

# Seasonal sedimentation of organic matter and contaminants in the Gulf of Finland

Harri Kankaanpää<sup>1)</sup>, Markku Korhonen<sup>2)</sup>, Anna-Stiina Heiskanen<sup>2)</sup> and Anna-Mari Suortti<sup>2)</sup>

<sup>1)</sup> *Finnish Institute of Marine Research, P.O. Box 33, FIN-00931 Helsinki, Finland*

<sup>2)</sup> *Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland*

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The levels of organic contaminants were analyzed in the accumulating material of the Gulf of Finland from April to October in 1996. Settling particles were collected at two locations: GF2 (open sea), and Schepelev (Neva Bay). The contaminants included in the study were: PCBs (7 congeners), DDT and its metabolites, HCHs, chlordanes, trans-nonachlor, and HCB. Sedimentation of total oil and total organic halogens (EOX) was also quantified. The average fluxes of the chemicals were calculated, and the total sedimentation to the whole Gulf of Finland accumulation areas were extrapolated from the flux values obtained for one open sea station. The sedimentation of total particulate carbon, nitrogen and phosphorus was also measured. The contribution of phytoplankton carbon (PPC) and other biogenic material to the total settled carbon was estimated. The sedimentation of the compounds was most intense during the times of increased dry matter accumulation. During the spring, diatoms were dominant in the settled material and phytoplankton comprised about 78% of total settled carbon. During the autumn, the effect of resuspension seemed important. The results from the trap at Schepelev indicated smaller fluxes of PCBs and DDTs than in the open Gulf, but the PCB concentration was high. With the exception of DDTs (90%), the Gulf of Finland was calculated to receive 1–9% of the reported total input of different contaminants to the Baltic Sea.

## Introduction

The ecological status of the Gulf of Finland is vulnerable since the Gulf's small water volume (approx. 1 100 km<sup>3</sup>) is affected by the activities of nearly 20 million people living in the surrounding area. The wastes from a large catchment area

of 420 000 km<sup>2</sup> also threaten the Gulf. With respect to organic contaminants, the most important source areas are the River Neva in the St. Petersburg region (Russia), and the Kymi River in the area of the town of Kotka (Finland), both of which have numerous industrial complexes of large production capacity.

Organohalogenes are known for their high toxicity and environmental persistency (Moore and Ramamoorthy 1984, Landner 1989, Paasivirta 1991), and are therefore a risk to aquatic organisms. Atmospheric deposition and diffuse sources are responsible for the loading of pesticides to the area (Helweg 1992, Østfeldt *et al.* 1994, Pacyna *et al.* 1994, 1996, Baltic Marine Protection Commission 1996, HELCOM 1996 and Baltscheffsky 1997). Approximately half of the emissions of PCBs originate from diffuse sources, including old electrical equipment (Baltscheffsky 1997).

Bottom sediments and sedimenting particles are key matrices for the analysis of contaminants in the Gulf of Finland. The sediments may act both as a temporary and permanent storage of contaminants, depending on the location and type of the sediment deposits. Because of the Gulf of Finland's active sedimentation, large quantities of contaminants are constantly removed from the water column to the sea floor. In order to get a comprehensive picture of the cycling of chemicals that occurs, knowledge of the sedimentation of the contaminants is essential. It has been suggested that eutrophication has accelerated the sedimentation, which may in turn reduce the bioavailability of toxic compounds to aquatic animals (Gunnarsson *et al.* 1995). Therefore, levels of contaminants both in biota and particulate material should be considered.

Seasonality and the species composition of the planktonic community have a crucial impact on sedimentation rates and the settling loss of organic material from the pelagic system in the Baltic Sea (Smetacek *et al.* 1984, Heiskanen and Kononen 1994). How sedimentation of contaminants is related to the seasonality of the downward flux of planktonic organisms is thus important to study *i.e.*, which ecosystem processes and key organisms are related to the deposition of organic contaminants to sediments.

The sources of organic pollution from the Finnish area are better known than those in Russian territory: knowledge of the amounts of organic compounds emitted from the St. Petersburg area is still inadequate. The most potent threat in the Kymi River/Kotka area is the wood processing industry: pulp bleaching, and previously used wood preservatives. These activities have released several harmful substances into the environment, such as polychlorinated dioxins and furans (Koistinen *et al.* 1995),

chlorophenolic compounds, and other chlorinated degradation products of wood lignin.

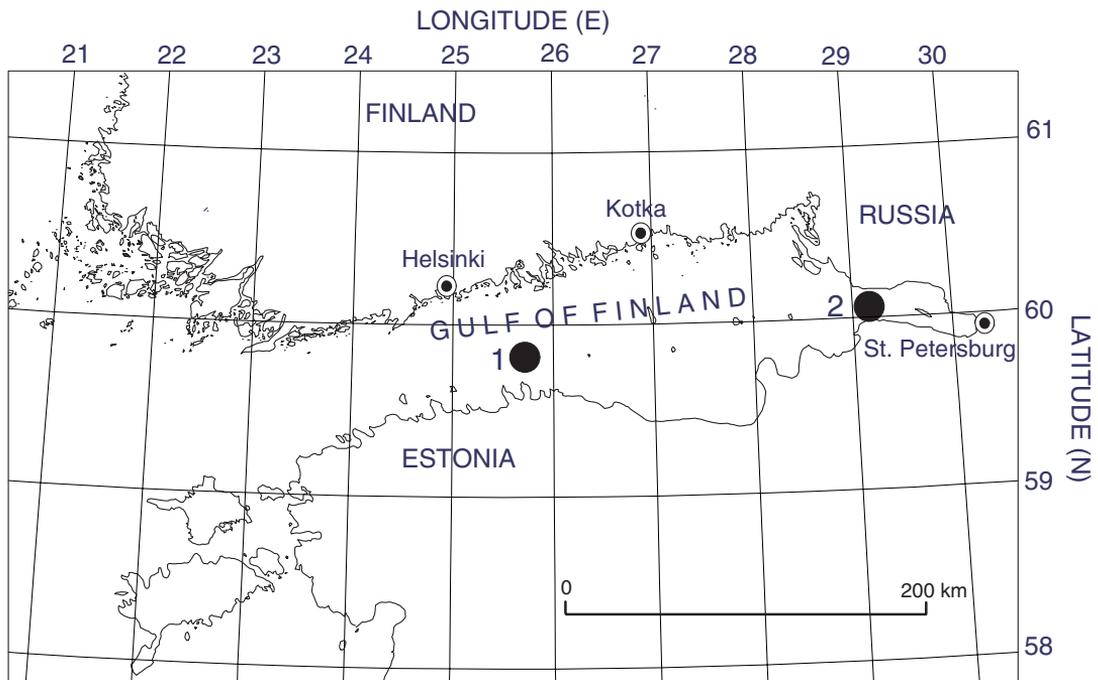
Recent studies have indicated that the sediments around Kotka (Fig. 1) contain 6–120  $\mu\text{g}$  of Cl  $\text{g}^{-1}$  dw, measured as EOX (Kankaanpää *et al.* 1997a), and that traces of organochlorine pollution can be seen up to 30 km from Kotka. Apparently, such a clearly observable elevation in the EOX content cannot be observed in sediments from the Neva Bay area (Kankaanpää and Tissari 1994a), so it seems that organochlorine pollution from the wood processing industry in that area does not exist. Otherwise, the eastern Gulf of Finland is affected by several anthropogenic hydrocarbons coming from traffic, incineration and spills of oil products, for instance the levels of the carcinogenic PAH Benzo[a]pyrene were high (over 90  $\text{ng g}^{-1}$ ) in the Neva estuary in 1994, and still up to 24  $\text{ng g}^{-1}$  in 1996 (Grigori Frumin unpubl.).

There are only a few previous reports on the levels of organohalogen contaminants in Gulf of Finland sediments. Pertilä and Haahti (1986) reported sum PCB levels, as Aroclor equivalents, of 60  $\text{ng g}^{-1}$  dw and sum DDT levels of 15  $\text{ng g}^{-1}$  dw in surface sediments at station XV-1 (SE of Kotka). Due to the lack of data on the sedimentation of contaminants, a series of experiments involving sediment traps were perceived necessary, and carried out within the framework of the International Gulf of Finland Year in 1996. The work was intended to provide information on the deposition rates of PCBs, DDTs, and organochlorine pesticides. This study thus concentrated on the organic substances.

The aims of this study were to obtain estimates of accumulation rates of harmful organic substances in different areas of the Gulf of Finland, and to estimate the share of the pollutants in the Gulf of Finland accumulating in the Baltic Sea. Moreover, the settling flux of phytoplankton and other biogenic particles was quantified from the samples collected from station GF2 in order to find out whether accumulation of organic contaminants was connected to the downward flux of biogenic material.

