SEDIMENT TO WATER FLUX OF PERSISTENT ORGANIC POLLUTANTS FROM CONTAMINATED FIBER BANKS IN THE BALTIC SEA

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Introduction

Lately, the presence of heavily polluted fiber banks located along the northern Baltic coast of Sweden have received attention as a source for persistent organic pollutants (POPs) to the aquatic environment. These fiber banks originate from the Swedish forest industry, which in the past has discharged large amounts of contaminated cellulose and wood fibers into the aquatic environment, material which has accumulated on the sea floor [1]. This fiber material has over time dispersed and mixed with natural sediment to form fiber rich sediments, which cover even greater areas of the seabed. Our previous study in the shoreline of the County of Västernorrland (Bothnian Sea) found high levels of chlorinated organic compounds, such as polychlorinated biphenyls (PCBs), in fiber bank areas [2]. Dispersion of POPs from sediment with very high organic content, such as fiber bank areas, is poorly investigated. The aim of the present study was therefore to investigate the dispersal of PCBs from fiber bank areas by quantifying diffusive sediment-water fluxes of PCBs from fiber banks, fiber rich sediments and of fiber less affected sediments using benthic flux chambers. The relationships between sorption of PCBs to sediment, fluxes of PCBs and sediment type were also investigated. In addition, passive samplers were deployed at different depths in the water column above one of the fiber banks to determine the water concentration of PCBs.

Materials and methods

Study area and samples

Two heavily polluted fiber bank areas, Väja (R) and Sandviken (Q), located in River Ångerman (N62°58′14″, E17°46′27″), Sweden were studied. A map of the sampling areas can be found elsewhere [2]. Sediment samples (*n*=19) were collected from the fiber bank, fiber rich sediment, and less affected sediment from both study areas. The sediment samples were stored cold (+4°C) prior to pore water analysis and then frozen (-18°C) until sediment analysis. Benthic flux chambers (*n*=5) were placed on the seabed for 32-34 days at the same sites as the sediment sampling. The design of the benthic flux chamber has been described in detail elsewhere [3]. Briefly, the flux chamber consisted of a cylindrical stainless steel chamber (Ø 250 mm, area 0.049 m^2, inner volume 3.4 L) containing a SPMD passive sampler (Exposmeter, Sweden, 0.92 m length, 534 cm^2 surface area, 75-90 µm thickness) filled with a strong absorbing phase (triolein). In addition, SPMD passive samplers (*n*=2), each mounted on a stainless steel spider (Exposmeter, Sweden, Ø 15 cm, height 5 cm) and placed in a stainless steel canister (Exposmeter, Sweden, Ø 16 cm, height 15 cm), were deployed in the water column at two different depths (2 m above the sediment and 7 m below the water surface) for 32-34 days to determine water concentrations above the fiber bank in Sandviken (Q). After sampling, the SPMDs were stored frozen (-18°C) until chemical analysis.

Extraction and clean up

Sediment samples (*n*=19) were Soxhlet extracted and cleaned up as previously described [2]. Three of the sediment samples were extracted and cleaned up in triplicate. In short, each sediment sample (5 g) was spiked with isotope-(^{13}C)-labelled surrogate standards and extracted with acetone: *n*-hexane (225 mL, 1:1, v/v, 24 hours). After extraction, sulfur was removed using cupper and the extracts were cleaned up on multilayer columns composed of activated silica (SiO_2, 3g), sulfuric acid treated silica (40% H_2SO_4:SiO_2, 6g) and sodium sulphate (Na_2SO_4, 3g). Each column was eluted with *n*-hexane (60 mL).

Polyoxymethylene (POM) strips were used to measure the dissolved concentration of POPs in sediment pore water of the sampled sediments (*n*=19). The pore water of three sediment samples were sampled in triplicate. The procedure for the PCBs to partition between sediment, water and POM (CS Hyde, Lake Villa, IL, USA) was performed as previously described [2]. After partitioning, isotope-(^{13}C)-labelled surrogate standards were added to the POM strips, which were then extracted with acetone:*n*-hexane (1:1, v/v, 20 + 20 mL) for 2 x 24 hours.

The SPMDs (samples *n*=5+2, field blanks *n*=2) were extracted with 2 x 150 mL *n*-hexane for 2 x 24 hours as described by Josefsson et al. [4]. Prior to extraction, isotope-(^{13}C)-labelled surrogate standards were added to each sample. The extracts were cleaned up on silica:sulfuric acid gel columns composed of activated silica ($SiO_{2,}$ 3g) and sulfuric acid treated silica (40% H_2SO_4:SiO_2 w/w, 6g) and the analytes were eluted with 60 mL *n*-hexane:dichloromethane (5:1 v/v, 60 mL).

