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UNDERSTANDING BIOACCUMULATION AND BIOTRANSFORMATION PROCESSES OF HIGH PRIORITY CONTAMINANTS IN FIBER BANKS SEDIMENTS IN THE NORTHERN BALTIC SEA

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Introduction

The Baltic Sea has been heavily affected by historical and current inputs of persistent organic pollutants (POPs). Pulp mills formerly operating along the Swedish coast were the major "primary" source of polychlorinated biphenyls (PCBs) and other POPs like dioxins generated by the chlorination of phenolic compounds naturally present in the wood. POPs, associated with fiber residues and discharged in the wastewaters and sludges, accumulated on the seafloor that led to the formation of so-called fiber banks. Despite that "primary" emissions in environment were effectively reduced or eliminated under the Stockholm Convention, "secondary" emissions (continuing release of POPs deposited in soil, water, sediment) are expected to dominate in the future (1,2). Climate change may increase both primary and secondary emissions, alter degradation rates, sediment properties, and the partitioning of POPs among the environmental compartments (3). Adequate monitoring, management and restoration of fiber banks regions is hampered by limited knowledge of sources of POPs to the contaminated areas as well as factors controlling fate and transport of POPs in the marine environment. The scientific literature on POP levels in sediment, water and biota in the Baltic Sea is large, but mainly descriptive.

The primary aims of this study were to investigate sediment-water-biota exchange of POPs, and to learn how differences in properties of contaminated sediments affect bioaccumulation and biodegradation of POPs. This was done by performing a microcosm experiment and measuring chiral and achiral polychlorinated biphenyls (PCBs) in different compartments: sediment, pore water, overlying water, suspended particles, and biota.

Many chemicals, including some PCBs, are chiral. They are produced and released into the environment with 1:1 (racemic) proportion of two mirror-image enantiomers. The enantiomer fraction can be calculated as EF = (+)/[(+)+(-)], where (+) and (-) refer to concentrations of enantiomers with these optical signs, or E1/(E1+E2), where E1 and E2 designate the first- and second-eluting enantiomers. A racemic compound has EF = 0.5. Enantiomers have identical physical and chemical properties so transport processes and abiotic reactions occur at the same rate and do not alter enantiomer distribution (4-6). However, in biotic systems, enzymes (which are also chiral) react selectively with POPs enantiomers through microbial degradation in water and sediments and metabolism in higher organisms (7). This results in non-racemic residues in e.g. fish (8) and invertebrates (9,10). By studying changes in chiral signatures, it is possible to follow environmental fate, e.g. degradation, metabolism, of POPs (5), and we are applying this concept in the fiber banks region.

Materials and methods

Bioaccumulation and sediment-to-water fluxes of PCBs in two fiber banks sediments, viz. Kramfors and Örnsköldsvik estuaries, plus one reference site (Norrbyn) outside the contaminated areas, were studied using two benthic species, the worm Marenzelleria spp. and marine clam Macoma balthica. These are two common species in the Baltic Sea, they have different feeding strategies, habitats and sediment bioaccumulation mechanisms.

Bioaccumulation experiment

The experiment was performed for 28 days in a temperature-controlled room at 8°C with a photoperiod of 16 h light:8 h dark (Figure 1). Test systems were monitored for physical-chemical parameters: temperature, pH, oxygen, nutrients (NH4+, NO3+NO2), conductivity and salinity. Fate and transport of PCBs in the microcosms were investigated by determining contaminants in sediment, water, pore water, overlying water, suspended solids and biota. Effects of species traits, feeding strategies were investigated by measuring bioaccumulation of PCBs in two benthic species after 4 weeks.

Samples were collected in the end of the experiment. Sediment, suspended particulate matter, and biota were extracted with toluene using Accelerated Solvent Extraction (ASE), and water by liquid-liquid extraction with hexane. Equilibrium pore water concentration of PCBs was determined in a series of sorption experiments using passive samplers, i.e. polyoxymethylene POM (11). Extraction recoveries were 79-124%, 95-113% and 85-119% for sediment, pore water and biota, respectively. All samples

were analyzed for PCBs using GC - low resolution MS with columns specific to the task: DB5ms for quantitative work and the cyclodextrin stationary phase CP-Chiral-Dex-CB for enantiospecific analysis.

Results and discussion

The concentrations of PCB7 (sum of PCB28, 52, 101, 118, 138, 153 and 180) in sediment pore water and biota are presented in Figure 2. The concentration of PCB7 in sediment was the highest for Örnsköldsvik sediment, 73 ng/g dry wt. (Class V according to the Swedish classification of contaminated sediments), followed by Kramfors, 20 ng/g (Class V), and then Norrbyn, 1.8 ng/g (Class III), sediments. The most abundant congeners were CB138, 153 and 180.