## Material and methods

The sampling stations were selected for their location at active sedimentation areas. Station GF2 has



**Fig. 1.** Location of the sediment traps in the Gulf of Finland. 1 = GF2. 2 = Schepelev.

been intensively studied since 1993, and the use of this open sea station was therefore agreed upon. The GF2 station represents somewhat of a background area, and probably receives a larger fraction of atmospheric input than more coastally situated stations. The Schepelev station was selected for use by the All-Russia Geological Research Institute, and was served by their research vessel. The location was assumed to reflect the output of contaminants from the St. Petersburg region. Fig. 1 shows the locations of the sediment traps.

### Collection of material

An automatic sediment trap (Technicap PPS 5/2, France) with a collection area of 1.0 m<sup>2</sup> and aspect ratio of 1.6 was placed at station GF2 (59°50.27' N, 25°51.58' E; DGPS navigation) at a depth of 64 m (20 m above bottom), and set to collect sedimenting material at 3-day intervals. The trap was equipped with 250 ml polypropylene bottles (24 pieces), each filled with dilute formaline solution (3%) containing 10 g l<sup>-1</sup> NaCl. The trap was serviced during the 178-day experiment (25 April–20 October 1996)

from R/V Aranda. A smaller single-bottle trap (opening area 0.0152 m<sup>2</sup>, aspect ratio 4, 250 ml collection bottle) was placed in the same mooring, 10 m above the sediment surface. Material was collected in this trap during each period between the deployment and retrieval of the automatic trap (three intervals of 42, 70 and 66 days). The periods of collection were: 25 April–16 May, 16–25 May, 25 May–6 June, 6–27 June, 27 June–18 July, 18 July–15 August, 15 August–14 September, 14–26 September, and 26 September–20 October 1996.

A Russian single-bottle trap (upper diameter 1.2 m, 1 l collection bottle) was placed in the vicinity of the Schepelev Cape (Fig. 1), Neva Bay at 60°03.85' N, 29°08.02' E (GPS navigation). The depth of the trap was 29 m (10 m above the bottom). Material was collected from 22 July–30 October 1996.

### Pretreatment of samples

After the collection of the samples, they were stored in a refrigerator at +4°C and transferred to the laboratory. Each sample was agitated to obtain homoge-

neous suspension, and an aliquot (2 ml) was taken for the determination of planktonic species (GF2 upper trap only). The aliquot was taken into account when calculating total accumulation rates and fluxes.

The sediment suspension was centrifuged at 2 000 rpm for 10 minutes (Heraeus Megafuge 2.0R), and the excess solution was removed. The particulate material was lyophilized (Edwards Freeze-dryer, Super Modulyo) for at least 24 h, and the dry weight was subsequently measured. Occasional individuals of *Monoporeia affinis* were removed with forceps. The dried material was homogenized using a planetary mill (Fritsch pulverisette 5) with zirconium oxide balls and bowls. Finally, part of the 3-day fractions (automatic trap) were combined to form nine samples that were subjected to chemical analyses. The three samples from the single trap at station GF2 were analyzed separately. One sample was obtained from the Schepelev station, and treated accordingly.

### Analysis of carbon, nitrogen and phosphorus

Material from the automatic trap and from the first period of the lower GF2 trap was analyzed. The small amount of material from the lower trap did not permit further nutrient analyses. The samples were combusted in oxygen, and the content of total particulate carbon (PC), not total organic carbon, and hydrogen (not reported) was measured using IR detection. Nitrogen was measured with a TC detector. The instrument used was the Leco CHN-600.

Determination of phosphorus was carried out in CEM MDS-2000 microwave digestion equipment using the microwave assisted nitric acid digestion draft EPA method 3051. The analysis of phosphorus was made with an ICP-AES using a Thermo Jarrell Ash Polyscan 61 E instrument.

### Quantification of settled phytoplankton biomass and other biogenic material

Subsamples for microscopic enumerations from station GF2 were combined to represent nine periods covering the seasonal cycle from 24 April until 20 October in 1996. The combined samples were diluted and the 3–5 most dominant phytoplankton species were enumerated from subsamples by using an

inverted microscope. At a minimum of 500 counting units in total, and at least 100 units of the 1–3 most dominant species were enumerated. A minimum of 20 random fields were enumerated (magnification  $\times 200$ ). The species' biovolumes and carbon contents were calculated according to the Recommendations of the Baltic Marine Biologists (Edler 1979), and those of dinoflagellate cysts (*Scrippsiella hangoei*) according to Heiskanen (1993).

Furthermore, subsamples of 2 to 5 ml were sieved through a 50 mm plankton net and concentrated by using the Utermöhl-method (Utermöhl 1958). Calanoid and harpacticoid copepods, cladocerans, mesozooplankton resting eggs and fecal pellets of planktonic crustaceans were enumerated by an inverted microscope (magnification  $\times 125$ ). The biomass of mesozooplankton was estimated by converting the biovolumes of the species to carbon by assuming carbon content of  $0.052 \text{ pg C m}^{-3}$  (Mullin 1969). Fecal pellet carbon contents were estimated by measuring the cylindrical or spheroidal dimensions of pellets and multiplying the obtained pellet volume by 0.11 (Bathmann *et al.* 1987).

### Analysis of extractable organic halogen (EOX)

The method is based on the procedure by Martinsen *et al.* (1988), as described by Kankaanpää and Tissari (1994b). An exact amount of 2.6–3.1 g (except Schepelev; 1.04 g) of sediment was placed in a Sovirel bottle and extracted with 75 ml of cyclohexane-isopropanol (4:1 v/v) first 2 h in ultrasonicator (Branson 3200) and then 16 h in a vertical rotator (Braun Certomat M) at 100 rpm. The mixture was centrifuged at 1 500 rpm for 10 minutes, and the supernatant was washed two times with 25 ml of 0.2 M  $\text{KNO}_3$  (pH 2) to remove inorganic halides. The extracts were concentrated using a rotavapor (Heidolph), and finally with nitrogen flow to a final volume of 1.9–4.6 ml (exact volume measured). All the solvents were HPLC grade and reagents p.a. grade.

The halogen content was determined using a Euroglas ECS 2000 halogen analyser (Euroglas BV, Delft, the Netherlands). The extracts (two or three replicates) were combusted in  $\text{O}_2$  at 850 C. The halogen content was expressed in chlorine equivalents. The quality of the analyses was assured by using standard solutions of 4-chlorophenol.

## Analysis of total oil

The oil analyses were carried out using the method of Semenov (1977). The determination of total oil content was carried out using extraction of the dried material (about 0.1 g) with  $\text{CCl}_4$  for one hour. The extract was filtered using a medium-wide-pore filter (cleaned with  $\text{CCl}_4$ ), and then applied to a column filled with activated alumina. The hydrocarbons were eluted from the column, and quantified using IR detection in the wavelength range of 3.5–3.7  $\mu\text{m}$  (2 700–2 860  $\text{cm}^{-1}$ ). An average value of the concentration range reported by the Russian laboratory for each sample was used for flux calculations.

## Analysis of PCBs, DDTs and organochlorine pesticides

A subsample of 1 to 4 g was weighed accurately and placed in the beaker and extracted three times successively with 100 ml of acetone:hexane (1:1, v/v) for three minutes with an Ultrasonic Cell Disruptor (Branson Sonifier B-15). After each extraction the sample was centrifuged at 3 000 rpm for 7 minutes (Heraeus Megafuge 1.0). The extracts were combined and the solvent was evaporated to near dryness in a rotavapor (Büchi RE-121) and redissolved into isooctane. The internal standard 1,2,3,4-tetrachloronaphthalene (Ultra Scientific) was added and the sample was purified with concentrated sulfuric acid until the solvent phase was colourless. Additionally, the elemental sulfur in sediment extracts was removed with copper chips. The sample was concentrated to a final volume of approximately 0.5 ml with a nitrogen blow-down technique. All the solvents and reagents were p.a. grade or better.