Instrumental analysis and QA/QC

Prior to instrumental analysis, each sample was reconstituted and volumetric standards were added. The samples were then analysed on a gas chromatograph (Agilent Technologies, 7890A) coupled to a triple quadrupole mass spectrometer (Agilent Technologies, 7010 GC/MS Triple Quad). The MS was run in MRM mode, using two transitions for each target analyte. For quality assurance, a procedural solvent blank was included in each batch of samples. Each sample was analysed for 20 PCB congeners; CB-28, -52, -77, -81, -101, -105, -114, -118, -123, -126, -138, -153, -156, -157, -167, -169, -170, -180, -189, -209. Results are presented as Σ_{20}PCB and as Σ_7PCB (CB-28,-52,-101,-118,-138,-153,-180) in **Figure 1 and 2**.

Results and discussion

Sediment and pore water concentrations

The sediment concentrations of PCBs in fiber banks, fiber rich sediments, and less affected sediments from Väja (R) and Sandviken (Q) are presented in **Figure 1A** on dry weight (d.w.) basis (ng g^{-1} d.w.). The highest PCB concentrations were found in the fiber banks in both study areas. The measured mean Σ_7PCB concentrations in Väja (28 ng g^{-1} d.w) and Sandviken (36 ng g^{-1} d.w.) are classified as very high levels (>15 ng g^{-1} d.w) according to standards established by the Swedish Environmental Protection Agency [5]. Significantly higher sediment pore water concentrations (pg L^{-1}) were also found in fiber bank sediments compared to fiber rich sediments and less affected sediments (one-way ANOVA, $p<0.05$) as shown in **Figure 1B.**

Relation between sorption, sediment to water flux and sediment type

The measured levels in sediment and pore water were used to calculate the coefficient of sorption (K_d) in fiber bank, fiber rich sediment, and less affected sediments. The sorption of PCBs was found to be significantly higher in fiber banks than in fiber rich sediment (one-way ANOVA, $p<0.05$) and in less affected sediments (one-way ANOVA, $p<0.05$). This is likely explained by the higher organic carbon content in the fiber banks (mean: 12%) compared to fiber rich sediments (mean: 3.5%) and of fiber less affected sediments (mean: 2.6%). The sorption of PCBs was also found to be significantly correlated (Spearman, $p<0.05$) with the hydrophobicity (log K_{ow}) of the PCBs. However, despite significantly higher sorption, the sediment-water flux of PCBs (ng m^{-2} day^{-1}) from fiber banks were significantly higher compared to fiber rich sediments (paired t-test, $p<0.05$) (**Figure 2**).

Conclusions and future perspectives

To our knowledge, this is the first *in situ* study presenting fluxes of POPs from fiber contaminated sediment areas. Our results demonstrate higher levels of PCBs in fiber bank sediments, but also higher sorption to this material than to surrounding sediments. In spite of high sorption to the fiber banks, sediment-water fluxes were found to be significantly higher from fiber banks than from surrounding areas. Overall, our study demonstrates the need to address fiber banks as sources for dispersal of POPs to the aquatic environment in the Baltic Sea and in other areas of the world where sediments impacted by fibers from the pulp, paper and board industry exist. The current study is part of TREASURE, a research project for which the ultimate goal is to develop a risk assessment method to identify fiber banks in most urgent need of remediation.

Acknowledgements

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References

1. Apler A, Nyberg J, Jönsson K, Hedlund I, Heinemo S-Å and Kjellin B (2014) *Fiberbanksprojektet-Kartläggning av fiberhaltiga sediment längs Västernorrlands kust*, Geological Survey of Sweden. SGU Report:2014:16.
2. Dahlberg A-K, Vogel L, Wiberg K, Apler A and Josefsson S (2016) *Organohalogen Compounds,* **78**, 572-575
3. Eek E, Cornelissen G and Breedveld GJ (2010) *Environmental Science & Technology,* **44**, 6752-6759
4. Josefsson S, Schaanning M, Samuelsson GS, Gunnarsson JS, Olofsson I, Eek E and Wiberg K (2012) *Environmental Science & Technology,* **46**, 3343-3351
5. Swedish Environmental Protection Agency, Report 4914 (1999) *Bedömningsgrunder för miljökvalitet – Kust och hav.*

