

## **Occurrence, Flux Estimates and Spatial Variations of Organochlorine Contaminants in Settling Particulate Matter in the northern part of the Baltic Sea.**

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### **INTRODUCTION**

Organic environmental pollutants such as hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCBz), DDT and its metabolites (DDTs), chlordane related compounds (CHLs), dieldrin and polychlorinated biphenyls (PCBs) are distributed globally by transport through air and water<sup>1</sup>. The Baltic Sea is reported to be highly contaminated of organic compounds<sup>2</sup>. Most literature is however focused on the concentrations in organisms or in sediments. In the aquatic environment these compounds can be dissolved in the water or be associated with particles depending on their hydrophobicity and organic carbon-water partition coefficients<sup>3,4</sup>.

Particulate matter in the aquatic environment can have a natural origin like dead biological material (detritus) and living plankton organisms, or have an anthropogenic origin<sup>5</sup>. This particulate matter can transfer pollutants into the food chains or to the sediments. Sediment trap sampling of settling particulate matter (SPM) during a longer period of time reflects the contamination in the water column<sup>5</sup>.

Sediment trap fluxes refer to the total amount of matter or compounds obtained in the traps per unit of time. Contributions may also be obtained from resuspension of sediments. The estimation of down fluxes of SPM associated compounds is of great interest for the general fate of organic pollutants since the sediments often serve as the final sink for these contaminants. Extrapolation of such flux estimations can also give an indication of the contamination load in a certain region. Earlier studies using sediment traps in the Baltic Sea region have been a fruitful tool to estimate loads of e.g. PCDD/Fs and PAHs in remote as well as anthropogenically influenced aquatic environments<sup>3,6,7</sup>.

The present study discusses the occurrence of organic contaminants in SPM and the spatial variations in terms of fluxes of the above listed chemicals in remote coastal and offshore waters in the Bothnian Sea and Bothnian Bay, respectively. An attempt is also made to use the obtained fluxes to estimate the total sedimentation of compounds in Bothnian Bay, Bothnian Sea as well as to the total Baltic Sea.

### **MATERIALS and METHOD**

Sediment traps were positioned in coastal and offshore stations in the Bothnian Sea and Bothnian Bay, respectively, in the northern Baltic Sea (Figure 1). These coastal stations are

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remote and have a high water exchange with the open sea. Sampling time, geographical coordinates, location depths and placement of the traps are given in Table 1.

Table 1. Characteristics of sediment trap sampling.

Local	SR5 (n=1)	F9 (n=1)	SN (n=1)	HF (n=2)
Sampling time (from)	17-jan-91	13-may-91	16-jun-92	17-aug-91
(to):	07-mar-92	18-nov-91	12-jun-93	26-aug-93
Latitude (N)	61°05'03"	64°42'50"	59°54'90"	65°34'72" and 65°34'86"
Longitude (E)	19°32'94"	22°04'32"	19°10'92"	22°45'70" and 22°45'95"
Depth (m)	115	116	41	24 and 26.5
Placement of trap from bottom (m)	15	15	10	10

n=number of samples

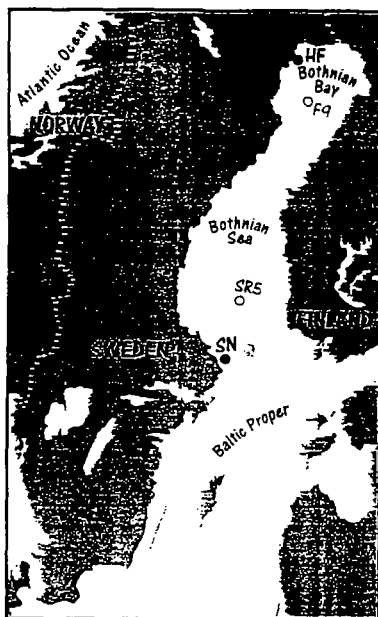


Figure 1. Sampling locations in the Baltic Sea.

A detailed description of the sediment traps and sampling technique is presented elsewhere<sup>8</sup>. In short, the sediment traps were self buoyant and bottom anchored. The trap contained cylindrical glass collection vessels in mounted PVC cylinders. Chloroform was used in the glass vessels for preservation of the trapped settling matter.

