, a thin layer of quiescent water at the sediment-water interface where the turbulent mixing is dampened. Diffusion is a slow process, and an increased diffusive path

length over which the concentration gradient is present (e.g. for buried contaminants) will decrease the diffusive flux. In addition to molecular diffusion, contaminants can also be remobilized from the sediment by colloidal diffusion, facilitated by bioturbation or other advective processes (80).

5.1.2 Advection of pore-water

Transport through advection is when the contaminants are transported due to their entrainment in a moving media. Examples of advective processes affecting the transport of POPs from sediment is the consolidation of sediment leading to an advective movement of pore-water from the sediment, ground-water discharge, and the effects of waves and tides in shallow areas. Advection can be the dominant transport mechanism close to land in coarse (sandy) sediments, where the permeability and hydraulic conductivity are high, but in more fine and compact sediment, such as the silt and clay found on accumulation bottoms, the advective rate decreases and other transport processes, such as diffusion, can dominate (105).

5.1.3 Resuspension

Particles with associated contaminants can be resuspended from the surface sediment by waves or currents, and anthropogenic activities such as bottom trawling can increase resuspension (106,107). As particles are resuspended to the water column, the labile fraction of contaminants can desorb to the water phase (108). Since the concentration of dissolved compounds is lower in the water column than in the sediment pore-water, desorption of POPs from the particle becomes more thermodynamically favourable in the water column. Schneider et al. (108) simulated resuspension events with PCB contaminated sediment, and found that 22% of resuspended PCBs were in the dissolved phase after 2 h, and 35% after 2 days. Repeated resuspension also revealed that the rapidly desorbing fraction was replenished, and with 4 days of resting time, only the most highly chlorinated congener (*penta*-CB) did not reach its original desorbed fraction.

5.2 Sediment-water biotic transfer

Another potential transport route of POPs from sediment to pelagic biota is the biotic transfer. The benthic organisms live in close contact with the contaminated sediment, and are an important link in the transfer of

contaminants from sediment through the benthic-pelagic food chain to fish and fish consumers such as seals, piscivorous birds, and humans. The POPs in the sediment are primarily taken up by the infauna by absorption from pore-water via dermal surfaces (skin or gills; 109,110) or by dietary absorption through the gut epithelium following ingestion of contaminated particles (111,112). As several studies have indicated, the relative importance of various uptake routes is affected by the physicochemical properties of the chemical (e.g. 113-115), with uptake from pore-water being potentially important for less hydrophobic compounds, and uptake from ingestion being more dominant for more hydrophobic compounds which sorb strongly to particles. Furthermore, differences in feeding strategies of the infauna (e.g. deposit-feeding or suspension-feeding) are also important for the bioaccumulation of POPs (116-119).

5.3 Bioturbation

Bioturbation, the mixing of particles and pore-water in the upper sediment layers by benthic organisms, has profound effects on the biogeochemistry of the sediment and the sediment-to-water fluxes of nutrients and contaminants (120-125). The importance of bioturbation was recognized already by Darwin in his studies on earthworms, as he stated: *"Worms have played a more important part in the history of the world than most persons would at first suppose"* (126). The bioturbating activity of the benthic organisms is a result of their feeding, burrowing and tube-construction, burrow ventilation (flushing of burrows with oxygenated water), and production of mucus and fecal pellets (120,121). By its bioturbating activity, the infauna increases the sediment-water interface area, and creates a mosaic of oxic/anoxic environments (121).

Bioturbation can both increase the sediment-to-water flux of POPs (125,127-129) and decrease it, by burying contaminants present at the surface (130,131). The interaction between the bioturbation and contaminant fate depends on several factors, such as the physicochemical properties of the POPs; the distribution of contaminants in sediment (e.g. present at the surface or buried); how strongly associated the contaminants are with the sediment; the number, size and bioturbation mode of the organisms; the possible effects of the contaminants on the organisms (e.g. survival and behavioural alterations); and the biogeochemistry of the sediment (123). Some researchers only include particle-reworking behaviour in the term bioturbation, while burrow flushing, which has an impact on pore-water movement, is classified as bioirrigation (132). Particle-mixing and bioirrigation have different impacts on the sediment contaminants (123). The

bioirrigation increases the oxygenation in the sediment, and increases the movement of freely dissolved or colloid-associated contaminants from the sediment (123). It is thus likely to influence less hydrophobic compounds more. Particle-mixing, on the other hand, has a larger impact on compounds with high log K_{ow} . In addition to direct impacts on contaminant fate and transport, the bioturbation can also have indirect effects on microorganisms, and thus influence the microbial degradation of organic matter and of contaminants (123).

5.3.1 Bioturbation modes

Since benthic organisms have different modes of mixing the sediment, they can be classified into functional groups based on their bioturbation mode. Five functional bioturbation groups have been outlined in literature (133): Biodiffusors are species that move particles randomly (omni-directionally) over short distances. The (upward) conveyors are vertically orientated species that feed at deeper sediment layers and egest at the sediment-water interface, and in contrast to the diffusive-like transport by the biodiffusors, this transport is non-local and unidirectional. The inverse (or downward) conveyors display the opposite transport behaviour, feeding at the sediment surface and egesting deeper in sediment. The regenerator group consists of species that moves sediment from deeper in sediment to the surface through their digging activity, and as burrows are deserted sediment moves into the burrow. Finally, bioirrigators/gallery-diffusors have their main bioturbating activity as they dig and irrigate their burrows. The impact of bioturbation on the transport of sediment contaminants depends on the functional groups present and dominating in the sediment.

5.3.2 Benthic species investigated in this thesis

In paper II and III, the investigated species were *Marenzelleria* spp. and *Monoporeia affinis*. *Marenzelleria* spp. is a recent invader in the Baltic Sea, observed for the first time in 1985 (134). It most likely entered the Baltic Sea via ballast water on ships and rapidly spread throughout the Baltic Sea (12), where it has become a dominating species in the benthic macrofaunal community in many areas (11,135). *Marenzelleria* spp. is found in soft bottoms at densities from <100 up to >30 000 individuals per m², with higher abundances in coastal than off-shore waters (136). Three morphologically similar *Marenzelleria* species are present in the Baltic Sea: *M. viridis*, *M. neglecta* and *M. arctica*, and the different species may differ in their behaviour

(137). *M. arctia*, which originates from the Arctic, is only found in the northern Baltic Sea, while *M. viridis* and *M. neglecta* are mainly found in the southern, eastern and western part of the Baltic Sea (137). *M. arctia* appear to prefer deeper habitats, while *M. neglecta* was found in nearby, more shallow areas (137). However, the species may co-occur (137), and the population in Paper II and III consisted of both *M. viridis* and *M. neglecta*. *Marenzelleria* spp. construct mucus-lines tubes down to 35-50 cm (13,14,135) and can be classified as a bioirrigator/gallery-diffusor. The amphipod *M. affinis*, a glacial relict in the Baltic Sea, dwells in the surface layer of sediment (138) and can be classified as a biodiffusor. *M. affinis* is a dominating soft bottom species in the benthic macrofaunal community in the northern Baltic Sea (139), but the population underwent a substantial decline around the year 2000. This decline is suggested to be caused by large run-off from land with terrestrial carbon and decreased phytoplankton bloom, leading to food shortage for the amphipods (140).