Organochlorine compound analysis was performed on a Hewlett-Packard gas chromatograph (Model 5890 Series II, Waldbronn, Germany) equipped with two  $^{63}\text{Ni}$  electron capture detectors (ECDs), two capillary columns HP-1701 and HP-5 (60 m  $\times$  0.25 mm i.d., film thickness 0.25  $\mu\text{m}$ ) and a HP7673 automatic sampler. Helium was the carrier gas with argonmethane (95%:5%, v/v) as the detector make-up gas. The injector and detector temperatures were 270 °C and 300 °C, respectively. The oven temperature programme was 90 °C for 3 min,

30 °C  $\text{min}^{-1}$  to 215 °C for 42 min and 5 °C  $\text{min}^{-1}$  to 270 °C for 10 min. Compounds were identified from both columns by comparing the relative retention times with known compounds, 1,2,3,4-tetrachloronaphthalene as an internal standard. Quantification is based on a standard mixture prepared by weighing neat crystals (Dr. Ehrensdoerfer, Germany) and dissolving them individually in isooctane, then mixing them together to make up the final solution in isooctane. Technical mixtures of Pyralene 3010 (Prodelec), Clophens A50 and A60 (Bayer) were only chromatographed for comparing the PCB pattern in the samples. These are considered to be similar to Aroclors 1242, 1254 and 1260, respectively. The analyzed CB congeners were CB 28, CB 31, CB 52, CB 101, CB 110, CB 118, CB 153, CB 105, CB 138, CB 187, CB 156 (not detected at station GF2), CB 180 and CB 170. Additionally CB 8 and CB 18 were analyzed from the Schepelev sample. The sum of seven CBs (sum7CB) consists of CB28, CB52, CB101, CB118, CB138, CB153 and CB180.

## Extrapolated depositions for the Gulf of Finland

Average flux value for each parameter was calculated using equation (1):

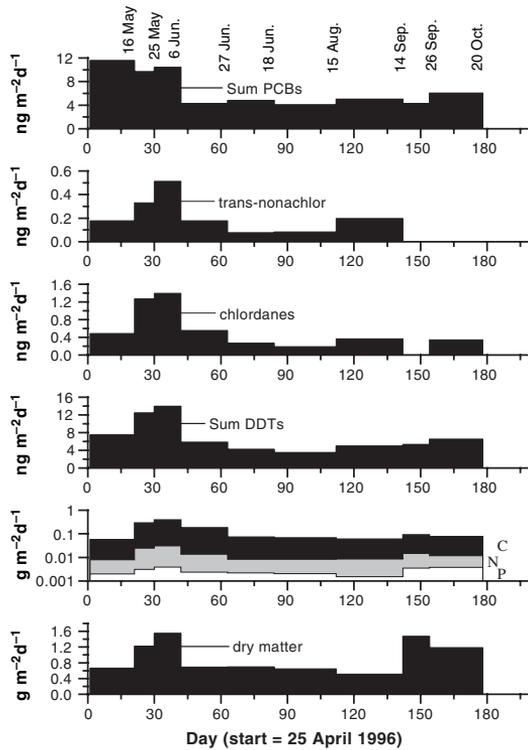
$$F_{\text{av}} = \sum_{i=1}^n m_i c_i t^{-1} A^{-1}, \quad (1)$$

where  $F_{\text{av}}$  is the average flux for each parameter,  $n$  is the number of collection periods,  $m$  is the amount of particulate matter accumulated during the collection period,  $c$  is the concentration of each parameter during the collection period,  $t$  is the duration of the experiment and  $A$  is the collection area of the sediment trap.

Total sedimentation at the GF2 station (automatic trap) was also calculated, and the total annual sedimentation estimate was calculated according to equation (2) and assuming constant sedimentation throughout the year. An estimate of 30% of active accumulation bottoms in the Gulf was used (Boris Winterhalter, Geological Survey of Finland, pers. comm.)

$$m_{\text{tot}} = F_{\text{av}} \times 365 \text{ d} \times 3 \times 10^{10} \text{ m}^2 \times 0.3, \quad (2)$$

where  $m_{\text{tot}}$  is the total annual sedimentation for each parameter, 365 d is number of days,  $3 \times 10^{10} \text{ m}^2$  is the area of the Gulf of Finland and 0.3 is the share of active accumulation bottoms.



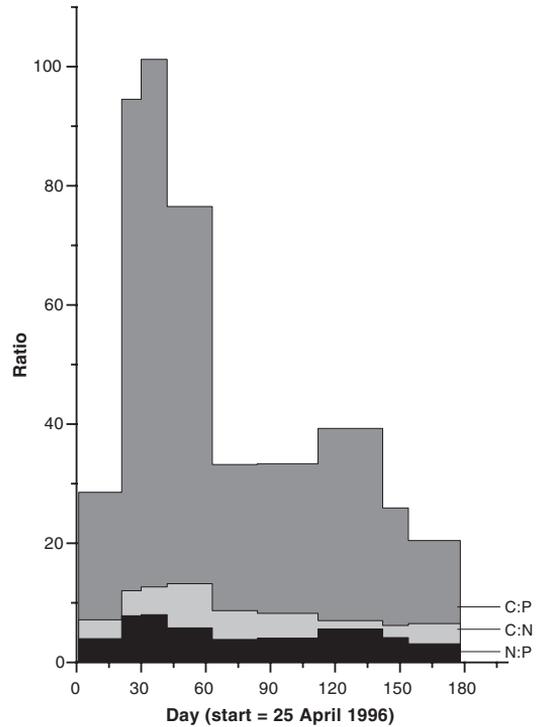
**Fig. 2.** Sedimentation of PCBs ( $\text{ng m}^{-2} \text{d}^{-1}$ ), trans-nonachlor ( $\text{ng m}^{-2} \text{d}^{-1}$ ), chlordanes ( $\alpha + \gamma + \text{oxy}$ ,  $\text{ng m}^{-2} \text{d}^{-1}$ ), DDTs (DDE+DDD+DDT,  $\text{ng m}^{-2} \text{d}^{-1}$ ), carbon ( $\text{g m}^{-2} \text{d}^{-1}$ ), nitrogen ( $\text{g m}^{-2} \text{d}^{-1}$ ), phosphorus ( $\text{g m}^{-2} \text{d}^{-1}$ ), and dry matter ( $\text{g m}^{-2} \text{d}^{-1}$ ) in the automatic trap at station GF2 during the experiment (25 April–20 October 1996). All Y axis values start from the X axis. Missing values indicate fluxes below the limit of detection.

## Results

### Accumulation in the open Gulf of Finland (station GF2)

#### Flux of particles and primary elements

The flux of total particulate material was 0.50–1.6, on average  $0.85 \text{ g m}^{-2} \text{d}^{-1}$ . Most of the material settled during the maxima, more during the second one (Fig. 2, lowest graph). Extrapolated total sedimentation was  $2.8 \times 10^6 \text{ t}$ . Most of the carbon ( $0.06\text{--}0.39$ , av.  $0.12 \text{ g m}^{-2} \text{d}^{-1}$ ) accumulated during the first maximum, less during the second one. Total sedimentation was  $355 \times 10^3 \text{ t C yr}^{-1}$ , and during the experiment  $170 \times 10^3 \text{ t C}$ . Most of the nitrogen ( $0.008\text{--}0.031$ , av.  $0.012 \text{ g m}^{-2} \text{d}^{-1}$ ) accumulated primarily during the first maximum, less during the sec-



**Fig. 3.** The C:P, C:N, and N:P ratios (from up to down) at station GF2 (automatic trap) during the experiment (25 April–20 October 1996). All Y axis values start from the X axis.

ond one. Total sedimentation was  $41\,000 \text{ t N yr}^{-1}$ , and  $20\,000 \text{ t N}$  during the experiment. Phosphorus ( $0.0015\text{--}0.0039$ , av.  $0.0025 \text{ g m}^{-2} \text{d}^{-1}$ ) sedimentation showed two maxima, and sedimentation during the second maximum was slightly stronger. Total sedimentation was  $8\,200 \text{ t P yr}^{-1}$ , or  $4\,000 \text{ t P}$  during the experiment. C:N varied between 6.2 and 13.2; a maximum occurred at first bloom. The C:P ratio was from 20 to 100; two maxima. N:P varied from 3.8 to 8.0, with two maxima. With respect to carbon, most of the nitrogen and phosphorus was deposited before and after the maxima. See Fig. 2 for fluxes and Fig. 3 for C:N:P relations. The flux ranges are listed in Table 1, and extrapolated sedimentation values in Table 2.