The clean-up procedure was a multi-residue method aimed to determine numerous organochlorine and polyaromatic hydrocarbon compounds<sup>9</sup>. Briefly, the samples were homogenised and extracted wet in a soxhlet (Dean Stark) apparatus with toluen (24h) and a mixture of hexane and acetone (59/41, 24h). The extracted organic phase was enriched using a polyethylene film dialysis technique<sup>10</sup>. The dialysis fraction was further split into two parts, of which 10% was used for analysis of organochlorine pesticides and bulk ( $\text{Cl}_3\text{-Cl}_{10}$ ) PCBs. This fraction was further cleaned on a Florisil column<sup>11</sup>. Before extraction an internal standard mixture containing a multitude of  $^{13}\text{C}$ -labelled and deuterated compounds was added. The internal standards used for quantification of compounds in this study were  $^{13}\text{C}$ -labelled lindane, *p,p'*-DDT, dieldrin, PCB#80 and #153. The analysis and detection was performed using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) instrumentation. The MS instrument was a Fisons MD800 operating in the electron impact (EI) mode using selected ion recording (SIR). The GC was a Fisons GC 8000 with a DB-5 (60x0.32 i.d) column.

The  $\Sigma\text{HCH}$  data is given as the sum of  $\alpha$ ,  $\beta$  and  $\gamma$ -HCH. The  $\Sigma\text{DDT}$  data is a sum of *o,p'*- and *p,p'*-DDT, DDD, DDE and *p,p'*-DDMU. Of 13 chlordane related compounds analysed in this study, only seven were reported above the detection limit. The  $\Sigma\text{CHL}$  is the sum of those detected compounds and includes *cis*-heptachlorepoxide, (*trans*- and *cis*-) chlordane and nonachlor, MC5 and MC6. The MC notations are abbreviations of compounds identified by Miyazaki *et al.*<sup>12</sup>. Finally the PCB data given is the summation of 68 tri- through deca-chlorinated PCB congeners<sup>13</sup>. Quantification was performed against an external quantification standard containing one PCB congener for each tri- through hepta-chlorinated PCBs. All other compounds in this study were present in this standard, except the chlordane MC compounds.

## RESULTS and DISCUSSION

The concentrations of the analysed compounds are presented in Table 2 on dry weight basis. The concentrations at the offshore (SR5 and F9) and coastal (SN and HF) stations, respectively, were similar for each chemical group compared. Generally, the concentrations at the offshore stations were approximately a factor of four to seven higher than the coastal stations. An explanation might be the lower percentage of total organic carbon (TOC) in the coastal stations (0.83 and 1.4%) compared to the offshore stations (4.9 and 5.2%) since a higher organic content may result in a higher absorbing capacity for the dissolved pollutants due to the high organic-water partition coefficient for these type of compounds. Biomagnification variations for plankton organisms between places, might also contribute to concentration differences.

Table 2. Concentrations (ng/g dry weight) of some organochlorines in settling particulate matter (SPM) in open sea and coastal locations in Bothnian Sea and Bothnian Bay, respectively. (For the locations of the collection sites, see Fig. 1).

Local	SR5 (n=1)	F9 (n=1)	SN (n=1)	HF mean (n=2)
$\Sigma\text{HCH}$	22	23	6.4	8.6
Hexachlorobenzene	3.4	3.2	0.49	0.69
$\Sigma\text{DDT}$	18	9.9	2.4	1.9
$\Sigma\text{Chlordanes}$	7.2	6.7	0.41	0.56
Dieldrin	9.5	22.3	0.75	1.6
$\Sigma\text{PCB}$	28	31	4.6	7.2
% Carbon (of dw)	5.2	4.9	1.4	0.83

n=number of samples, dw=dry weight

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The two traps at the HF location, separated by approximately 50 m, had similar compound concentrations and flux values. No compound deviated more than 20% from the mean values given in Tables 2 and 3. Additional blank samples run in parallel with the samples contained some minor residues of lower chlorinated PCBs and hexachlorobenzene. No corrections for the blanks were made since they were well below 10% of any calculated value in the samples.

The chemical composition profiles for each sampling station are presented in Figure 2. The profiles are similar between the sampling stations. Some differences can however be seen e.g. ΣHCH are the most abundant group at the coastal stations (SN and HF) and ΣPCB at the offshore stations (SR5 and F9). The somewhat higher values for ΣDDT in SR5 and dieldrin in F9 also deviate from the general picture.

