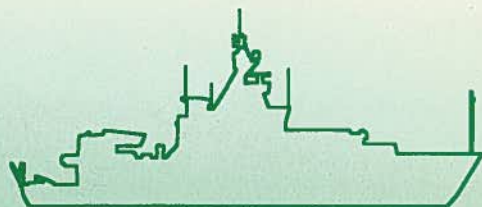HARRI KANKAANPÄÄ

Sedimentation, distribution, sources and
properties of organic halogen material
in the Gulf of Finland

MONOGRAPHS

of the

Boreal Environment Research

BOREAL ENVIRONMENT RESEARCH

SCOPE OF THE JOURNAL

Boreal Environment Research is an international interdisciplinary journal publishing original articles, reviews and short commentaries devoted to studies of various aspects of the boreal environment and its natural resources in particular on environmental problems, their assessment, understanding and management, as well as on the sustainable use of natural resources in the fields of atmospheric, terrestrial, aquatic, marine and fisheries sciences.

Boreal is interpreted in a wide sense, i.a. including polar, subpolar and northern temperate conditions, biomes or ecosystems. The journal is a forum for emphasizing a holistic approach to environmental sciences, linking pressures via sources of pollution to the occurring in the various media. Articles dealing with monitoring, experimental, theoretical and modelling studies as well as their combination are all welcome.

EDITORS-IN-CHIEF

Prof. Hannu Lehtonen
Department of Limnology
P.O. Box 27
FIN-00014 University of Helsinki, Finland

Dr. Sylvain Joffre
Finnish Meteorological Institute
P.O. Box 503
FIN-00101 Helsinki, Finland

EDITORIAL OFFICE

SUBMISSION OF MANUSCRIPTS

Four copies of the manuscript are to be sent directly to the appropriate Editor-in-Chief. Manuscripts related to aquatic, marine and fisheries sciences to Prof. Hannu Lehtonen, and those related to atmospheric and terrestrial sciences to Dr. Sylvain Joffre. Indicate clearly to whom the correspondence should be sent, and include the telefax number and, when available, the e-mail address. On a separate sheet, submit a list of four qualified and unbiased referees with complete names and addresses.

SUBSCRIPTIONS

6

Harri Kankaanpää

Sedimentation, distribution, sources and properties of organic halogen material in the Gulf of Finland

Sedimentation, distribution, sources and properties of organic halogen material in the Gulf of Finland

Harri Kankaanpää

As clear as mud

Contents

List of original publications

This thesis is based on the following original papers, which are referred to in the text by their respective Roman numerals:

I   Kankaanpää H. & Masuku C. P. 1992. Adsorbable organic halogen compounds (AOX): determination in sea sediments. *Chemosphere* 24: 1331-1345.

II   Kankaanpää H. & Tissari J. 1994a. Background levels of EOX and AOX in the sediments of the Gulf of Finland - molecular weight distribution of EOX in the sediments. *Chemosphere* 28 (1): 99-116.

III   Kankaanpää H. & Tissari J. 1994b: Analysis for EOX and AOX in two industry influenced coastal areas in the Gulf of Finland. Levels of EOX and AOX in the Kotka region, Finland. Levels of EOX in the Neva Bay, Russia. *Chemosphere* 29 (2): 241-255.

IV   Kankaanpää H., Laurén M., Mattson M. & Lindström M. 1995. Effects of bleached kraft mill effluents on the swimming activity of Monoporeia affinis (Crustacea, Amphipoda) Lindström. *Chemosphere* 31 (11/12): 4455-4473.

V   Kankaanpää H., Laurén M., Saares R., Heitto L. & Suursaar Ü. 1997. Distribution of halogenated organic material from anthropogenic and natural sources in the Gulf of Finland catchment area. *Environmental Science and Technology* 31 (1): 96-104.

VI   Kankaanpää H., Vallius H., Sandman O. & Niemistö L. 1997. Determination of recent sedimentation in the Gulf of Finland using ^{137}Cs in the Gulf of Finland. *Oceanologica Acta* 20, in press.