In Paper IV, the bioaccumulation in the gastropod *Hinia reticulata* and the polychaetes *Hediste (Nereis) diversicolor* and *Nereis virens* (collectively treated as *Nereis* spp.) was investigated. These species are omnivores. Both taxa burrow in the sediment, but since *H. reticulata* ventilates with its siphon to the overlying water, it inhabits the sediment surface (~3 cm), while *Nereis* spp. constructs deeper (down to >20 cm), often U-shaped tubes (141). *H. reticulata* can be classified as a biodiffusor, since it has a bulldozer-like activity in the surface sediment, while *Nereis* spp. construct galleries that they bioirrigate, thus increasing the sediment-water interface area (142).

5.4 Comparison of sediment-water abiotic transport processes

Valsaraj et al. (143) estimated the time required for a POP (*tri*-CB) to leach from a sediment layer 10 cm in depth by different transport processes (Table 2). The precise values are, of course, dependent on the environmental conditions, for instance the extent of advection and erosion, but what is apparent is the major impact that bioturbation can have on the sediment-water transport. A study comparing the remobilization of a *tri*-CB between systems with physical resuspension (paddle) and with bioturbation by *M. affinis* and *Marenzelleria* sp. reached the conclusion that bioturbation can be equally important as physical resuspension for POP remobilization from sediment (144).

Table 2. The rate of different sediment-water transport processes for remobilization of a *tri*-CB from a model sediment. Based on Valsaraj et al. (143).

Transport processes	Characteristic time
Molecular diffusion (retarded by sorption)	1 900 yrs
Colloid-facilitated transport	1 500 yrs
Sediment erosion	10 yrs
Sediment movement (bed load transport)	2 days
Aquifer interactions	4 000 yrs
Local advection	69 000 yrs
Bioturbation	10 yrs

5.5 Sediment-to-water flux and benthic bioaccumulation of buried contaminants (Paper II and III)

The hypothesis for Paper II and III was that the sediment-to-water flux and bioaccumulation of buried POPs would depend on the vertical distribution of the POPs and of the bioturbating species. Selected PCB and PBDE congeners were placed at three depths in sediment (2.0-2.5 cm, 5.0-5.5 cm, and 10.0-10.5 cm; Figure 15). The sedimentation rate can vary widely between different areas, but with a median sedimentation rate for the different Baltic Sea sub-basins of 0.8 to 3.7 mm per year (145), the layer at 10 cm would have been deposited 27 to 125 years ago. The remobilization of the buried POPs and the bioaccumulation were studied in treatments with either the native species *Monoporeia affinis* (*Mo*) or the invading polychaete *Marenzelleria* spp. (*Mz*; Figures 16 and 17) during an 8-week experiment. Both species feed at the sediment surface (146,147), but as mentioned, they differ considerably in their vertical distribution (14,138).

5.5.1 Sediment-to-water flux of buried contaminants

The flux (particulate and apparently dissolved) of buried contaminants was significantly higher in treatments with *Mz*, compared to treatments with *Mo* or treatments without macrofauna (controls). This demonstrates that the invasion of *Mz* in the Baltic Sea can lead to increased remobilization of buried contaminants. The remobilization was inversely related to the burial depth of the POP congeners, with higher fluxes from shallow layers (2.0-2.5 cm > 5.0-5.5 cm > 10.0-10.5 cm; Figure 18), but remobilization occurred from layers down to at least 10 cm. The flux in *Mo* treatments was similar to the flux in controls, and it is probable that the burrowing depth of *Mo* at the

density in this experiment (220 ind. m^{-2}) did not reach even the contaminants buried at 2 cm depth.

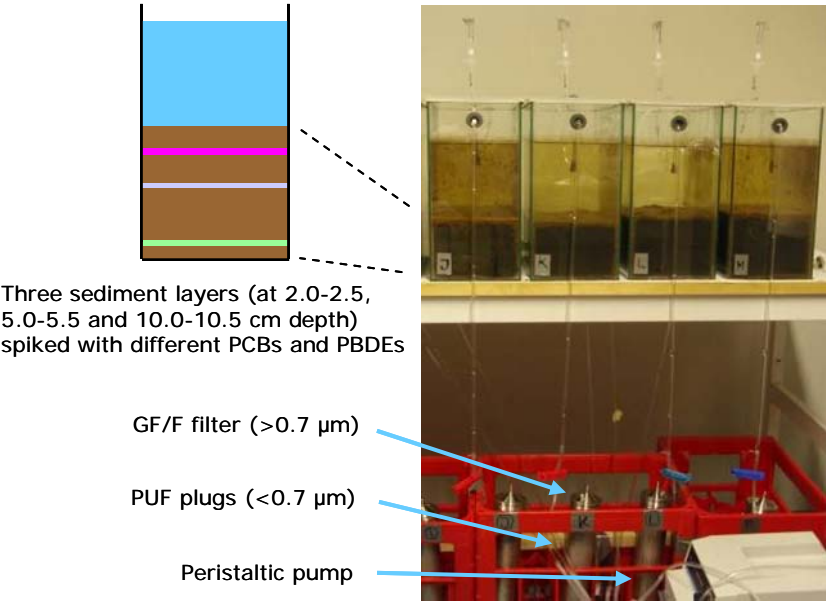


Figure 15. The experimental setup for the studies in Papers I and II.



Figure 16. *Marenzelleria* sp.

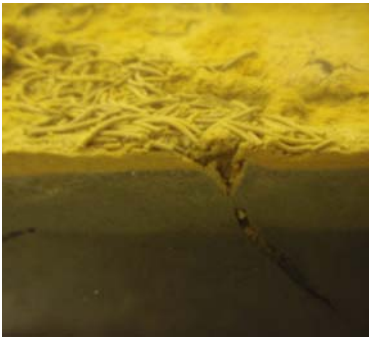


Figure 17. Fecal pellets around *Marenzelleria* burrow

The fluxes were inversely correlated to the hydrophobicity ($\log K_{ow}$) of the congeners, for all burial depths (Figure 18). As apparent from Figure 18, the flux of a compound with a $\log K_{ow}$ value of 6 was around twice as high as for a compound with a $\log K_{ow}$ value of 7.5. Since the less hydrophobic congeners partition to pore-water to a higher extent, the increased flux for the less hydrophobic congeners indicates that pore-water movement, as a result of bioirrigation by *Mz*, is an important sediment-to-water transport route for the buried POPs. The importance of bioirrigation is in accordance to what was observed by Hedman et al. (148) when studying the effect of bioturbation by *Mz* on contaminants present at the sediment surface. An increased amount of *Mz* burrows was also found to increase the hydraulic conductivity of the sediment in both laboratory and field experiments (14). On the other hand, there have been reports of *Mz* bioturbation affecting both particle and pore-water transport (149). In Paper II, calculated mass transfer coefficients (MTCs; see Paper II) for the sediment-to-water flux of (apparently) dissolved contaminants showed an increase by up to 14 times in *Mz* treatments compared to systems without bioturbation, with a corresponding enhancement by up to 21 times for the particulate phase. There was substantially less movement of particles than of pore-water, according to the lower MTCs ($\times 10^{-6}$) for the particulate phase than the (apparently) dissolved phase, but as a result of the hydrophobicity of the POPs and their partitioning to particles, the contribution from the particulate phase transport could still be of similar magnitude as the dissolved phase transport.