The high scavenging capacity of SPM, the limited biotransformation in particles and plankton organisms, and the dominating atmospheric input in remote water areas, result in profiles that describe the situations in both the water column and the above air.

The magnitude of the fluxes (ng/cm<sup>2</sup>/year) at each station are presented in Table 3. The stations in the Bothnian Sea have higher fluxes than respective offshore and coastal stations in the Bothnian Bay. Since we believe that air transport is the main source in remote water areas for the analysed compounds, variations in fluxes between the locals might be mainly controlled by differences in fluxes of organic matter and biological production. It is difficult to evaluate variations in biological production between the stations. In general, the particulate flux of organic carbon and biological production decreases from south to north in the Baltic Sea. Notable are the differences in fluxes of SPM between coastal and offshore stations (Table 3). These are approximately a factor five higher in the coastal stations (SN, HF) as compared to the offshore stations (SR5, F9) in the Bothnian Sea and the Bothnian Bay, respectively. Despite this fact the fluxes in respective offshore station is somewhat higher for most of the compound groups.

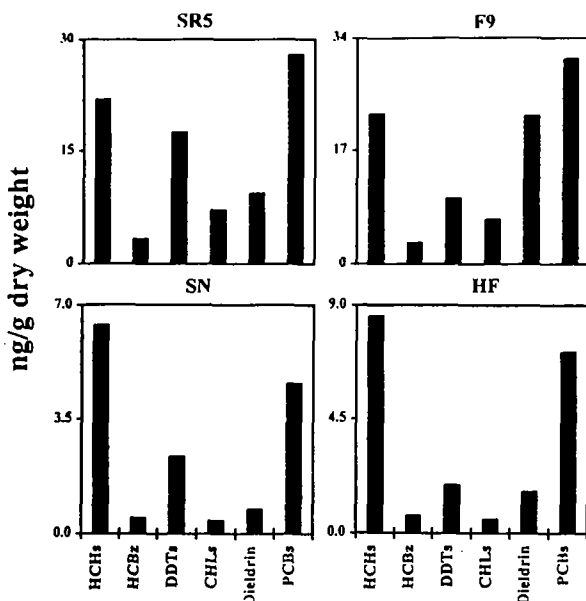


Figure 2. Composition profiles of organochlorine compounds in offshore and coastal locations in the Bothnian Sea (SR5 and SN) and the Bothnian Bay (F9 and HF) in the northern Baltic Sea.

Table 3. Sediment trap fluxes ( $\text{ng}/\text{cm}^2/\text{year}$ ) of some organochlorine compounds in open sea and coastal locations in Bothnian Sea and Bothnian Bay, respectively. Amount settling particulate matter (SPM) ( $\text{g}/\text{cm}^2/\text{year}$ ) (dry weight) are also given for each local. (For the locations of the collection sites, see Fig. 1).

Local	SR5 (n=1)	F9 (n=1)	SN (n=1)	HF mean (n=2)
$\Sigma\text{HCH}$	1.3	0.78	2.0	0.98
Hexachlorobenzene	0.20	0.11	0.15	0.080
$\Sigma\text{DDT}$	1.1	0.34	0.74	0.22
$\Sigma\text{Chlordane}$	0.43	0.23	0.13	0.065
Dieldrin	0.57	0.77	0.23	0.19
$\Sigma\text{PCB}$	1.7	1.1	1.4	0.83
SPM	0.060	0.034	0.31	0.17

n=number of samples

A rough estimation of annual sedimentation of compounds in the total Bothnian Sea and the Bothnian Bay using the fluxes in SR5 and F9, respectively, resulted in approximately 1100 kg  $\Sigma\text{PCB}$  and 700 kg  $\Sigma\text{DDT}$  for Bothnian Sea and 390 kg  $\Sigma\text{PCB}$  and 130 kg  $\Sigma\text{DDT}$  for the Bothnian Bay. In addition, an extrapolation from the SR5 values to total sedimentation in the whole Baltic Sea resulted in approximately 7 ton  $\Sigma\text{PCB}$  and 4 ton  $\Sigma\text{DDT}$ .

In summary, many organochlorine compounds can be found in SPM. A higher organic carbon content in such matter will result in higher adsorption of these compounds. The fluxes of compounds are higher in the Bothnian Sea than the Bothnian Bay probably due to a higher organic carbon content and biological production in the south.

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