The concentrations of dissolved PCB7 in sediment pore water were 16 pg/L in Örnsköldsvik, 8.6 pg/L in Kramfors, and 9.5 pg/L in Norrbyn. All three sediment pore waters were characterized by high abundance of low molecular congeners, e.g. CB28, 52 and 101.

Lipid-normalized concentrations of the PCB7 in Marenzelleria spp. after 1 month of exposure were 245 ng/g in Örnsköldsvik sediment, 383 ng/g in Kramfors sediment and 164 ng/g in Norrbyn sediment. As for Macoma balthica, concentrations were 1096 ng/g in Örnsköldsvik sediment, 175 ng/g in Kramfors sediment and 241 ng/g in Norrbyn sediment. The most abundant congeners in the macroinvertebrate samples were CB101, 138, 153, and 180. In general a good agreement between PCB profiles in sediment and invertebrates was observed, which suggests that sediment was a primary source of PCBs to invertebrates. In addition, the analysis of PCB profile in Macoma balthica revealed higher (compared to Marenzelleria spp.) importance of lower chlorinated congeners, e.g. CB101, indicating importance of pore water as a source of PCBs in that species.

Figure 3 shows a log-log plot of the lipid-water partitioning ratio K_lipid/W and organic carbon normalized sediment-water partitioning coefficient K_oc versus the chemicals' K_ow, demonstrating the clear difference between the sorptive capacities of lipids and sediment OC: K_lipid/W exceeded K_oc by 1-2 orders of magnitude in Norrbyn, however K_lipid/W were comparable to K_oc in Kramfors and Örnsköldsvik sediments.

Biodegradation and biotransformation processes in fiber banks sediment were studied by determining the proportions of chiral PCB enantiomers in water, Macoma balthica, and sediment. The concentration of all chiral PCBs in Marenzelleria spp. (except CB149) was below detection limits.

CBs 95, 136, and 149 were racemic in Norrbyn and Kramfors sediments suggesting that the source is likely unweathered pollution or lack of enantioselective metabolism. The nonracemic EFs of CB132 and 174 indicate that microbial degradation has occurred stereoselectively, possibly by reductive dechlorination. EFs in sediment, pore water and biota agreed in some cases, and not in others. In principle, EFs in pore water should be the same as in sediment, and differences in biota will occur only if there is enantioselective metabolism. Further analysis is required before conclusions can be drawn.

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Figure 1. Experimental set-up.

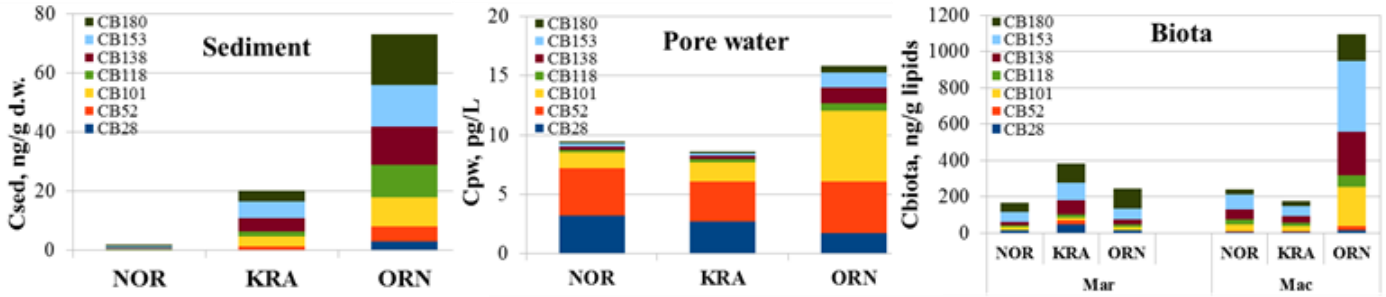

Figure 2. Concentration of PCB7 in sediment, pore water, *Marenzelleria* spp. and *Macoma balthica* in Norrbyn, Kramfors, and Örnsköldsvik sediments.