VII   Kankaanpää H., Korhonen M., Suortti A. -M. & Heiskanen A. -S. Seasonal sedimentation of organic matter and contaminants in the Gulf of Finland. Accepted for publication in *Boreal Environment Research*.

Papers I to IV are reprinted with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK. Paper V is reprinted, with permission, from Kankaanpää, H., Laurén, M., Saares, R., Heitto, L. and Suursaar, Ü. 1997. Distribution of Halogenated Organic Material in Sediments from Anthropogenic and Natural Sources in the Gulf of Finland Catchment Area. Environmental Science & Technology 31 (1): 96-104. Copyright American Chemical Society. Paper VI is printed with permission from Gauthier-Villars and paper VII with permission from the publisher of the Boreal Environment Research.

Some unpublished results are also presented.

Corrections to original publications

Paper II, page 99, second row in abstract and page 112, third row in conclusions: 2.5 should be replaced by 6.0. Paper II, page 114: TOC % should be TOC mg g^{-1}. Paper V, page 102: dry matter sedimentation rate should be 0.51 kg m^{-2} a^{-1}. Paper V, page 103: the annual sedimentation of EOX is 56 t.

The author's contribution

In paper I the author was responsible for planning and carrying out the research. Dr Christopher Masuku assisted with preparing the manuscript and correcting the English. In papers II and III the author planned the experimental set-up, made the data-processing and drafted the manuscripts. Chemical analyses were carried out by Mr Jorma Tissari, who helped in developing new analytical methods, in interpreting the results obtained and in preparing the manuscripts. In paper IV the author initiated the project, made most of the data processing and drafted the manuscript. The experimental part with aquaria was planned and supervised by Dr Magnus Lindström. Ms Madeleine Mattson and Ms Marjo Laurén carried out the compilation of activity recordings. Ms Riitta Olsonen assisted in the statistical calculations. All the co-authors assisted in preparing the manuscript.

Most of the responsibility for paper V was shouldered by the author, who planned and supervised the sediment cruise in the Gulf of Finland, carried out most of the data analysis and interpreted the results. Chemical analyses were carried out by Ms Marjo Laurén and Mr Henrik Österlund. Ms Riitta Saares supervised the EOX analyses at the Finnish Environment Institute and provided validation data and some of the information concerning the Lake Saimaa. Mr Lauri Heitto and Mr Ülo Suursaar provided information concerning local industrial loading, to the River Kymi and Estonian waters respectively. The co-authors assisted in the preparation of the manuscript.

The greatest part of paper VI was planned and written by the author, as was the sampling, measurements and calculation of sedimentation rates and fluxes. The co-authors provided data and assisted with finalising the manuscript. Raw data was also obtained from Dr Alexander Rybalko and Dr Yury Mikheev.

In paper VII the planning of the sediment trap study was made by the author and chemical analyses by Ms Anna-Mari Suortti, Ms Sari Väänänen and Mr Vesa Pimiä. The author was responsible for the calculations and the writing of most of the material on chemical results. Mr Markku Korhonen assisted with the practical work and with the manuscript. Ms Anna-Stiina Heiskanen wrote the parts on the characteristics of sedimenting material and Ms Suortti assisted with those on the chemical analyses and PCB patterns.

List of abbreviations

AC	activated carbon
ANOVA	analysis of variance
AOCl	adsorbable organic chlorine
AOX	adsorbable organic halogen
BKME	bleached kraft mill effluent
CB	chlorobiphenyl
Chl a	chlorophyll a
Chl RC I	chlorophyll RC I
DL	detection limit
DDT	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane
DDTs	DDT and its primary metabolites
DGPS	differential global positioning system
dw	dry weight
E	east
ECD	electron capture detector
ECF	elemental chlorine-free
EMI	Estonian Marine Institute
EOBr	extractable organic bromine