Figures

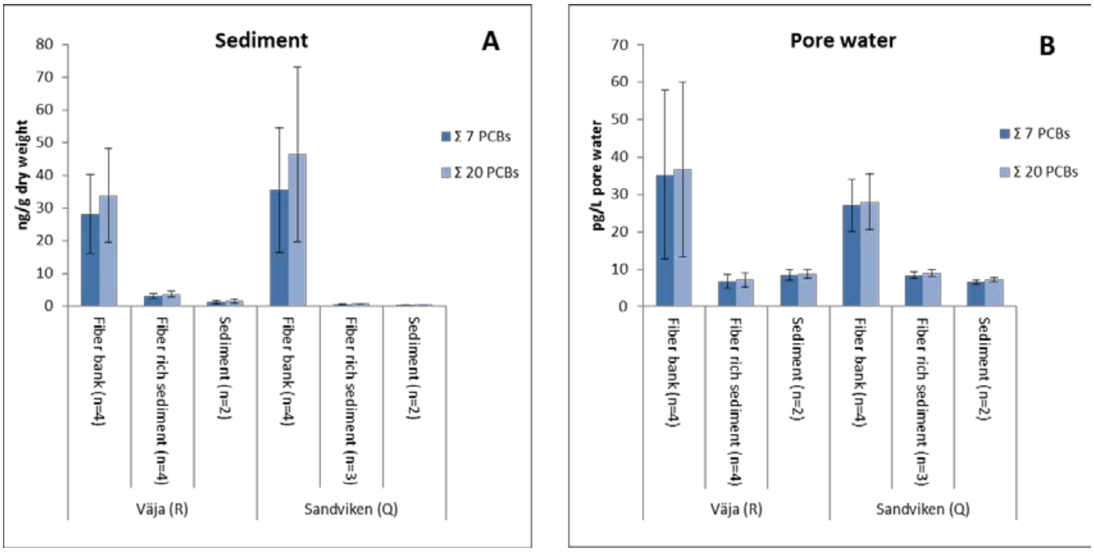

Figure 1. PCB concentrations in sediment (ng g^{-1} d.w., Figure 1A) and pore water (pg L^{-1}, Figure 1B) presented as Σ_7PCBs and Σ_{20}PCBs. Error bars show the standard deviation for *n* number of samples.

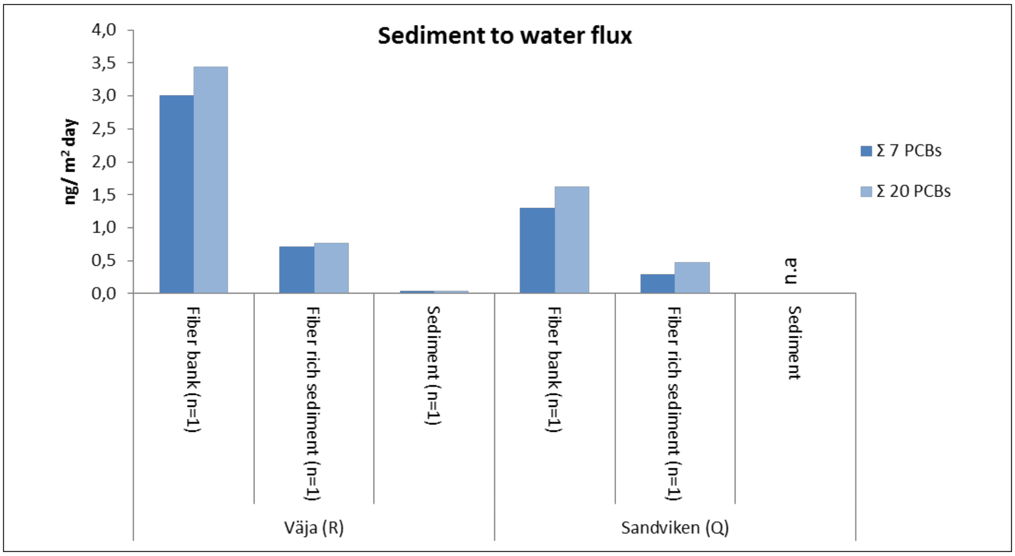

Figure 2. Sediment to water flux of PCBs (ng m^{-2} day^{-1}) from fiber bank, fiber rich sediments and of fiber less affected sediments in Väja (R) and Sandviken (Q). n.a = not analysed.