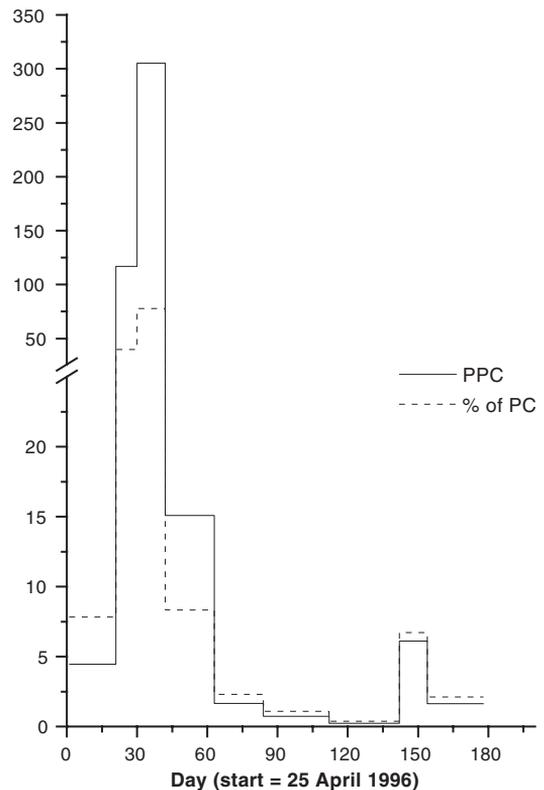
#### Phytoplankton

Sedimentation of phytoplankton carbon (PPC) was highest at the end of May and in early June (between 25 May and 6 June). The average daily PPC

flux ( $305 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) was estimated to contribute about 78% of total particulate carbon (PC) sedimentation during the same period (Fig. 4). Thereafter, the settling flux of phytoplankton declined and remained low for the rest of the study period. Diatoms (Bacillariophyceae) contributed more than 98% of the total settled phytoplankton biomass, the chain forming diatom *Achnanthes taeniata* Grönow being the most dominant species (about 70% of total PPC). Other important species were *Chaetoceros* spp., *Diatoma tenuis* Agardh, and *Skeletonema costatum* (Greville) Cleve corresponding to 10, 10, and 8% of total PPC, respectively, during the peak PPC sedimentation period at the end of May (Table 3). The same species dominated the settled material throughout the spring period and were still numerous in June when PPC sedimentation had already declined.

Numbers of the dinoflagellate *Scrapsiella hangoei* (Schiller) Larsen resting cysts started to increase in late May and peaked in June when total PPC was 15% of the PC sedimentation (Table 3). Their contribution to the total settled PPC (up to 70% of total PPC) was significant only after the major diatom sedimentation was already over.

Cyanobacteria (especially *Aphanizomenon* cf. *flos-aquae* Ralfs ex. Bornet & Flahaut) were abundant in settled material during the early autumn (15 August–14 September; Table 3). However, the flux of PPC was less than 2% of total settled PC for most of the summer period (Fig. 4). In late September (14–26), the flux of diatoms (about 80% of PPC) consisted of *Skeletonema costatum*, (Table 3) increased slightly, contributing to 7% of the total settled PC (Fig. 4).



**Fig. 4.** Sedimentation of phytoplankton carbon (PPC;  $\text{mg C m}^{-2} \text{ d}^{-1}$ ) and contribution (percentage) of PPC to total settled carbon (dashed line; % of PC) between 26 April and 20 October 1996 at station GF2

#### Mesozooplankton and other biogenic material

All (combined) sediment trap samples from GF2 were checked for possible swimmer contamina-

**Table 1.** Range of fluxes and average fluxes (in parenthesis) for dry matter and contaminants at different trap stations. SCP = Schepelev. N.D. = not detected. N.A. = not analyzed.

Parameter	Location (depth)		
	GF2 (64 m)	GF2 (74 m)	SCP (29 m)
Dry matter ( $\text{g m}^{-2} \text{ d}^{-1}$ )	0.50–1.6 (0.85)	3.0–4.4 (3.7)	0.03
t-nonachlor ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	0.08–0.51 (0.34)	0.4–1.0 (0.7)	N.D.
Chlordanes ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	0–1.4 (0.45)	1.6–3.1 (2.3)	0.02
HCHs ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	1.4–14.3 (3.4)	6–18 (11)	0.03
HCB ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	0.23–0.93 (0.51)	1.8–3.2 (2.6)	0.01
s7PCBs ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	4.3–11.6 (6.2)	40–58 (50)	3.3
DDTs ( $\text{ng m}^{-2} \text{ d}^{-1}$ )	3.5–14.0 (6.5)	31–37 (34)	0.23
EOX ( $\mu\text{g m}^{-2} \text{ d}^{-1}$ )	1.4–21.6 (6.1)	N.A.	0.49
Total oil ( $\mu\text{g m}^{-2} \text{ d}^{-1}$ )	220–900 (320)	N.A.	N.A.

tion due to diurnal vertical migration of copepods and cladoceran zooplankton. Calanoid copepods (mainly *Acartia* spp. and *Eurytemora* sp. adults and copepodits) were found in trap material during the late summer and early autumn periods. The maximum number enumerated was approx. 230 copepods  $m^{-2} d^{-1}$ . Cladocerans (such as *Podon*

**Table 2.** Extrapolated total sedimentation for the Gulf of Finland (kg) according to the results from the automatic GF2 trap, and percentage of the total input estimated for the whole Baltic Sea (from <sup>1</sup>Baltscheffsky 1997; <sup>2</sup>Baltic Marine Protection Commission 1996). Cl-equiv = calculated sedimentation of chlorine from PCB, DDT and pesticide data.

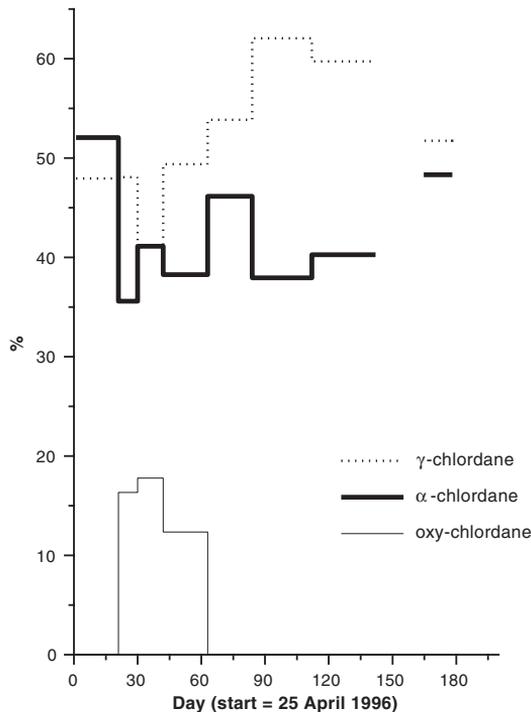
Parameter	Total (kg) exp	Annual	% of input to the Baltic Sea (annually)
Dry matter	$1.4 \times 10^9$	$2.8 \times 10^9$	—
C	$1.7 \times 10^8$	$3.6 \times 10^8$	—
N	$2.0 \times 10^7$	$4.1 \times 10^7$	—
P	$4.0 \times 10^6$	$8.2 \times 10^6$	—
Trans-nonachlor	0.25	0.51	—
Chlordanes	0.75	1.5	—
HCHs	5.3	10.9	—
$\gamma$ -HCH	1.9	4.0	1.5 <sup>1)</sup>
HCB	0.90	1.6	—
s7PCBs	10.0	20.6	3 <sup>1)</sup>
Total PCB	33	60	9 <sup>1)</sup>
DDTs	10.0	20.6	90 <sup>1)</sup>
EOX	9 700	20 000	—
Cl-equiv	19	42	—
Total oil	$510 \times 10^3$	$1.06 \times 10^6$	1–6 <sup>2)</sup>

*polyphemoides*, *Evadne nordmannii*, and *Bosmina coregoni maritima*) were found in trap material throughout the summer period reaching the maximum numbers of approx. 200 cladocerans  $m^{-2} d^{-1}$ . Harpacticoid copepods were also found in trap material but always in very low numbers ( $< 50$  harpacticoids  $m^{-2} d^{-1}$ ). The maximum biomass of the possible swimmers (i.e. the total biomass of the species mentioned above) was estimated to be 0.54 mg C  $m^{-2} d^{-1}$ , corresponding to less than 1% of total settled PC. Thus it was evident that contamination of organic material fluxes due to vertically migrating crustacean zooplankton was insignificant in the measurements of total carbon flux.

Vertical flux of fecal pellets was elevated during two study periods, namely between 25 April and 16 May, and in the autumn between 29 September and 22 October. During the first period, pellets of an oval shape and generally less than 200  $\mu m$  long and less than 40  $\mu m$  in diameter (presumably deriving from copepods), were frequent in trap samples reaching the total pellet volume flux of 0.1  $mm^3 m^{-2} d^{-1}$  and estimated to correspond to a C-flux of 10  $\mu g C m^{-2} d^{-1}$ . In autumn, pellets of a cylindrical shape, a diameter of approx. 100  $\mu m$  and a length varying between 100  $\mu m$  and 700  $\mu m$  (presumably deriving from mysids), became numerous in trap material. The volume flux of pellets was approx. 3.7  $mm^3 m^{-2} d^{-1}$ , corresponding to a total carbon flux of 0.41 mg C  $m^{-2} d^{-1}$ . However, even the maximum flux of feces in the autumn was less than 1% of total PC flux during the same period, indicating that the settling flux of crustacean

**Table 3.** Sedimentation of the principle phytoplankton species and groups (Flux: mg C  $m^{-2} d^{-1}$ ) and their share of the total phytoplankton carbon flux at station GF2 (as a percentage, %) (*A. taeniata* = *Achnanthes taeniata*, *S. hangoei* cysts = *Scrippsiella hangoei* cysts, Aphaniz. = *Aphazomenon* cf. *flos-aquae*) during the different sediment trap collection periods in 1996.