EOCl	extractable organic chlorine
EOX	extractable organic halogen
EROD	7-ethoxyresorufin-*o*-deethylase
ES	electrospray
FIMR	Finnish Institute of Marine Research
FINNARP	Finnish Antarctic Research Program
FEI	Finnish Environment Institute
GPS	global positioning system
GSF	Geological Survey of Finland
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HELCOM	The Baltic Marine Environment Protection Commission - Helsinki Commission
HMW	high-molecular-weight
HPLC	high performance liquid chromatography
ICES	The International Council for the Exploration of the Sea
IR	infra red
Lat	latitude
LMW	low-molecular-weight
LOI	loss on ignition
Lon	longitude
MALD	matrice assisted laser desorption
MFO	multi-function oxygenase
MS	mass spectrometry
MWD	molecular weight distribution
N	north
NAA	neutron activation analysis
OCP	organochlorine pesticide
PAH	polyaromatic hydrocarbon
PCC	polychlorinated catechol
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDE	polychlorinated diphenyl ether
PCDF	polychlorinated dibenzofurans
PCG	polychlorinated guaiacol
PCP	polychlorinated phenol
PCB	polychlorinated biphenyl
r	coefficient of correlation
RP	reversed phase
S	south
σ	standard deviation
SEC	size exclusion chromatography
TC	total carbon
TCF	total chlorine-free
TLC	thin layer chromatography
TOC	total organic carbon
TOX	total organic halogen
UV	ultraviolet
VIS	visible
VSEGEI	All-Russia Geological Research Institute
W	west
ww	wet weight
X	halogen

In the following sections, the term 'organochlorine' is used when discussing specific chlorinated compounds or pulp mill effluents or sediments that are clearly affected by BKME. The term 'organohalogen' is used when the source of the organic halogen is none of the above, or when describing material that contains halogens other than chlorine, or material that is of natural or unknown origin.

Sedimentation, distribution, sources and properties of organic halogen material in the Gulf of Finland

Harri Kankaanpää

Finnish Institute of Marine Research, P.O. Box 33, FIN-00931 Helsinki, Finland

Abstract

In Gulf of Finland sediments, non-specific sum parameters for organic compounds, extractable organic halogen (EOX) and adsorbable organic halogen (AOX) were used to estimate total organohalogen levels and the distribution of organohalogens from both natural and anthropogenic sources. Estimations of the coverage, natural production and total amounts of halogenated organic material were made using mainly EOX, ^{137}Cs dating, and sediment trap studies. Geographically, the study concerns mainly the Gulf of Finland, but includes some parts of its catchment area. Sediments for the organohalogen analyses were collected from 113 coring sites around the study area, and from two sites in the Gulf of Bothnia and also from the Weddell Sea, Antarctica.

An AOX method for marine sediments was applied first to sediments from Bothnian Bay, from the vicinity of a pulp mill, where total organohalogen concentrations reached 590 µg Cl g^{-1} dw in the surface sediment. The same method was later used for Gulf of Finland sediments. A modified EOX method was applied to quantify lipophilic organohalogens in sediments. The analytical methods were validated and found reliable. The contribution of interfering inorganic halides was negligible. The EOX method was also used in combination with a SEC-HPLC method developed for determining molecular weight distribution of sediment extracts. The AOX and EOX results from the non-polluted areas indicated that, in the non-polluted areas, the total organohalogen levels were high (up to 10-13 µg Cl g^{-1} dw or 150-200 µg Cl g^{-1} C measured as EOX) compared with the levels of specific organochlorine compounds chlorophenolics, PCBs, DDTs and organochlorine pesticides.