A comparison of the distribution of POPs between the particulate (filter) and apparently dissolved (PUF) phases in the water column showed that the distribution to the particulate phase increased with increased burial depth of the congeners (Figure 3 in Paper II). The variation in particle-dissolved distribution as a result of burial depth suggests that the pore-water movement is enhanced in surface layers compared to deeper layers.

5.5.1 Sediment contamination profile

Sediment cores showed low mixing of contaminated particles in both *Mz* and *Mo* treatments (Paper III). For instance, the POP concentrations in the surface sediment layer (0-1 cm) were generally <1% of the concentrations at the layer where they had been placed originally. On the other hand, the concentrations of originally buried POPs at the surface layer of *Mz* treatments were significantly higher than in *Mo* treatments, and it was also

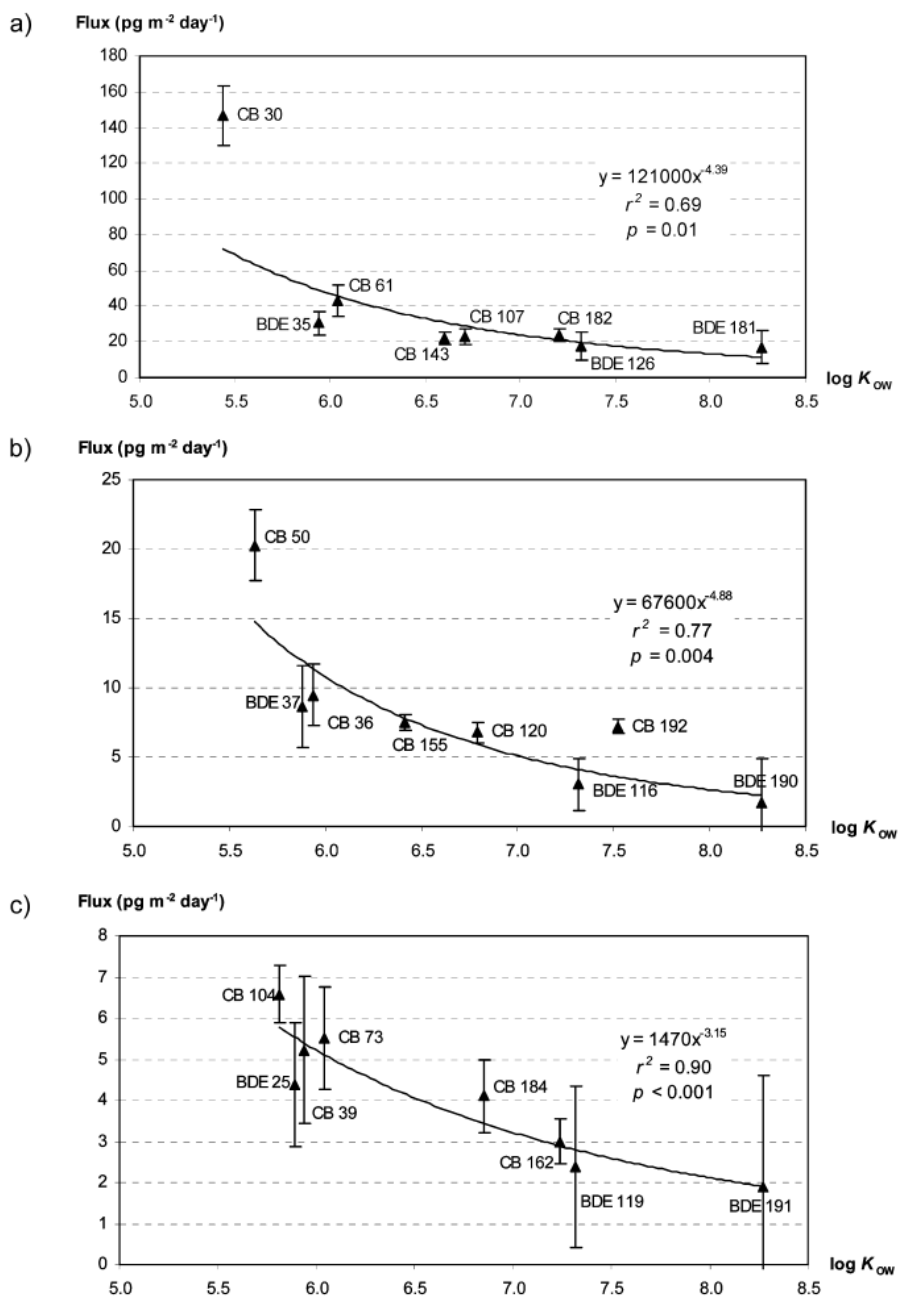


Figure 18. Fluxes ($\text{pg m}^{-2} \text{day}^{-1}$) of buried congeners in *Marenzelleria* spp. treatments as a function of $\log K_{ow}$, from the a) 2 cm, b) 5 cm and c) 10 cm depth. Figure from Paper II.

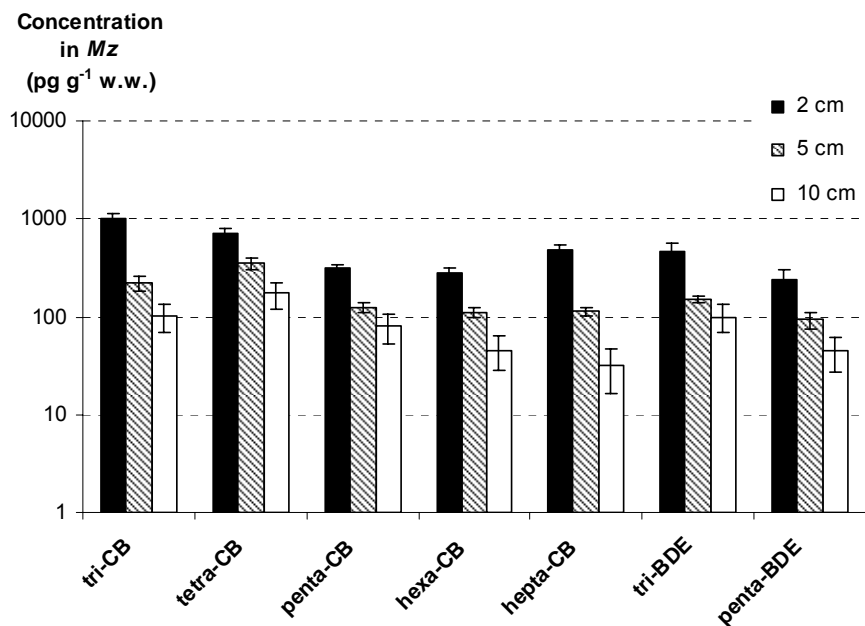
higher than in the layer below (1-2 cm). These observations suggest a transport of buried contaminants to the sediment surface in *Mz* treatments, as a result of fecal pellet deposition (Figure 17) or contaminant deposition by sedimentation from the water column. The increased levels in the surface sediment as a result of *Mz* bioturbation will lead to increased exposure to previously buried POPs also for species with shallower bioturbation depths.