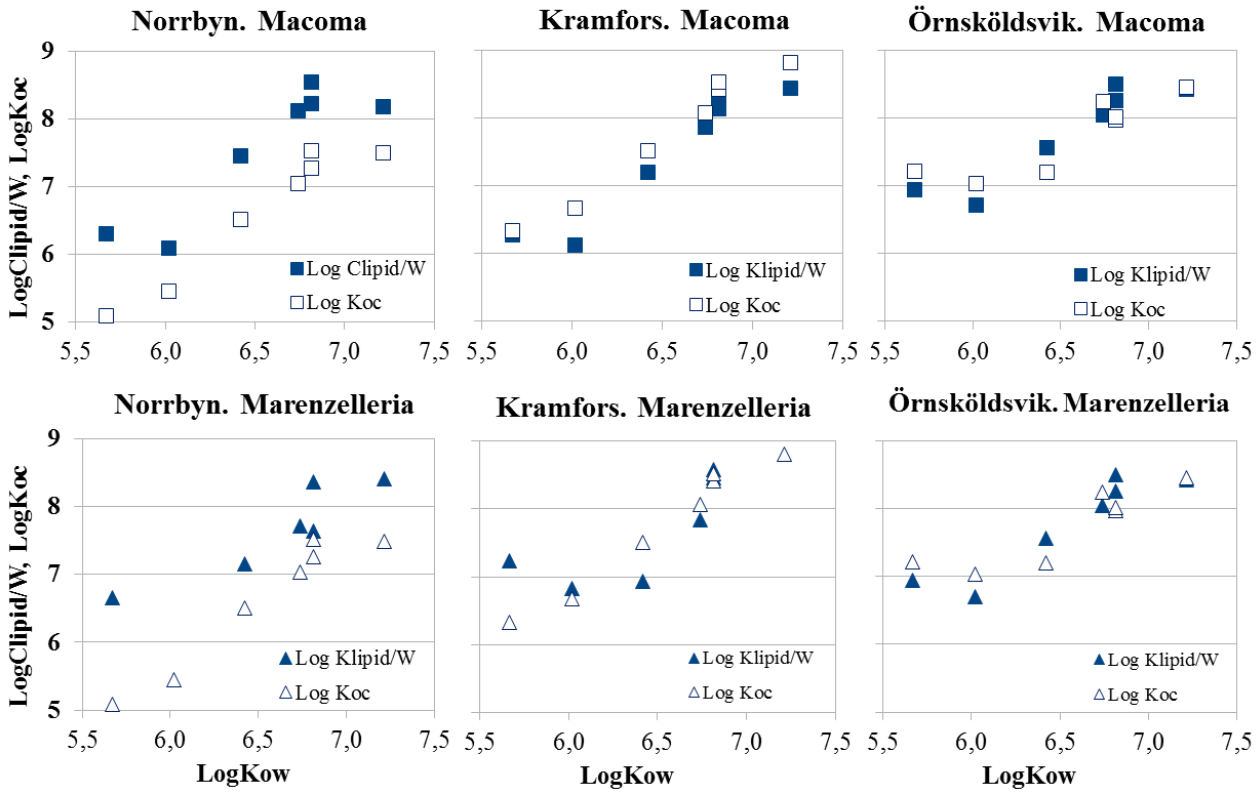

Figure 3. PCB Log BAF for *Marenzelleria* spp. and *Macoma balthica* based on pore water concentrations determined with the POM-SPE method.

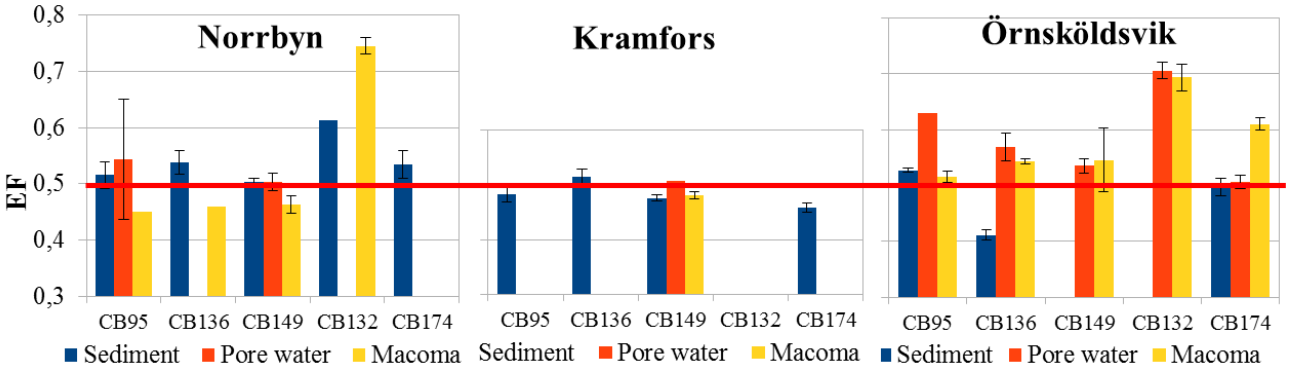

Figure 4. Enantiomer fractions (EF = E1/(E1+E2)) for CB95, 136, 149, 132, and 174 in sediment, pore water and biota samples.