HPLC, MS, and NMR techniques were used to characterise the organic compounds present in the EOX pool. The molecular weight distributions revealed practically no differences between polluted and natural sediments. The similarity of the MWDs in all samples suggested that the pollutants from pulp mill effluents bind to the dominating natural organic material. The molecular weight distribution and the results of spectrophotometric analyses showed that the extractable organic material is very homogeneous in Gulf of Finland sediments, and proved that molecular weight distribution cannot be used as an indicator of pollution from pulp and

paper industry. Most of the EOX was polar, furthermore detailed characterization of the natural EOX material was difficult using MS and NMR, and the MS results were not in agreement with the SEC results. Fragments from chlorophylls were observed and algal pigments were important constituents of the extracts.

In 1994, anthropogenic organochlorines were found still in relatively high concentrations (up to 116 µg Cl g^{-1} dw) in the sea-bed of the Kotka area. Chlorinated compounds from the pulp industry may thus still pose a potential but localised threat in the Gulf of Finland. Due to the recent reduction in chlorine use and the fact that clean sediments are rapidly covering the polluted layers, the environmental impact of the pulp mills is diminishing. Except in a few cases there was no evidence of pollution from pulp industry in the eastern and southern Gulf of Finland.

Biological effects of bleached kraft mill effluents (BKME) from a pulp mill were studied under laboratory conditions using *Monoporeia affinis* Lindström as an indicator species. The animals showed adverse effects after exposure to BKME, but the effects seemed not to be chronic, which indicates that reducing BKME output may improve the state of benthic populations in recipient areas. Pollution from the pulp and paper industry does not seem to be threatening the Gulf of Finland as a whole, and monitoring total organohalogen in the Gulf of Finland is on recommended in selected areas, preferably in February-March when the contribution of natural production is least.

Results from sediment trap studies and ^{137}Cs dating yielded sedimentation rates of 0.60 cm a^{-1}, 0.85-4.1 g m^{-2} d^{-1} (dry matter) and 6-17 µg Cl m^{-2} d^{-1} (EOX) in sedimentation areas. In sediment trap material, PCBs, DDTs and pesticides together contributed only 0.2% and chlorophenolics less than 5% of the EOX flux. Total quantity of organohalogens in Gulf of Finland surface sediments sampled in 1994 was estimated at 80 tons, of which natural organohalogens contributed 72 tons. As a conclusion, it is possible to say that emissions from anthropogenic sources in the Kotka-Kymi River area cannot explain the observed levels and, at present, natural production, mainly by spring diatoms, appears to be the major source of the organohalogens present in Gulf of Finland sediments.

---

1 Introduction

Chlorinated organic compounds, especially the non-polar compounds, are dangerous because of their persistent character, their facile tendency to incorporate in lipids (fats), their tendency to bioaccumulate, and other biological effects. Although their non-chlorinated analogues are usually considered less dangerous, some of them are also toxic in the ecosystem. Today, most pulp mills use of chlorine-free bleaching processes and total emissions of chlorine chemicals have been reduced markedly, but not completely. It should be noted however that the discharge of non-chlorinated chemicals is substantial. The ecosystem of the Gulf of Finland is naturally vulnerable to pollution of all kinds, including organohalogen compounds. The water volume is small (1100 km^3) in relation to the catchment area (420000 km^2), where 20 million people live.

During the past decades the industry and environmental protection organisations have quarreled about the benefits and risks of using and producing organohalogens, especially organochlorine compounds (see e.g. Anonymous 1992, Yosie 1996). Although the controlled use of several pesticides and chlorine disinfection has improved the quality of life of millions of people, the misuse and uncontrolled emissions of chlorinated compounds, as well as several accidents, has made them very unpopular in the public eye and justifiably so. Thousands of scientific reports show these compounds are dangerous to living organisms (e.g. Landner 1989, Moore and Ramamoorthy 1984, Paasivirta 1991). While there is risk attached to the use of many chlorine chemicals, the environmental effects of a large number of compounds are not known well enough. One aspect of the problem is that all of the compounds themselves have not been identified, for instance in BKME. Also, general knowledge on the character of the organic matter in marine environment is still poor (e.g. Johnson *et al.* 1992).