Period	<i>A. taeniata</i>		Total diatoms		<i>S. hangoei</i> cysts		Aphaniz.		Total cyanobacteria	
	Flux	%	Flux	%	Flux	%	Flux	%	Flux	%
25 Apr.–16 May	1.3	29	4.5	100						
16–25 May	86	73	117	100	0.1	0.1				
25 May–6 Jun.	216	71	304	99	1.7	0.6				
6–27 Jun.	10	66	11	76	3.6	24				
27 Jun.–18 Jul.	0.4	24	0.1	0.5	1.2	72				
18 Jul.–15 Aug.	0.1	19	0.3	40	0.4	60				
15 Aug.–14 Sep.			0.03	12			0.14	64	0.20	88
14–26 Sep.			5.0	81	0.3	4.4	0.2	3.4	0.9	14
26 Sep.–20 Oct.			1.2	72	0.2	12			0.3	16



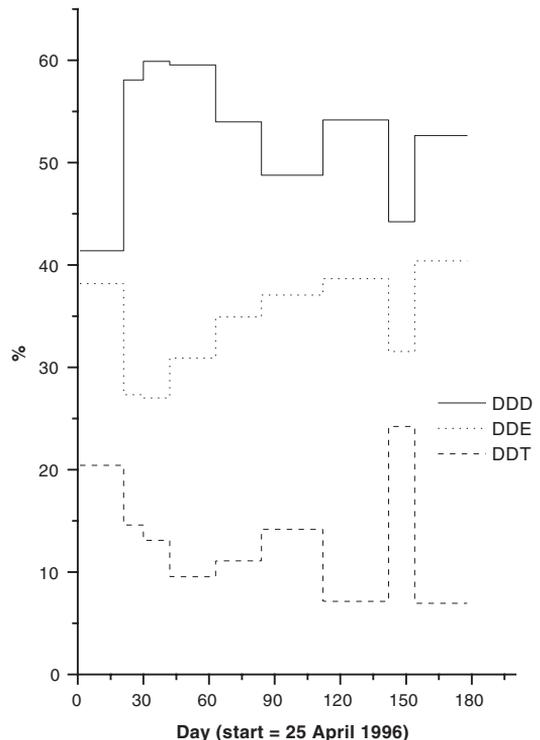
**Fig. 5.** Proportions (%) of  $\gamma$ -,  $\alpha$ -, and oxy-chlordane at station GF2 (automatic trap) during the experiment (25 April–20 October 1996). Zero values indicate levels below the limit of detection.

feces was insignificant in comparison to the vernal phytoplankton flux and detrital carbon flux during summer.

Another type of biogenic material, occasionally abundant in the settled material were mollusc (*Bivalvia*) larvae in early summer (4 600 larvae  $m^{-2} d^{-1}$ ) and mesozooplankton resting eggs (having a diameter of approx. 50  $\mu m$  and a total flux up to 13 000 eggs  $m^{-2} d^{-1}$ ) in late summer and autumn. Rotifer thecae (*Keratella* spp.) were also numerous in the settled material during summer. Their carbon contents were not estimated, but it was unlikely that their contribution to the total flux would have been more than 1% of total PC flux at any time of the study.

### Pesticides

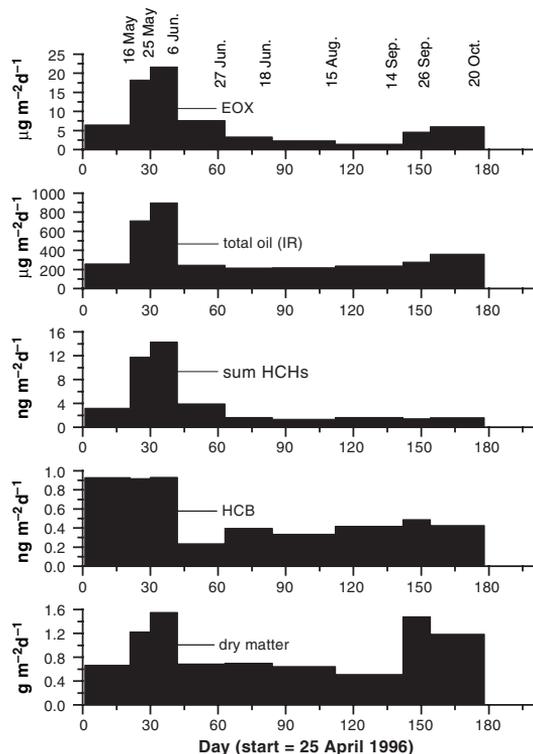
Most of trans-nonachlor (0.08–0.51, the average 0.34  $ng m^{-2} d^{-1}$ ; Table 1) accumulated during the first bloom; less before the second accumulation maximum (Fig. 2). Extrapolated amounts of trans-



**Fig. 6.** Proportions (%) of DDE, DDD, and DDT at station GF2 (automatic trap) during the experiment (25 April–20 October 1996).

nonachlor were 0.25 kg during the experiment, and 0.51  $kg yr^{-1}$  (Table 2). Chlordanes (0–1.4, on average 0.45  $ng m^{-2} d^{-1}$ ; Table 1) accumulated predominantly during the first maximum (Fig. 2). The amounts of isomers were  $\gamma > \alpha > oxy$ , oxy-chlordane being observed only during the first accumulation maximum (Fig. 5). The proportion of the  $\gamma$  isomer increased during the experiment while the amount of  $\alpha$  isomer decreased. Yearly sedimentation was 1.5 kg, and during the experiment 0.75 kg (Table 2).

The highest levels of DDTs (3.5–14.0, on average 6.5  $ng m^{-2} d^{-1}$ ; Table 1) were observed during the first maximum, as illustrated in Fig. 2. Their amounts decreased thereafter, and increased during the second accumulation maximum. Metabolites of DDT predominated, so that  $DDD > DDE > DDT$ . Generally, the amounts of DDT decreased during the experiment, but temporarily increased during the second maximum. Apart from the beginning of the experiment, the flux of DDE increased and that of DDD decreased (Fig. 6). The extrapolated sedimentation of DDTs was 20.6  $kg yr^{-1}$  or 10.0 kg during

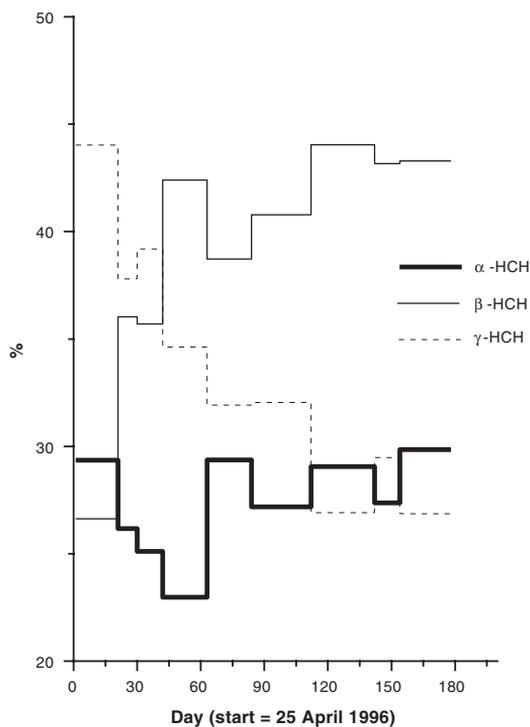


**Fig. 7.** Sedimentation of EOX ( $\mu\text{g Cl m}^{-2} \text{d}^{-1}$ ), total oil ( $\mu\text{g m}^{-2} \text{d}^{-1}$ ), HCHs ( $\text{ng m}^{-2} \text{d}^{-1}$ ), HCB ( $\text{ng m}^{-2} \text{d}^{-1}$ ), and dry matter ( $\text{g m}^{-2} \text{d}^{-1}$ ) to the automatic trap at station GF2 during the experiment (25 April–20 October 1996).

the experiment (Table 2).

