Inventories and emissions at a PCB contaminated site – Differences in emission rates from aquatic and terrestrial matrices

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Introduction

Although the concentration of PCBs in the environment have undergone a significant decline since the 1970s, PCBs are still present almost everywhere on earth. To assess the contribution of continuous emissions of PCBs to the global cycling of this contaminant, a better knowledge of the magnitude of the current sources is needed. Different contaminated media can be expected to release PCBs at different rates. Further, it is necessary investigate how differences in physico-chemical properties for different PCBs affects the emission rate from contaminated media. In this study, the leakage of PCB from a contaminated semi-enclosed small bay (the Örserum bay) in the archipelago outside Västervik on the Swedish east-coast is described. During the activities of a paper-mill for recycled paper several hundred kg PCB was released to the Örserum bay. Similar amounts are also found in a fibre separation basin and a deposit for sediments dredged from the bay. The deposit was created in the 1970s and was by 1996 covered with vegetation. Its volume is approximately 53 000 m^3 and the surface is relatively dry as opposed to the fibre separation basin which is soaked with water up to the surface most of the year. The fibre separation basin covers an area of 22 500 m^3 and the depth of the fibre layer is in average 2 m. In this study leakage processes of PCBs from different types of contaminated matter were investigated. The quantified PCB fluxes were volatilisation from the deposit, advective flux with groundwater, advective flux with water out from the bay, and volatilisation from the bay's water. The quantification of these fluxes was based on direct measurements and model calculations when necessary.

Materials and methods

Samples were taken from sediments, sediment traps, air, groundwater, baywater, the sediment deposit and the fibre separation basin. Volatilisation of PCBs from the deposit was measured with steel hoods.

Samples were Soxhlet extracted in toluene with Deans-Stark trap for water removal. H_2SO_4 / KOH / neutral SiO_2-gel columns were used for further clean-up. Analysis was done on a Fisons GC8000/MD800 (EI, single ion recording mode) and the PCB congeners were quantified against ^{13}C-labelled standards.

Results and discussion

In the sediments a clear concentration gradient of ΣPCB was found. Most of the PCBs were located in the inner part of the bay. The chemical profile in the inner part of the bay was similar to Aroclor 1242 as opposed to the profile found outside the bay which more resembled Aroclor 1254 and background location profiles from the Baltic Sea. The total amount of PCB found in the sediments of the bay was 80 kg. Also in the fibre separation basin a distinct concentration gradient was found. In the top 0-1 m layer the concentration of ΣPCB was 74 $\mu g\ g^{-1}$ while it was only 3 $\mu g\ g^{-1}$ in the bottom 3 to 4 m layer. All homolog groups showed a similar pattern, which was unexpected. The increasing organic carbon partition coefficients with increasing degree of chlorination implies lower mobility in an organic rich matrix. However, the observed effect may be an indication of that organic colloids and small particles may enhance the advective transport of more hydrophobic compounds in the ground. The mobility with groundwater organic colloids has been shown to increase with increasing hydrophobicity of the compound [1]. Still, only ca 3 % of the total amount of PCBs in the fibre separation basin has reached depths below 3 m. The total content of ΣPCB in the fibre separation basin was 600 kg. The dredged sediments in the deposit contained concentrations more similar to those found in the sediments in the inner part of the bay 34±6.5 $\mu g\ g^{-1}$. The total amount of PCB was estimated to 350 kg.

The concentration of PCB in air over the sediment deposit was significantly elevated. The vapour phase of ΣPCB was 30 times higher above the deposit than over the control site, 3100 ± 950 vs. 110 ± 65 pg m^{-3} respectively.

The volatilisation flux from soil to air of ΣPCB at the deposit was 19 ± 11 $\mu g\ m^{-2}\ d^{-1} g^{-1}$, which was three orders of magnitude higher than at the control site. The amount of ΣPCB annually volatilised from the deposition was estimated to 100 g. Calculated transfer velocities were higher at the control site than at the deposit.