5.5.2 Bioaccumulation of buried contaminants

Similar to the sediment-to-water flux, the bioaccumulation of buried contaminants was higher by *Mz* than by *Mo* (Figure 19). This supports the observation that the burrowing depth of *Mo* has not reached the buried contaminant layers (>2 cm depth). The biota concentrations were negatively correlated to the congener burial depth for both species (Figures 19a and b). Additional analyses of the concentrations of native PCB congeners, which unlike the buried congeners had not been added to the sediment and had an even vertical distribution in the sediment, revealed similar concentrations in both species (6.5-780 pg g⁻¹ ww in *Mz*; 6.6-1 400 pg g⁻¹ ww in *Mo*), in contrast to the buried congeners. These results clearly demonstrate that the vertical distribution (burrowing depth) of the species affected their accumulation of buried contaminants, even though both species feed at the same depth in sediment (surface feeders).

The buried contaminant concentrations were 2-36 times higher in *Mz* than in *Mo* on a ww basis (average 12 times; Figure 20). In contrast, the tissue concentrations of evenly distributed native contaminants were similar in both species, with an average *Mz/Mo* concentration ratio of 1.4 ± 0.92 . The higher accumulation of buried contaminants by *Mz* was especially pronounced for the less hydrophobic congeners ($\log K_{ow} \leq 6$), which mirrors the hydrophobicity trend for the increased sediment-to-water fluxes, and reflects the bioirrigating behaviour of *Mz*. The invasion of *Mz* in the Baltic Sea can thus give increased transfer of buried POPs, especially less hydrophobic congeners, in the aquatic food webs, but this is also dependent on the extent of predation on *Mz*, which is likely to be relatively well-protected due to its deep-burrowing behaviour.

a)



b)

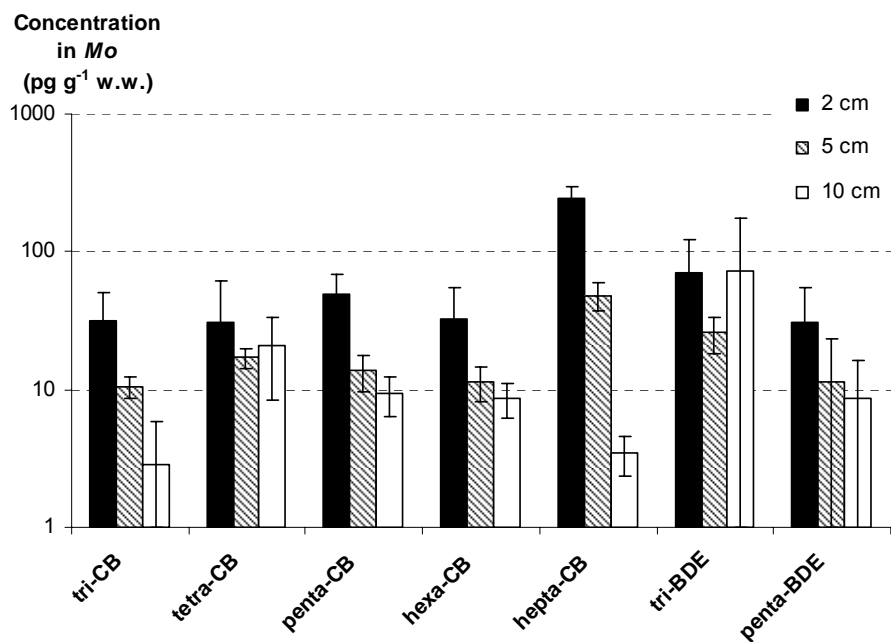


Figure 19. Concentration of PCB and PBDE congener spiked at different sediment depths (2.0-2.5, 5.0-5.5 and 10.0-10.5 cm) in tissue of a) *Marenzelleria* spp. (*Mz*) and b) *M. affinis* (*Mo*), with confidence intervals (95%). Figure from Paper III.

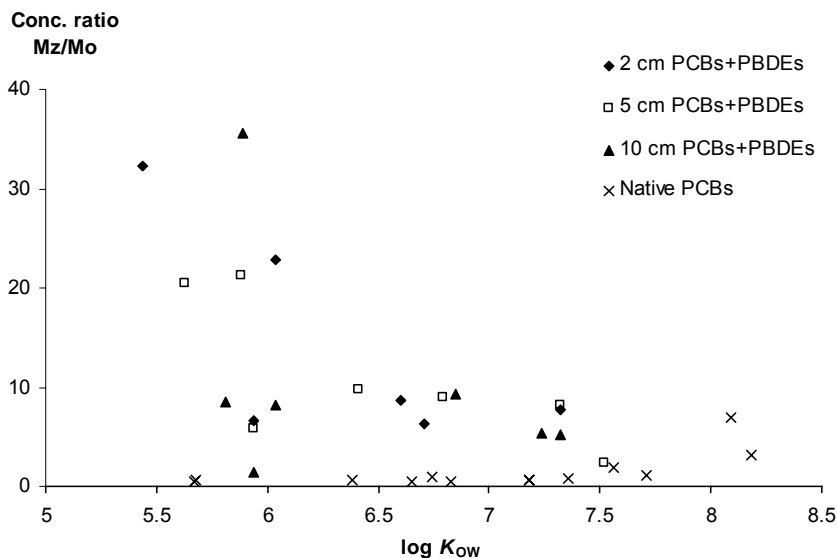


Figure 20. The ratio between concentrations in *Mz* and *Mo* (ww basis) compared to the log K_{ow} of the congeners. Figure from Paper III.

For *Marenzelleria* spp., biota-sediment accumulation factors (BSAFs) for the buried congeners were negatively correlated to hydrophobicity, while for the native congeners, the correlation was positive. The differing hydrophobicity trends for buried and native contaminants in *Mz* indicate that the uptake routes may differ as a result of the differing locations in sediment, assuming that steady-state exposure has been reached for both groups during the 8-week experiment. For the native contaminants, which are present in the sediment surface layer, ingestion may be an important route, while for buried contaminants uptake via burrow water can be more dominating. A better congener agreement was found between the water column concentrations and *Mz* tissue concentrations than between surface sediment concentrations and *Mz* tissue concentrations, which also points at uptake from pore-water being an important route.

6. Active capping to decrease contaminant transport from sediments

If sediments contain such high levels of contaminants that they pose a risk to the surrounding environment, the sediments need to be remediated. There is little information on the extent of sediment contamination and remediation needs worldwide, but estimates by the US Environmental Protection Agency state that approximately 10% of the sediment in surface waters of the USA is so contaminated that it poses a risk for fish, other wildlife, and humans (150). The remediation of sediment aims to eliminate, or at least limit, the transport of contaminants to overlying water and to benthic fauna. The remediation methods can be divided into methods performed in place (*in situ*), for instance capping, and methods performed after dredging of contaminated sediment (*ex situ*) (105). The choice of method depends on the extent of risk the contamination poses, and on other site-specific characteristics, for instance whether the sediment constitutes an erosion, transport, or accumulation bottom.

6.1 Sediment remediation methods

6.1.1 Monitored natural recovery

Monitored natural recovery, or natural attenuation, can be applied when the natural processes occurring in the area are enough to reduce the risk to acceptable levels (151). Even though the contamination of the sediment poses a risk, this risk is considered acceptable, and the ongoing processes such as contaminant degradation or sedimentation of clean matter on top of the sediment are enough. Thus, no active remediation measures are taken.