The accumulation of HCHs (1.4–14.3, on average  $3.4 \text{ ng m}^{-2} \text{d}^{-1}$ ; Table 1) occurred predominantly during the first particulate matter accumulation maximum (Fig. 7). The extrapolated value was  $10.9 \text{ kg yr}^{-1}$ , or  $5.3 \text{ kg}$  during the experiment. In the beginning of the experiment, the dominating HCH component was  $\gamma$ -HCH, but  $\beta$ -HCH was the most abundant thereafter, and the amount of  $\gamma$ -HCH decreased (Fig. 8). The share of lindane ( $\gamma$ -HCH) was on average  $1.2 \text{ ng m}^{-2} \text{d}^{-1}$ , or  $1.9 \text{ kg}$  in total during experiment ( $4.0 \text{ kg}$  yearly, Table 2).

The sedimentation of HCB ( $0.23$ – $0.93$ , on average  $0.51 \text{ ng m}^{-2} \text{d}^{-1}$ ; Table 1) happened before and during the first bloom, but was quite even throughout the experiment (Fig. 7). Sedimentation slightly increased again during the second particulate matter accumulation maximum. Total sedimentation was  $1.6 \text{ kg yr}^{-1}$ , or  $0.90 \text{ kg}$  during the experiment (Table 2). The observed pesticide concentrations are summarised in Table 4.



**Fig. 8.** Proportions (%) of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCH at station GF2 (automatic trap) during the experiment (25 April–20 October 1996).

### PCBs

In this study the sum of PCBs includes the environmentally most investigated congeners CB 28, CB 52, CB 101, CB 118, CB 138, CB 153 and CB 180. Other PCB congeners were also investigated but they are not reported here. The s7PCBs ( $4.3$ – $11.6$ , on average  $6.2 \text{ ng m}^{-2} \text{d}^{-1}$ ; Table 1) showed the highest sedimentation before and during the first particulate matter accumulation maximum, decreasing thereafter but increased slightly around the second maximum (Fig. 2). Total sedimentation was  $20.6 \text{ kg yr}^{-1}$ , and during the experiment  $10.0 \text{ kg}$  (Table 3). See Table 4 for PCB concentrations.

### Total chlorine content according to individual organochlorine compounds

The sedimentation of chlorine that can be explained by the PCBs, DDTs, and pesticides was

calculated by taking into account the content of chlorine in the compounds. The percentages (by weight) used were 63% (PCBs), 50% (DDTs), 72% (t-nonachlor), 70% (chlordanes), 73% (HCHs), and 75% (HCB). An estimate for 42 kg of Cl yr.<sup>-1</sup> was thus obtained (Table 2).

## EOX

Sedimentation of total organic halogen (EOX; 1.4–21.6, on average 6.1 g  $\mu\text{m}^{-2}\text{d}^{-1}$ ; Table 1) at station GF2 was largest during the spring maximum (Fig. 7). Extrapolated sedimentation during the experiment (178 d) was 9 700 kg, and annually 20 000 kg (Table 2). See Table 4 for EOX concentrations.

## Oil Products

Total oil (220–900, on average 320  $\mu\text{g m}^{-2}\text{d}^{-1}$ ; Table 1) showed the strongest sedimentation during the first bloom, and less during the second maximum (Fig. 7). The extrapolated annual oil sedimentation for the gulf area of accumulation was 1 060 t, or 510 t during the experiment (Table 2). See Table 4 for total oil concentrations.

## Results of the single-bottle trap at station GF2

The same parameters (except EOX) were determined from the lower sediment trap at station GF2. The summarized results are listed in Table 1. The deposition rates of organochlorine compounds and elements were higher than observed for the automated conical trap 10 m above this cylindrical trap. All the concentrations were at the same level as the upper trap, but the particle accumulation rate was about four times higher, and the sedimentation of contaminants around five times higher. HCHs were deposited about three times more efficiently.

## Sedimentation at Schepelev

Dry weight accumulation was only 0.03 g  $\text{m}^{-2}\text{d}^{-1}$  (Table 1) but may be slightly underestimated since part of the accumulated material could not be re-

moved from the collection bottle. The effect of this error is however smaller than 10%. The concentration of PCBs (7 congeners) was high: 110 ng  $\text{g}^{-1}\text{dw}$ , but taking into account the rather small dry weight accumulation of only 3.1 g, the final deposition rate of PCBs was 3.3 ng  $\text{m}^{-2}\text{d}^{-1}$  (Table 2). This is of the same order as at station GF2. However, the elevated concentration, and the PCB pattern suggest the effect of recent input of the technical Aroclor mixture (type 1242 and 1254). Also, two CB congeners, CB 8 and CB 18, not found in other samples, were detected. With the inclusion of these congeners, the total flux was 5.5 ng  $\text{m}^{-2}\text{d}^{-1}$  (average at GF2). Deposition of DDT and its metabolites, and other pesticides was much lower compared with open sea levels. The concentrations of HCB,  $\gamma$ -HCH, chlordanes, and DDTs were however of the same order. Only  $\alpha$  and  $\beta$  HCH occurred at slightly lower levels than at GF2.

Concentration of EOX reached 16  $\mu\text{g g}^{-1}\text{dw}$ , which was higher than the average EOX level of 7.6  $\mu\text{g g}^{-1}\text{dw}$  at GF2. Here also, the flux was low, only 0.5  $\mu\text{g m}^{-2}\text{d}^{-1}$ , due to a low particle accumulation rate.

## Discussion

### Sedimentation of biogenic material in relation to contaminant sedimentation

The sinking flux of organic matter was largely mediated by the sedimentation of diatoms (mainly

**Table 4.** Average concentrations and concentration ranges of organic contaminants (ng  $\text{g}^{-1}\text{dw}$ , except for EOX and total oil;  $\mu\text{g g}^{-1}\text{dw}$ ) at station GF2 (automatic trap) during the experiment (25 April–20 October 1996). N.D. = not detected.

Parameter	Average	Range
Trans-nonachlor	0.25	N.D.–0.39
Chlordanes	0.60	N.D.–1.0
HCHs	3.7	0.95–9.6
$\gamma$ -HCH	1.3	0.3–3.6
HCB	0.6	0.3–1.4
s7PCBs	8.0	2.9–17.5
Total PCB	27	9.7–58
DDTs	7.7	3.6–11.3
EOX	6.6	2.7–14.9
Total oil	380	190–580

*Achnanthes taeniata*) during the spring period. Such phenomenon is one result of a generation of transparent exopolymer particles (TEP), subsequent aggregation and rapid sinking from the euphotic surface layer (Alldredge *et al.* 1993, Crocker and Passow 1995).

Rapid sedimentation of vernal diatoms at the end of the spring bloom is a typical phenomenon in the most boreal and temperate coastal waters. In the coastal Gulf of Finland *A. taeniata* is often an important species in the settled material at the end of spring bloom as well (Heiskanen and Kononen 1994).

Resting cysts of the common vernal dinoflagellate *Scripsiella hangoei* were abundant in the settled material during June (Table 3). Their maximum settling flux was considerably lower (approx.  $5.7 \times 10^6$  cysts  $m^{-2} d^{-1}$ ) than in the coastal Gulf of Finland, where fluxes up to  $700 \times 10^6$  cysts  $m^{-2} d^{-1}$  have been measured (Heiskanen 1993).

Several diatom species have been shown to contain high levels of lipids when nutrients are depleted from the growth medium (Taguchi *et al.* 1987, Tadros and Johansen 1988). Elevated lipid concentrations of particulate matter have been also observed upon termination of the vernal diatom bloom in the Gulf of Finland (Autio *et al.* 1990). This would imply that settling diatom debris would have high lipid content when the major part of biomass is sinking after nutrients are exhausted from the surface layer.

Cyanobacteria may form extensive blooms and surface accumulations in the Baltic Sea during summer (Kahru *et al.* 1994), but their contribution to the downward flux of organic matter is generally negligible (Heiskanen & Kononen 1994). At the end of August, high numbers of *Aphanizomenon* were found in the settled material (Table 3). However, the contribution of PPC was less than 1% of the total particulate carbon settled during the same period.

Crustacean swimmers can form a considerable part of organic carbon flux (Lee *et al.* 1992). During the present study, however, the numbers of crustacean zooplankton, capable of extensive vertical movements in the water column, was low in sediment trap material. Their estimated contribution to the total particulate carbon flux was always less than 1%. Thus the flux of organic material (C, N, or P) or downward transport of organic contaminants could not have been due to the accumulation of vertically

migrating organisms.