The two film-model [2, 3] were applied to the measured concentrations in air and the bay's water. The estimated volatilisation flux from the bay's water was 200 g.

The concentration of PCBs in the groundwater varied significantly between different wells. The highest concentration was found in the groundwater retrieved from the fibre separation basin, which could be expected since that water was in direct contact with fibres containing the highest concentrations of PCBs. The amount of ΣPCB leaching to the bay via groundwater was estimated to 5 g per year.

PCBs are also transported out of the bay with advective transport of the bay's water. The average turnover time of 1.75 d for the entire bay equals an exchanged volume of 600 000 $m^3\ d^{-1}$. Combined with the measured concentration of particulate and dissolved PCBs in the outer part of the bay and on the outside of the bay this was used to estimate the annual amount of ΣPCB out of the bay. This flux was significant, 700 g per year.

A model developed by Chen [4] was used to calculate the diffusive flux of PCBs from the sediments to the water column of the bay. Model calculations [3] were also used to assess the

amount of PCBs desorbed from resuspended particles. A budget for the Örserum bay was assembled (Figure 1) and the calculated sediment release fluxes were found to be 3 times higher than the two estimated output fluxes. This indicates that the output fluxes were not overestimates. In total, approximately 1 ton ΣPCB exists in the bay and 1 kg is annually emitted from the area. These investigation also revealed that the PCBs in the bay were considerably more mobile than the PCB on land. Only 0.01 % of the PCBs on land were emitted annually whereas as much as 1 % per year was emitted from the bay's sediments.

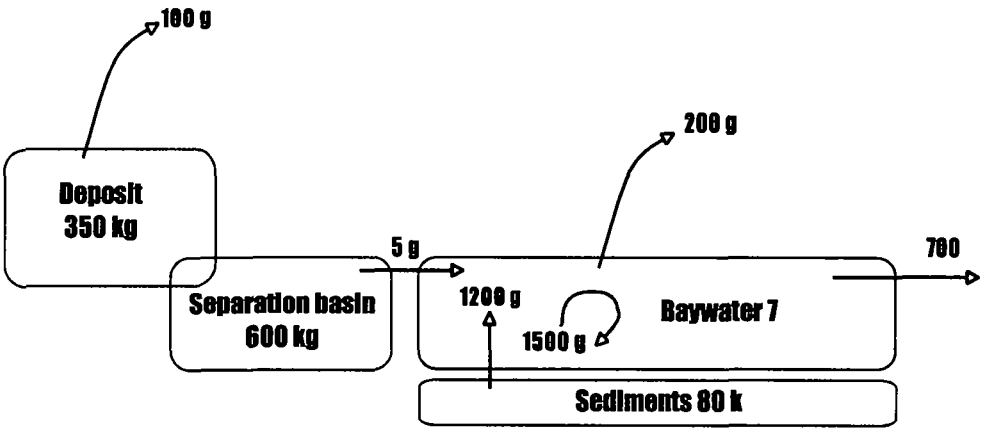

Figure 1. Content and annual fluxes of ΣPCB in the Örserum bay summarised in a budget.

Congener specific analysis also allowed an assessment of how physicochemical properties of different PCB congeners affected the mobility and fluxes. Vapour pressure and hydrophobicity were the two governing properties. 90 % of the PCBs that volatilised from the ground of the deposit consisted of tri- and tetra-chlorinated congeners and less than 0.5 % consisted of the highly hydrophobic hepta- and octa-chlorinated congeners. Similarly, di- to tetra-chlorinated congeners accounted for 97 % of the net volatilisation flux from the bay's water surface. As opposed to the volatilisation fluxes the advective flux of PCBs out of the bay involves a significant particle mediated transport, enhancing the mobility of the highly chlorinated more hydrophobic congeners. This emission route accounted for 96-100% of the total release of the hexa- to octa-chlorinated congeners. Still, of the total emission of PCBs from the area nearly 90 % consisted of di- to tetra-chlorinated congeners.

References

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