Sediment trap fluxes, residence times and surface sediment concentration variability of PCBs, PCDD/Fs and PAHs in the Baltic.

Broman. D.#, Bandh, C.#*, Ishaq, R.#*, Näf, C.#, Pettersen, H.#*, Zebühr, Y.#

Aquatic Chemical Ecotoxicology, Department of Zoology and *Department of Analytical Chemistry, Stockholm University, S-106 91 Stockholm, Sweden.

Introduction

In the aquatic environment the sorption dynamics of hydrophobic organic compounds (HOCs) are of crucial importance for the total turnover of these compounds in water, which includes processes like pelagic recirculation, sedimentation and sediment remobilization. The dynamic interactions of HOCs between the particulate, dissolved and truly dissolved fractions are also of great ecotoxicological importance since in many cases they control the bioavailability of a compound. Although there is an enormous variation, in both composition and sorption abilities, in the materials summerized in the two terms particulate and dissolved matter, these sorption dynamics are often modelled with a few sorbent and solute characteristics. One commonly used way to predict the behaviour of a HOC in water is by discussing the particulate organic carbon (POC) - water partition coefficient (K_{POC}) of the compound in question¹. The ability of POC to sorb HOC is of central importance since POC is both the major constituent in biological particulate matter as well as surface cover on most inorganic aggregates.

The sink for particulate matter and particle-associated HOCs is the accumulation bottom sediments. Because of the high K_{POC} displayed by many HOCs and because of the high organic carbon content in the settling matter, the accumulation bottom sediments will be of great importance for the deposition and turnover of HOCs in the aquatic environment.

The aquatic environment of the Baltic Sea has for a long time been exposed to great loads of hydrophobic organic compounds (HOCs) due to outlets from numerous emission sources in the countries surrounding the Baltic Sea as well as from long range transport from other countries. The load of HOCs, such as PCDDs, PCDFs (PCDD/Fs) and PAHs, in various water areas of both near source, and background load character, on the Swedish Baltic coast has been shown i earlier studies²⁻⁵. In the present study attempts are made to estimate the load of primarily PCBs and PAHs, but also of PCDD/Fs, on the total area of the Baltic Sea. This is evaluated in terms of the PCB and PAH content in a large number of surface bottom sediments, from several parts of the Baltic Sea, as well as the PCB, PAH and PCDD/F content in settling and suspended particulate matter collected with sediment traps and water filtration, respectively, at stations located in open sea areas of the Baltic (see figure).

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Approach and Achievements

Surface sediment samples (0-1 cm) were collected with core samplers at 37 locations (during 1991) in the Bothnian Bay, Bothnian Sea, Gulf of Finland and Baltic proper (see figure) at various depths ranging from 43 to 250 m.

Sediment traps were moored at 4 different locations; one in the Bothnian Bay, one in the Bothnian Sea and two in the Baltic proper. The depth at these locations varied between 120 to 170 m and the traps were all located at distance of 15 m from the bottoms. The sampling period was from May to November 1991 for the trap in the Bothnian Bay and from January 1991 to March 1992 for the other three sediment traps.

The sediment traps were of a self-suspended buoyant type with cylindrical collection vessels of glass contained in a gimbal-mounted PVC cylinders. The trap design and anchorage technique used are described in detail elsewhere⁶. To avoid microbial activity in the collected material chloroform was used as a preservative in the collection vessel as described by Broman *et al.*³.

The filtering of water for the collection of the dissolved and particulate fractions were made at 7 stations in the open Baltic (see figure). The equipment used consisted of a glass fiber filter for the particulate fraction followed by polyurethane foam plugs for the dissolved fraction. More details of the filtration procedure can be found elsewhere⁵.

All samples were sonicated and then Soxhlet extracted with toluene for 24 hours. The water was removed during extraction with a so called Dean-Stark trap which was attached to the Soxhlet apparatus⁷. Prior to extraction nine ¹³C-labeled PCB standards (2,2',5,5'-TCB (#52), 3,3',4,4'-TCB (#77), 2,2',4,5,5'-PnCB (#101), 2,3,4,4',5-PnCB (#118), 3,3',4,4',5-PnCB (#126), 2,2',3,4,4',5-HxCB (#138), 2,2',4,4',5,5'-HxCB (#153), 3,3',4,4',5,5'-HxCB (#169) and 2,2',3,4,4',5,5'-HpCB (#180)) and four PAH standards (2-methylantracene, D₁₂-perylene, picene and dibenzo(a,i)pyrene) were added. To the samples analyzed for their content of PCDD/Fs eight ¹³C-labeled standards were added (2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PnCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD). Clean-up and analyses procedures of the PAHs, PCBs and PCDD/Fs can be found elsewhere^{3,5,8}.

The PCB compounds analyzed were the corresponding native isomers of the ¹³C-labeled standards given above plus 2,4,4'-TriCB (#28), 2,3',4,4'-TCB (#66) and 2,3,3',4,4'-PnCB (#105) and the PAHs analyzed were 19 compounds ranging from three-ringed phenanthrene to six ringed coronene. The PCDD/Fs analyzed were all 17 2,3,7,8-substituted isomers and the sum of all congener groups.

The gross flux of particle-associated contaminants to a certain water area can preferably be measured with sediment traps of adequate design. In the material collected with sediment traps deployed for longer periods of time is also found, indirectly, a significant part of the previously dissolved matter and non-settling suspended matter and thereby also the PCBs, PCDD/Fs and PAHs associated to these materials. Dissolved organic carbon (DOC) can for instance have a glueing effect which facilitates particle aggregation processes and results in incorporation and adsorption of DOC to particulate matter?

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The settling particulate matter (SPM) found in the sediment traps are by definition the materials of which the bottom sediments are built. In the bottom sediment, however, there are several biotic and abiotic processes which alter the composition of the settled material and thereby also the concentrations of HOCs. Further, there are also physical processes like resuspension which makes it difficult to regard the surface sediments as only to consist of newly sedimented material.

The first preliminary results of the surface bottom sediment data (27 samples) show a variation of the PAH concentrations (nineteen compounds) between 0.1 and 6 μ g/g on a dry weight basis and between 15 and 55 μ g/g on an organic carbon (OC) weight basis. The concentrations of PCBs (a sum of isomers #77, #101, #138, #180) showed a variation between approx. 20 and 1000 pg/g on a dry weight basis and between approx. 2 and 15 ng/g on an OC weight basis (22 samples).

The sediment trap samples and the remainder of the surface bottom sediment samples are under evaluation and the results of the total flux of both PCBs and PAHs on the Baltic Sea as well as the total load on bottom surface sediments of these compounds in the different geographical areas of the Baltic will be presented.

With data on the HOC concentrations in suspended particulates and in settling particulate matter (i.e. the filtered and sediment trap collected samples) it will be possible to calculate and also to compare earlier estimates¹⁰ of the settling velocities and residence times found for HOCs in open Baltic water. The filtered material will also give an indication of the variation found in the water mass as well as the momentary content of HOCs the mixed surface layer of the Baltic as described in earlier studies^{5,10}.

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