The flux of large feces in late autumn may have been connected to the abundance of organisms producing these (presumably originating from Mysids) and simply to the high sinking rates of such large pellets. Feces have been anticipated to be a significant part of the downward flux of organic carbon (Honjo and Roman 1978, Angel 1984). However, in the central Gulf of Finland (GF2) the contribution of fecal carbon was always less than 1% of total PC flux being thus shadowed by the contribution of PPC in spring and that of detrital carbon in summer and autumn.

### Effect of resuspension

The settled material from autumn contained only 6–12% carbon compared with 26% during the spring bloom (result not shown). This, together with the low contribution of PPC during the autumn, suggests that the settled material from autumn contained substantial amounts of resuspended material. This is also evidenced by the abrupt change in DDT, DDD and DDE proportions, which approached the percentages prevailing during the spring bloom (Fig. 6). However, since bottom sediments were not analyzed, this is not concrete evidence. Although the main trap was 20 m above the sea-floor, the strong autumn winds were capable of generating currents strong enough to resuspend the sediments. Looking at the high flux rates for the lower GF2 trap, where the carbon content was only 10% during the first 42-day interval, resuspension to at least 10 m above the bottom seems to take place, although a focussing effect may also play a part. Furthermore, the traps had different aspect ratios (1.6 and 4), which may affect the retaining of particles. In the light of these observations, the installation of the traps may need to be planned so that the effect of resuspension is minimized. On the other hand, it is also important to estimate the contribution of secondary effects on the accumulating matter. Such studies in the Gulf of Bothnia indicated that, episodically, the resuspension had a great effect on the total sedimentation at one metre above bottom (Juntura *et al.* 1996).

In the coastal Gulf of Finland resuspension has been estimated to contribute approx. 17 and 24% of

total carbon sedimentation during spring and summer, respectively, while the rest was estimated to derive from primary sedimentation (Heiskanen and Leppänen 1995). In the archipelago region of coastal Sweden it was estimated that resuspension increased the primary settling flux of organic carbon by 50%. Generally, primary C sedimentation varied between 60–100% of gross C sedimentation (Blomquist and Larsson 1994). However, their study was carried out in the shallow archipelago region (total depth of stations varied between 27 and 42 m), and resuspension probably had greater impact on total sedimentation than in the open Gulf of Finland, where the stations studied are generally deeper (here 84 m), and their distances from shore are greater. Nevertheless, our results indicate that at times resuspended material may contribute to a significant part of settled material.

### Accumulation rates in the Gulf of Finland

The average accumulation rate observed for station GF2 during 1996 was  $0.85 \text{ g m}^{-2} \text{ d}^{-1}$ , which is lower compared with estimates of  $1.4 \text{ g m}^{-2} \text{ d}^{-1}$  (Kankaanpää *et al.* 1997a) in a similar trap study. The reason for this difference is probably the cold weather conditions that prevailed during summer 1996. By using  $^{137}\text{Cs}$  dating, an average sedimentation rate of  $1.1 \text{ g m}^{-2} \text{ d}^{-1}$  for the whole Gulf, and  $1.4 \text{ g m}^{-2} \text{ d}^{-1}$  for the GF2 station were obtained (Kankaanpää *et al.* 1997b). It thus seems that (1) the flux estimates obtained for the upper GF2 trap are realistic, (2) the accumulation rate during 1996 was lower than that of 1995, and (3) the rates from trap and  $^{137}\text{Cs}$  studies agree.

### Accumulation of organic contaminants in the open sea

The extrapolated sedimentation values are only indicative due to the limited data set. The temporal variations of accumulation rates demonstrated that the contaminants are removed from the water column as they become part of the particulate material. There was also less active accumulation throughout the observation period. It may be possible that the downward transport of organic contaminants could be connected to the algal biosynthesis of lipids and

subsequent sedimentation of lipid-containing phytodetrital material during the spring bloom. This, together with the large number of particles with high adsorption capacity, may explain the dominant accumulation of the contaminants during the spring.

Of the measured organochlorines, the most abundant ones (in order of abundance) were the PCBs, followed by DDTs, HCHs, HCB, chlordanes, and trans-nonachlor (Fig. 2, Fig. 7, Table 1 and Table 2). Since the studied sum of seven PCBs corresponds to approximately 30% of the total amount of PCBs in technical mixtures like Clophens A50 and A60 or Aroclors 1254 and 1260 (calculations based on the data in Schultz *et al.* 1989), the total amount of sedimenting PCBs can be estimated at  $60 \text{ kg yr}^{-1}$ .

The proportions of the different isomers and metabolites show interesting changes during the experiment (Fig. 5, Fig. 6 and Fig. 8). For DDTs, there is a constant dominance of DDD, but after the spring bloom the share of DDE gradually increases while the amount of DDT decreases. The trend indicates the conversion of the deposited DDT to DDE. Of the HCHs, the share of the  $\gamma$ -isomer clearly diminished throughout the experiment, and the  $\beta$ -isomer dominated from summer to the end of the collection. Therefore, the monitoring of lindane should be complemented with the monitoring of  $\beta$ -HCH, which is almost as abundant as lindane during the spring maximum.

The relative proportions of different CB congeners changed somewhat during the experiment: there was a slight decrease of less chlorinated CB 28 and CB 52, and a slight increase of more chlorinated CB 153, CB 138 and CB 180 towards the end of the collection period.

Compared with the lindane deposition estimate of approx.  $30\text{--}50 \text{ ng m}^{-2} \text{ d}^{-1}$  (Jaarsveld *et al.* 1993), the fluxes obtained in this study are much smaller (average of  $1.2 \text{ ng m}^{-2} \text{ d}^{-1}$ ). This may be due to the rather high water solubility of HCHs (Loganathan and Kannan 1994), allowing most of the lindane from the atmosphere to stay in the water phase. Compared with the results of  $15 \text{ ng g}^{-1} \text{ dw}$  of DDTs and  $60 \text{ ng g}^{-1}$  of PCBs as Aroclor (Perttilä and Haahti 1986) from station XV1 (eastern Gulf of Finland), or  $21 \text{ ng g}^{-1} \text{ dw}$  of PCBs and  $5 \text{ ng g}^{-1} \text{ dw}$  of DDTs from the western Gulf of Finland (Østfeldt *et al.* 1994), the present average concentrations (Table 4) in the open sea were lower:  $7.7 \text{ ng g}^{-1} \text{ dw}$  of DDTs, and also  $8.0 \text{ ng g}^{-1} \text{ dw}$  of

s7PCBs (27 ng g<sup>-1</sup> as Aroclor). Further comparisons of organochlorine concentrations cannot be made since bottom sediments were not analysed in this study. The total areal share of PCBs (as Aroclor) to the Gulf of Finland was about 9% of the reported deposition to the Baltic Sea (Baltscheffsky 1997). This value is of the same order as the areal share of the Gulf (approx. 8% of the Baltic Sea).

With respect to the extractable organic halogen (EOX) content, the specific organochlorine levels observed in this study can explain only about 0.2% of the halogens detected as EOX at station GF2 (Table 2). This observation is therefore further evidence for the earlier observation of intense natural production of organohalogens at sea (Kankaanpää *et al.* 1997a), which may be due to the biosynthesis of intracellular compounds in algae, or accumulation of excreted compounds onto particles during blooms. The extrapolated annual sedimentation of EOX was 20 t, while it was estimated at approx. 56 t in 1995 (Kankaanpää *et al.* 1997a). The concentration range of EOX was 2.7–14.9 µg Cl g<sup>-1</sup> dw (Table 4), being of the same order as observed earlier for surficial sediments during the peak of primary production (Kankaanpää *et al.* 1997a).

Surprisingly high deposition rates were observed for the oil total (up to 900 µg m<sup>-2</sup> d<sup>-1</sup>, or 1 060 t annually), although the Baltic Sea as a whole has been reported to receive much higher quantities of oil: 20 000–70 000 t annually (Baltic Marine Protection Commission 1996). The possible contribution of natural compounds affecting the IR detection of oil at a 3.5–3.7 µm wavelength has not been estimated. According to the monitoring results of total oil in the Gulf of Finland (Finnish Institute of Marine Research, monitoring data), the average levels in surface water (0–1 m) have been 0.3–3.6 µg l<sup>-1</sup> (the average 1.0 µg l<sup>-1</sup>,  $\sigma = 0.8$  g l<sup>-1</sup>,  $n = 23$ ) during 1992–1996. Using the average concentration for extrapolation, the whole 30 000 km<sup>2</sup> × 1 m water element ( $3 \times 10^{13}$  l) has contained approximately 30 t of oil during the 1990s. Considering the oil content of water and that oil is preferably adsorbed by sediments, the estimates can be realistic. The main source of the oil may be the intentional dumping of bilge-water from ships, which has been reported to be frequent in the area. No earlier results (using the fluorometric method), however, exist for the oil content in sediments from the open sea, nor for oil concen-

trations in deep water.