6.1.2 Dredging

One option for remediation of sediment is dredging, which physically removes the contaminated sediment from the site. This may be the only viable option if the remediation is done at e.g. navigational channels, where the water depths has to be maintained, or in sediments constituting erosion or transport bottoms, where a substantial movement of sediment is occurring (152). The large benefit of dredging is that the contamination is removed from the site. However, dredging is not a remediation method in itself, as the dredged sediment has to be dealt with afterwards. The sediment can for instance be disposed off by landfilling or treated by incineration, bio-

remediation, or stabilisation/solidification (105). One drawback with dredging is the risk of spreading POPs from the sediment *ex situ*, by leaching or by volatilization from the contaminated sediment when deposited on land (153,154). Other serious drawbacks are the risk of spreading the contamination in the aquatic environment during the dredging, and the incomplete removal of contamination from the site, as a contaminant residual will be left after the dredging (155). Concentrations in the surface sediment do not always decrease, or do not decrease enough to reduce the risks to biota sufficiently, after a dredging operation (152,155,156).

6.1.3 *In situ* capping

In *in situ* capping, the natural recovery is enhanced by placing a layer of clean material at the sediment-water interface to isolate the contaminated sediment from the water column and sediment infauna. The cap usually consists of 30 cm or more of sand or other mineral materials (105). The purposes of the cap are to protect the contaminated sediment from erosion (resuspension of particles), to isolate the contaminated sediment from benthic organisms, and to reduce the transport processes in the sediment (157). This is achieved by increasing the path length that the sediment contaminants have to traverse to reach the water column, both for dissolved contaminants and for contaminants transported with particles/colloids.

The sediment-cap-water system can be modelled as consisting of five parts (157): the underlying sediment, the chemical isolation layer, the bioturbation layer, the sediment-water interface (i.e. the benthic boundary layer), and the overlying water. The cap is thus divided into the chemical isolation layer and the bioturbated layer. In order for the chemical isolation layer to have sufficient thickness, the extent of bioturbation is therefore generally the dimension-determining factor for the cap (105). After the cap has been placed on the sediment, sediment contaminants will start to move upwards through the cap, eventually leading to a breakthrough, and a new, lower steady-state flux from the sediment will be established, as the resistance to mass transfer processes has increased as a result of the increased path length provided by the cap layer (157,158).

In systems where the diffusive transport is dominating, good capping efficiency of POPs can be achieved even with thin non-sorbing mineral cap material. Eek et al. (158) observed that with a 1 cm cap of crushed limestone or gneiss the sediment-to-water flux of PCBs and PAHs was reduced to 3.5-7.3% of the flux in uncapped sediment systems. In systems with higher ad-

vective flows, however, the contaminants migrate faster through the cap (159,160). For instance, Go et al. (160) predicted the breakthrough time before steady-state flux was reached for a 30 cm sand cap in a diffusion-controlled system to 1000 years, while it was reduced to 100 years in an advection-controlled system. In order to achieve an efficient cap in systems not controlled by diffusive flow, increased cap thickness or the addition of an active, sorbing material can be required (159,160).

6.1.3.1 Active capping

The active capping technology has recently become an area of intense research and development. Active capping is performed with a material that interacts with the sediment contaminants to reduce their bioavailability (159,161). A thinner cap can therefore be placed while retaining the efficiency of the cap, and this approach is also termed thin-layer capping. The thin-layer approach can be less destructive for the benthic ecosystem than the conventional capping. Unlike conventional capping, the aim is not to accomplish an isolation of the contaminants, but to decrease their bioavailability by the interactions with the active material. The interaction between the contaminants and the active material can be both a sequestering of the contaminants, or a reaction with the contaminants (sometimes referred to as “reactive capping”).

A material commonly suggested for the remediation of POPs in sediment is activated carbon (AC), based on research demonstrating high sorption of POPs such as PCBs and PAHs to black carbon and other carbonaceous geo-residues (89,90). Due to the strong sorption to AC, pore-water concentrations are lowered, which decreases the flux of dissolved contaminants from sediment to water. Mixing of sediment with AC (2-4%) has in several laboratory studies reduced POP sediment pore-water concentrations, sediment-to-water flux, and bioaccumulation by various infauna (119,161-166). The reduced bioaccumulation after AC amendment can not be explained solely by decreased uptake due to reduced pore-water concentrations. It is also probable that tissue concentrations are lowered due to reductions in the uptake after ingestion, i.e. a lower availability of contaminants in the gut system (119,165). McLeod et al. (167) investigated the absorption efficiency of PAH and PCB in the clam *Macoma baltica*, and found that the gut absorption efficiency for AC-associated CB 52 was <2%, which is lower than the 40-90% absorption efficiency observed when the PCB congener was associated with peat, coke, anthracite, char, wood or diatoms.

6.1.3.2 Materials for active capping

AC is a promising material for active capping of POPs, due to its high sorption capacity, with a high specific surface area (e.g. 761 m²/g), high total pore volume (e.g. 0.58 cm³/g) and low average pore diameter (e.g. 3.0 nm) (90). Other proposed materials for active capping of organic contaminants are *inter alia* coke (159,161,164,168) and bentonite clay (169), although AC generally exhibits superior sorption properties (159,161,164). There have also been suggestions of “reactive” caps for POPs, where AC impregnated with iron/palladium (Fe/Pd) nanoparticles would accomplish both a sorption and dechlorination of PCBs (170). In Paper IV, AC and lignin were investigated as active materials. Lignin is together with cellulose and hemicellulose one of the most common building blocks in wood, and it is a by-product in the manufacturing of pulp and paper. The lignin used in Paper IV was kraft lignin extracted from black liquor by the LignoBoost refining process.

6.1.3.3 Placement of an active cap

One crucial step in the capping of contaminated sediment is the placement of the sorbent material to the sediment. The materials used in ordinary, ‘passive’, capping, such as sand and gravel, have densities that make them relatively easy to place as a cap layer because of rapid settling to the sea floor. The low density of active materials such as AC, on the other hand, makes the placement in uniform, thin layers difficult, particularly in moving water (171). Generally, three different approaches are distinguished (172):

- 1) The cap is placed as a geotextile on the sediment surface, and sand is placed on top to secure the geotextile and provide a clean habitat for benthic biota (171).
- 2) The sorbent is mixed with the surface sediment, e.g. AC into the tidal flat at Hunter’s Point Shipyard in San Francisco, USA (173,174).²
- 3) The sorbent is mixed with a passive carrier, and placed as a thin slurry on top of the sediment surface

The two first approaches are more destructive for the habitat of the benthic fauna, as in approach 1 a completely new habitat consisting of clean sand is created instead of the original sediment, and in approach 2 the sediment,

² This approach is termed ‘capping’ throughout the thesis, although it strictly is not a cap.

with its fauna, is mixed. In the capping experiment included in this thesis (Paper IV), the third approach was applied.

6.2 The effect of thin layer capping on sediment-to-water flux and benthic bioaccumulation of PCDD/Fs, OCS and HCB (Paper IV)

In paper IV, the efficiency of active capping was explored both in terms of reducing the flux of dissolved POPs from sediment to the overlying water, and in reducing the bioaccumulation by two benthic taxa, the gastropod *Hinia reticulata* and the polychaetes *Nereis* spp. The POPs investigated were the 2,3,7,8-PCDD/Fs, HCB and OCS. Four factors were presumed to potentially influence the sediment-to-water flux and the bioaccumulation: the cap thickness, the choice of active material, the choice of passive (carrier) material, and bioturbation. The three first factors were varied in an experimental design: the cap thickness was 0.5-5 cm; the active material was AC, kraft lignin (LG), or no active material; and the passive material was marine clay sediment (CL), coarse limestone material (CO), or fine limestone material (FI; boxes with different cap treatments displayed in Figure 21). Bioturbation can increase the sediment-to-water flux of POPs under capping-like conditions (Paper II), and bioturbating animals were added to the experimental boxes to resemble real-world conditions. However, this factor was not varied (equal numbers and approximately equal biomass of all species added to each box).

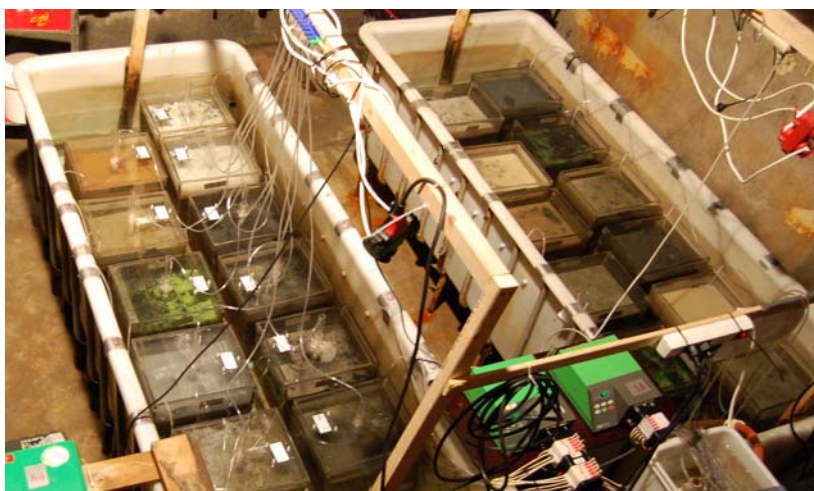


Figure 21. Boxes with different cap treatments during the experiment in Paper IV. Photo by M. Schaanning.

6.2.1 Sediment-to-water flux

A decrease in the sediment-to-water flux with increased cap thickness was observed. This decrease was larger for AC-amended sediment than LG-amended sediment or sediment without active capping material (Figure 22). The use of different types of passive material did not result in statistically significant differences. At a cap thickness of 3 cm, AC-amended sediment reduced the sediment-to-water flux of HCB, OCS and PCDD/Fs (on a TEQ basis) to 5, 10, and 20%, respectively, of corresponding fluxes for uncapped sediment. For the LG-amended cap, the fluxes were reduced to 19, 21, and 38%, respectively, while the decrease for caps without active material was less marked, and fluxes were reduced to 47, 41, and 60%, respectively (Figure 22, Figure 23). The decrease in flux was not as pronounced as the decrease observed by Zimmerman et al. (161), where a cap layer of AC of only 2 mm thickness placed on top of a marine sediment reduced the flux of PCBs to 11%. Similarly, Eek et al. (158) found that 1 cm of a mineral cap (crushed limestone or gneiss) without active materials reduced PCB fluxes to 7% of the fluxes in controls without cap. The differences observed between these studies and the study in Paper IV were likely to be due to the presence of bioturbating macrofauna in the systems of Paper IV, which increased the transport processes. In addition, the capping efficiency can depend on the hydrophobicity of the analyte (see section 6.2.4).

6.2.2 Bioaccumulation by two benthic species

The effects of cap thickness and addition of active material on the bioaccumulation by the amphipod *Hinia reticulata* were similar to the effects observed for the sediment-to-water flux, with addition of AC reducing the bioaccumulation more than amendments without active material or with LG. A 3 cm cap with AC decreased the *H. reticulata* tissue concentrations of HCB, OCS and PCDD/Fs to 1.1, 0.9 and 4.7%, respectively, compared to uncapped systems (Figure 23). The decrease in tissue concentrations with increased cap thickness was more pronounced for *H. reticulata*, the species dwelling closer to the sediment surface, than for the polychaetes *Nereis* spp. that constructed burrows deeper in sediment. For *Nereis* spp., the tissue concentrations decreased to 8, 11 and 26% of concentrations without cap for HCB, OCS, and PCDD/Fs, respectively (Figure 23).

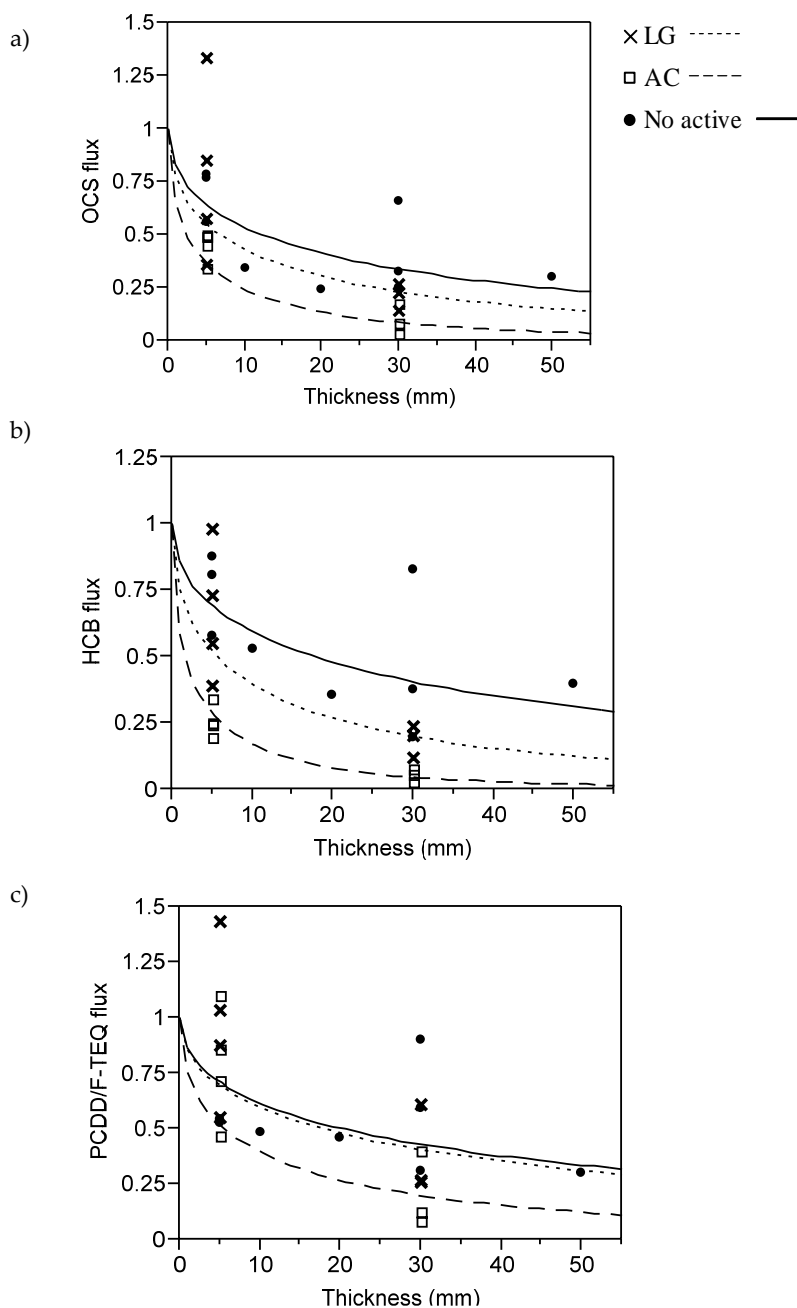


Figure 22. Decrease in sediment-to-water flux (sampled using SPMDs) with increased cap thickness; regression lines grouped by the type of active material for a) OCS, b) HCB, and c) PCDD/Fs (on TEQ basis). Fluxes were normalized to the average flux from uncapped sediment, which was defined as 1. Figure from Paper IV.