We compared our results of total deposition with the preliminary estimates of Lund University (Department of Ecology), reported in Baltscheffsky's overview (Baltscheffsky 1997), for the sedimentation of the whole Baltic Sea area. According to the comparison, the share of the gulf for the different contaminants is of the order of 1–90%, depending on the contaminant (Table 2). For contaminants other than DDTs, the share (1–9%) of the deposition of contaminants to the Gulf of Finland is comparable with the gulf's areal share (8%) of the Baltic Sea. This agreement by itself does not, however, guarantee the correctness of the deposition values.

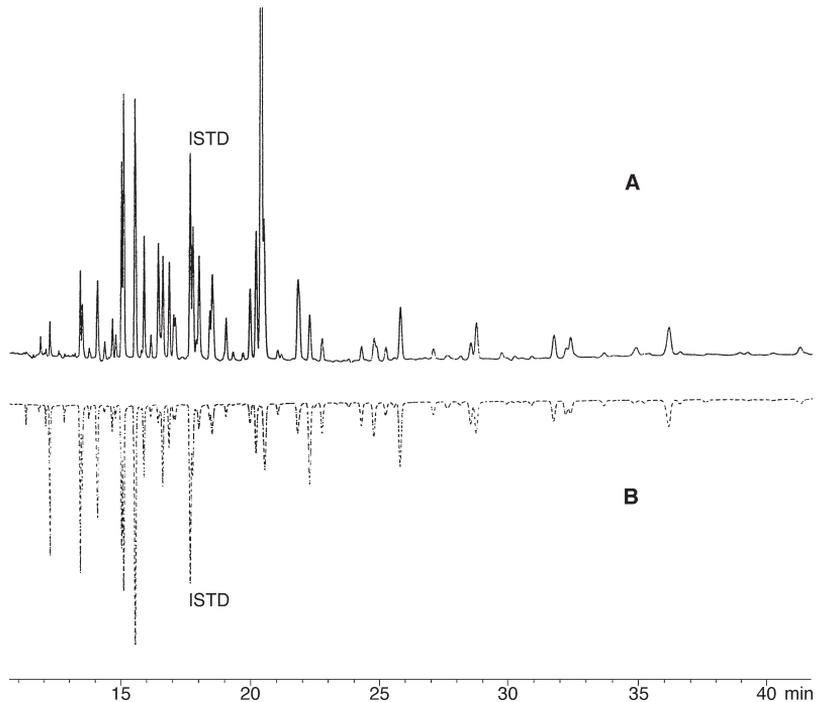
The highest percentage of 90% obtained for DDTs suggests that the condensation of DDTs may occur more efficiently in the Gulf of Finland area than in lower latitudes. This high percentage can, however, be due to as well inaccuracies in one of the deposition estimates. This problem remains to be solved in the future.

### Accumulation of PCBs and HCHs versus air deposition and emissions

Several kinds of processes have affected the fate of organochlorines in air and aquatic ecosystems. Atmospheric transport and the tendency towards cold condensation distribute pesticides used in warmer areas towards the northern areas. In the deposition of the Nordic region, certain chemicals which have been banned for several years can be found.

The organochlorines are dissolved in aquatic ecosystems in very low concentrations. They willingly bind to different kinds of particles. Humic substances and small particles, consisting of a large surface area, are the most suitable for binding. Lipophilic organochlorines are also easily accumulated in animals consisting of lipid and organochlorines are bioconcentrated on the predators situated in the upper trophic levels. Large amounts of the organochlorine contaminants are however deposited.

The extrapolated value of accumulation of 7 PCBs was about 20.6 kg yr.<sup>-1</sup> and that of total PCBs about 60 kg yr.<sup>-1</sup> for the Gulf of Finland (as calculated for accumulating areas, which were about 30% of the total area). The same value for



**Fig. 9.** Mirrored ECD-chromatograms (column HP-5) of the Schepelev trap sample (A) and a mixture of Pyralene 3010 and Clophen A50 in relative concentrations 2:1 (B). ISTD = internal standard. Chromatographic conditions are given in the material and methods section.

HCHs was  $10.9 \text{ kg yr}^{-1}$ . Calculated emissions of total PCBs in southernmost Finland (Finnish Environment Institute, unpublished data) along the coast varies between  $0.4\text{--}4 \text{ kg per } 100 \text{ km}^2 \text{ yr}^{-1}$ . Approximated to the whole Gulf of Finland (if using 20% of the maximum PCB emissions) the amount of PCB deposition would be  $240 \text{ kg yr}^{-1}$  for the Gulf. Because the dominating wind direction is south-westerly and the emissions used are from the northern coast of the Gulf of Finland, this can only be an approximation.

The measured bulk deposition of total PCB in the Evo area, situated about 100 km north of Helsinki, has been about  $0.9 \text{ kg per } 100 \text{ km}^2 \text{ yr}^{-1}$ . Calculated for the whole Gulf of Finland area this means about  $270 \text{ kg yr}^{-1}$  (the same values for HCHs are  $0.6 \text{ kg per } 100 \text{ km}^2 \text{ yr}^{-1}$  and  $180 \text{ kg yr}^{-1}$  for the gulf). In the project 'POPs Cycling Baltic' (Pacyna *et al.* 1996) the amount of  $85 \text{ kg yr}^{-1}$  for direct emissions and river inflow of total PCBs has been used for the Gulf of Finland.

If the approximated sedimentation to the emission and deposition values are compared, the sedimentation of total PCBs in the Gulf of Finland is about 10% (27% of the amount used in 'POPs cycling Baltic') and HCHs less than 5%.

### Accumulation in the Schepelev area

In general, the low accumulation rate (Table 2) at Schepelev was due to the collection being after the spring bloom, but the accumulation rate in this particular area may also be lower than at station GF2. The low rate was somewhat surprising when considering the hydrography of the area and the rather high sedimentation rates observed in the eastern Gulf of Finland (Kankaanpää *et al.* 1997b). The composition and high concentration of different PCB congeners in the Schepelev trap sample indicated that the source of PCB had been an Aroclor-type mixture. The overall PCB pattern very strongly resembles the combination of technical mixtures Pyralene 3010 and Clophen A50 (or Aroclors 1242 and 1254 respectively), as shown in Fig. 9. This is quite expected, since the technical PCB-mixtures Trichlorodiphenyl and Sovol, which have been used in the former USSR, are similar to Aroclors 1242 and 1254 respectively (Ivanov and Sandell 1992). The estimation of total PCBs is now more difficult because the PCBs studied are not the main contributors in Aroclor 1242 (Schultz *et al.* 1989), but a rough estimate is that the sum of seven PCBs is about 20% of the total PCBs,

suggesting the total PCB to be 17 kg yr.<sup>-1</sup>.

Although such contamination can originate from the St. Petersburg area, or possibly the Schepelev Cape area, it cannot be completely excluded that the high concentrations were caused by unintentional contamination on the research vessel, with the results needing to be verified with additional samples. The elevated EOX also evidenced organochlorine pollution at Schepelev, where all the measured organochlorine compounds explained approx. 0.5% of the EOX, which suggests that percentages of this magnitude indicate the presence of anthropogenic organochlorines from sources other than the pulp industry.

### Future aspects

Present monitoring of chlorinated contaminants in the study area includes only two-year-old herring. From the viewpoint of comparability of contaminant level data, the use of herring in monitoring is justified, but gives only a limited amount of information on the levels of contaminants in throughout the ecosystem. The accumulation rates obtained allow a more precise estimation of the cycling and mass balances of the harmful substances. We think that the studies on contaminants in sediments should be carried out more frequently than before. In practice, bottom deposits along the gulf should be analyzed for harmful substances, such as those analyzed in this study (except EOX), and additionally PAHs.

The chemical, biological and physical mechanisms related to accumulation and transportation of contaminants should be studied in order to better understand processes which affect the channeling and enrichment of contaminants in the coastal ecosystems. Calculation of mass budgets and balances provide information on the levels of contaminants in the environment, but do not provide insight to the mechanisms that govern the cycling and transportation of these substances in the natural environment.

To conclude, the accumulation of contaminants in general does not cause concern for the gulf's ecosystem. However the situation in the eastern gulf and Kymi River estuary needs to be better evaluated to assess the local risks of dioxins, PCBs and other organochlorines. It must be em-

phasized that the extrapolated results are based on observations from only one open sea station, and therefore the fluxes may be different in other regions. Due to the great variability in both temporal and areal sedimentation, it is necessary to measure the accumulation of contaminants in several locations, which would allow the calculation of accumulation rates even more precisely.

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