A comparison between the reduction in sediment-to-water fluxes and in the bioaccumulation by *H. reticulata* and *Nereis* spp. shows that the efficiency of the caps is clearly better for *H. reticulata* than for *Nereis* spp. (Figure 23). The magnitude of reductions is often similar for the sediment-to-water fluxes and *Nereis* spp. concentrations. Furthermore, the contamination in the surface layer of the cap in the 3 cm cap treatments was low compared to the contaminated sediment, suggesting generally low mixing of contaminated particles. This indicates that bioirrigation by *Nereis* spp. can be an important factor for the sediment-to-water flux of contaminants. Results observed for *Marenzelleria* spp. in Paper III suggest a similar scenario, as there was a higher degree of similarity between the patterns of buried congeners in *Marenzelleria* spp. tissue and the water phase (particulate + apparently dissolved) than between the tissue and the surface sediment.

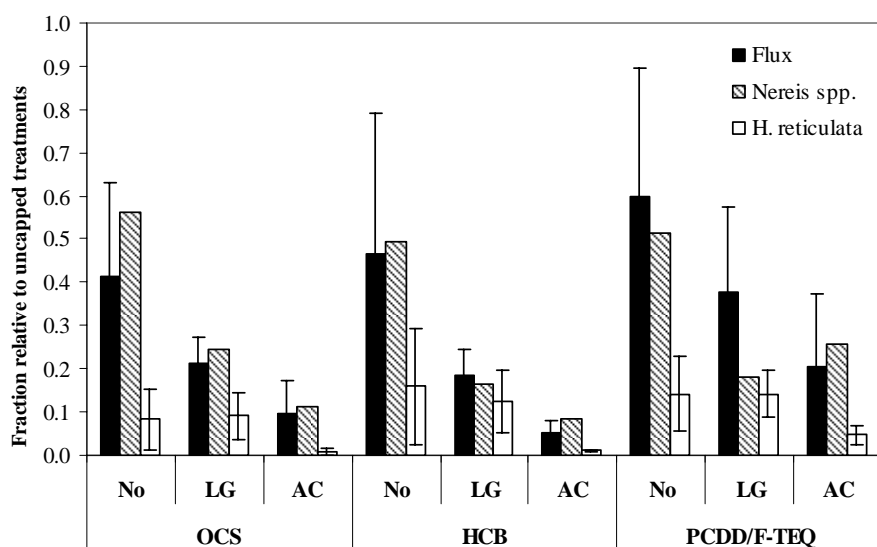


Figure 23. Comparison between the reduction in POP sediment-to-water flux and bioaccumulation in *Nereis* spp. and *H. reticulata*, for the 3 cm cap treatments without active material ("No"), with LG, or with AC. Error bars denote ± 1 standard deviation. Figure from Paper IV.

6.2.3 Potential effects of bioturbation on sediment-to-water flux

In bioturbated systems, the sediment-to-water flux of buried POPs is increased compared to non-bioturbated systems, as demonstrated in Paper II. In the beginning of the experiment in Paper IV, each box had equal density and similar biomass of animals, but at the end of the experiment, differences in the survival and biomass of *Nereis* spp. between treatments

were observed. Even though the survival measured at the end of the experiment is not a direct measure of the extent of bioturbation during the experiment, this still indicates that the extent of bioturbation could have differed between the treatments. The experiment was not designed to evaluate the effects of bioturbation on the sediment-to-water flux, but to assess if the capping efficiency was related to the survival of *Nereis* spp., the HCB flux was plotted against *Nereis* spp. survival (Figure 24; 3 cm cap and uncapped treatments). A covariation between *Nereis* spp. survival and sediment-to-water flux can be discerned, as the flux increases with increased survival. At similar survival, however, the flux is still lower in AC treatments than in capped treatments without active materials, which in turn have a substantially lower flux than control treatments without caps. For more hydrophobic substances, there were indications of an even larger increase in sediment-to-water fluxes with increased *Nereis* spp. survival than for HCB, which might be related to colloid-facilitated transport. This shows that experiments on capping with bioturbation as a variable are needed, preferably combined with sampling of different fractions of POPs in the water phase. Furthermore, the link between bioturbation and sediment-to-water fluxes implicates that if the addition of a capping material improves the habitat for the benthic organisms, the consequences may be increased bioturbation intensity and higher POP fluxes, although the fluxes would most likely still be lower than from uncapped sediment.

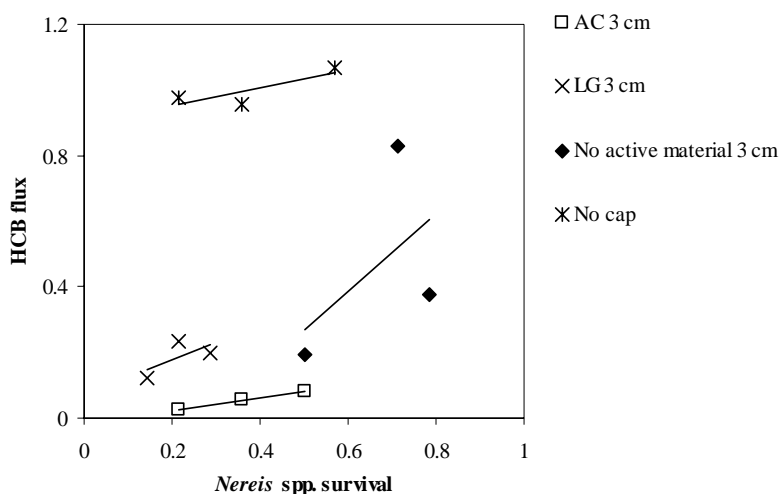


Figure 24. The HCB sediment-to-water flux compared to *Nereis* spp. survival for uncapped treatments and 3 cm cap treatments. Figure from Paper IV.

6.2.4 Effect of congener hydrophobicity on capping efficiency

The reduction in POP flux and bioaccumulation was higher for HCB and OCS than for PCDD/Fs (e.g. Figure 23). This varying capping efficiency for the POPs is related to differences in hydrophobicity, with the flux reduction being inversely related to the K_{ow} of the substances (Figure 25).

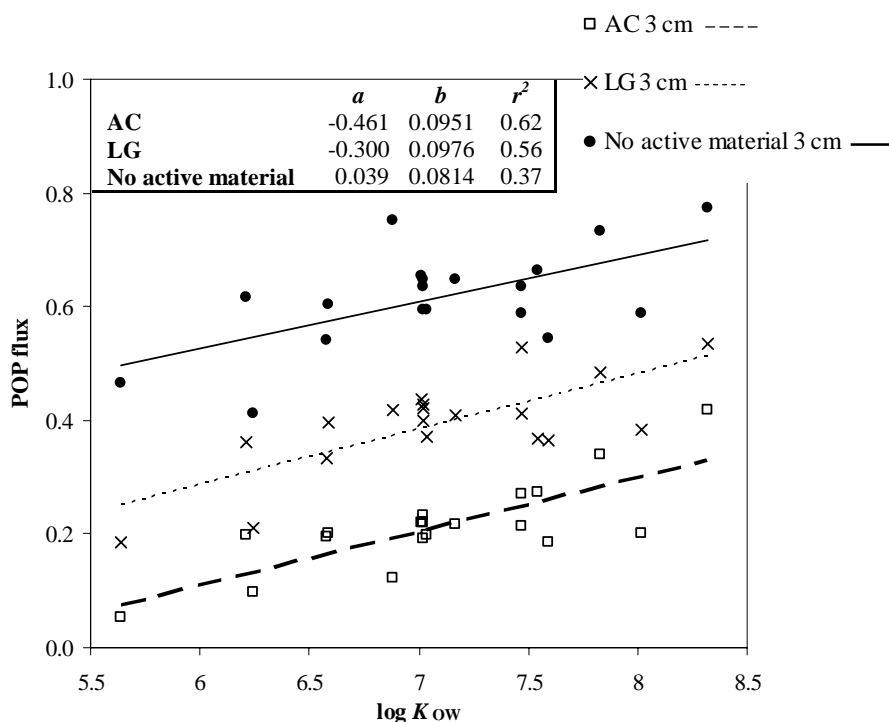


Figure 25. Reduction in the sediment-to-water fluxes of POPs (HCB, OCS, PCDD/Fs) from 3 cm cap treatments as a function of congener hydrophobicity. Fluxes are relative to the average fluxes in uncapped treatments, which were defined as 1. All three regressions ($\text{POP flux} = a + b \times \log K_{ow}$) had slopes significantly different from zero ($p < 0.05$, $n = 19$).

The same trend was observed for all 3 cm cap treatments, regardless of whether the active material was AC, lignin, or no active material was present. Similar observations of higher capping efficiency for less hydrophobic compounds have been made for PCBs and PCDD/Fs in several other studies after AC amendment of sediment and soil (119,161,162,164,166, 173,175). The suggested explanation is the difference in mass transfer rates between sediment/soil particles and AC for different compounds (161,164), with the more hydrophobic POPs displaying slower inter- and intraparticle

diffusion due to their stronger sorption to surfaces (so-called sorption-retarded diffusion; 164). More hydrophobic POPs are more resistant to desorption from the sediment particles and are sequestered more slowly by the added sorbent. It therefore takes longer time to reduce their bio-availability compared to less hydrophobic congeners (161,166). Considering that the same trend was observed regardless of the type of active material (AC, LG or no active material) in Paper IV, a contributing explanation to the observed decreased capping efficiency for more hydrophobic compounds can be colloid-facilitated transport. The distribution to colloids (and particles) generally increases with increased hydrophobicity, and the transport of colloids would be promoted by increased advective transport of pore-water due to e.g. bioirrigation by *Nereis* spp.

7. Conclusions and future perspectives

This thesis has demonstrated the importance of contaminated sediments as secondary sources of POPs. It has also illustrated the influence of bioturbation by different benthic organisms on the sediment-water dynamics. *Marenzelleria* spp., a group of sibling species that recently invaded the Baltic Sea, were found to increase the remobilization of buried POPs to the water column compared to a native species. They also accumulated the buried contaminants, and the trophic transfer of buried contaminants in the benthic-pelagic food web can thus increase with the establishment of these species. *Marenzelleria* spp., which burrow deeper in sediment than native Baltic Sea species, have potential to remobilize contaminants previously considered to be buried at a safe depth. By reintroducing contaminants from deeper sediment layers into circulation in the aquatic environment, the time frame for natural attenuation of contaminated sediments will be extended.

To enhance the natural attenuation and remediate contaminated sediments, thin-layer capping can be a viable option. In this thesis, promising results of thin-layer capping were seen for POPs such as PCDD/Fs, even when the bioturbation depth of the species present extended below the cap layer. The thickness of the cap was an important factor for the reduction of sediment-to-water fluxes and benthic bioaccumulation, and the efficiency of the cap increased with the addition of active materials that enhanced the sorption of the POPs. Amendment with activated carbon reduced fluxes and bioaccumulation more than amendment with kraft lignin. An important issue for further research is the development of active materials that are efficient in sequestering pollutants and sustainable from an environmental and economic perspective. The long-term efficiency of the active materials should also be investigated, since organic matter present in the sediment might decrease the efficiency of active materials by blocking sorption sites, and the active materials may degrade over time. Of utmost importance is the development of remediation methods that can function for both organic and inorganic contaminants, as contaminated sites often contain a mixture of contaminants.

For the future remediation of contaminated sediment sites in Sweden, it is essential to increase the knowledge on the efficiency of thin-layer capping in brackish environments, for organic as well as inorganic contaminants. Furthermore, the understanding on how bioturbation by *Marenzelleria* spp. impacts the remobilization of contaminants from sediment and the efficiency of thin-layer caps should be improved. The establishment of these species in

the Baltic Sea, with a high density in coastal regions, is likely to have implications especially for contaminated sites in coastal areas. Considering that *Marenzelleria* spp. have become dominating benthic species in many areas, but it is unclear to what extent the three species of this genus in the Baltic Sea differ in e.g. their feeding behaviour and bioturbation, research on the individual *Marenzelleria* species should be carried out. More knowledge is also needed on the role of *Marenzelleria* spp. in the aquatic food web.

The importance of bioturbation by bioirrigator/gallery-diffusor species on the remobilizations of POPs from sediment was demonstrated in this thesis, for both *Marenzelleria* spp. and *Nereis* spp. Even though POPs are hydrophobic and primarily sorb to particles, the flux from sediment to water was impacted by bioirrigating activities. The presence of burrows and tubes increases the sediment-water interface area and the hydraulic conductivity in the sediment, and could increase the advective transport in the sediment and facilitate the movement of colloids with associated POPs. The lower capping efficiency observed in Paper IV for the sediment-to-water flux of more hydrophobic compounds compared to less hydrophobic compounds may be related to colloid-facilitated transport, followed by desorption in the water column. It would therefore be valuable to measure not only the freely dissolved fraction of POPs in the water column overlying contaminated sediments, but also the particulate and colloidal fractions, in order to increase the understanding on how the transport from sediments occur.

Although the continuous dispersal of legacy-POPs from contaminated sediments is a problem for the aquatic environment, areas with diffuse contamination should not be neglected. Studies with refined characterisation of the quality and quantity of different size fractions of particles/colloids and associated POPs in the water column are needed also in background areas. For instance, the substantial decrease in PCDD/F water concentrations observed at a coastal Baltic Sea site in May (Paper I) warrants a more temporally dense sampling to establish if and to what extent a link exists between the increased sedimentation during the spring bloom and the decrease in PCDD/F water concentrations, as this has implications for the water-to-sediment transport. The understanding on the fate and transport processes of POPs in the aquatic environment should thus be improved, not only in areas close to point sources, but also in areas of diffuse contamination.

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