During the past few decades, the main anthropogenic source of organic chlorine compounds in the Baltic Sea, and the Gulf of Finland, has been the pulp and paper industry (Wulff and Rahm 1993). Although use of elemental chlorine has almost completely stopped, many of the factories are still using chlorine dioxide, which can also produce chlorinated lignin derivatives and may contain elemental chlorine as an impurity. Despite improved processes, emissions from factories around the Gulf of Finland remain rather high. For instance, the Sunila pulp mill near Kotka emitted approx. 220 t of AOX in 1995.

Several reports exist on the presence of natural organohalogens in the terrestrial and aquatic environments (for excellent reviews, see e.g. Gribble 1994, Grimvall and de Leer 1995). According to these reports the naturally occurring organohalogen compounds are common in both environments, but the amounts in the sea are not calculated. Algae and fungi are, for example, organisms which synthesise chlorinated, brominated and iodinated molecules. Since algae are common in the Gulf of Finland and the sea water is full of substrates (chloride and bromide), it is reasonable to expect that the natural organohalogens are synthesised and common. One of the key questions in the organohalogen debate is the magnitude of the contribution of natural production to the total organohalogen budget in sea. If natural production has a significant share it means that chlorinated and other halogenated compounds cannot in general be classified as dangerous, but as common and essential products of and for marine organisms.

The most common parameters for estimating the total levels of organohalogens in the environment are the sum, or group-parameters, EOX, EOCl, AOX, AOCl, etc. These parameters do not provide information on the chemical character of the constituents measured and since the composition of total organic halogen material is important, other chemical methods are also needed. The extremely complex character of both pulp mill-derived and natural organohalogen compounds in sediments makes the determination of composition difficult. Several methods for characterisation have been used, including chemical oxidation, chromatography, spectroscopy, etc. In spite of these efforts less than 10% of the EOX has been fully characterised (Table 1). In most cases, organohalogens have been classified simply according to their polarity and acidity.

Especially in the Baltic Sea sedimentation processes are important, e.g. removal of organic compounds from the water-column. Although sedimentation has a great impact on the flow and cycling of chemicals in the Gulf of Finland, the process of sedimentation is a complex phenomenon, not well understood. Sediments from the Baltic Sea contain more organochlorine compounds than sediments from the Oceans; for instance in the North Sea in general PCBs and DDTs occur in much lower concentrations than in the Baltic Sea. The concentration range of different organochlorine compounds (chlorophenols, PCBs, DDTs, chlorinated benzenes) in Baltic sediments is usually 1-100 ng g^{-1} ww (Grøn 1990). Heavy loading from local industrial and urban sources, the closed structure of the Baltic Sea and high sedimentation rates explain, to a large extent, the high levels. In the Baltic, study of sediments is therefore all the more important.

Table 1. Character of EOCl and EOX in Baltic Sea sediments. [1]Södergren *et al.* 1993. [2]Remberger *et al.* 1990. [3]Østfeldt *et al.* 1994. [4]Lund Kvernheim *et al.* 1993. [5]Martinsen *et al.* 1994. [6]Martinsen *et al.* 1988. [7]Wesén *et al.* 1990. [8]Wesén 1988. [9]Reemtsma and Jekel 1996. [10]Martinsen *et al* 1992. $K_{o/w}$ = octanol-water partition coefficient. GPC = gel permeation chromatography. RPTLC = reverse phase thin layer chromatography.

PARAMETER	RESULT (technique, source)
Identified	<10%[1]
	ca. 8% (in cyclohexane)[2]
	1-5%[3]
Specific compounds	Cl and non Cl alkenoic acids, alkanoic acids, terpenes, Cl-resin acids, non-BKME products[2] ,methyl esters[4]
EOCl of TOCl	30%[5]
EOCl of AOX	1%[6]
lipophilicity	90% very lipophilic ($K_{o/w}$ > 10[6])[5]
bio-accumulability	$K_{o/w}$ 10[5]..10[7] (RP-TLC)[7]
	20%, $K_{o/w}$ >1000
persistency	3-31% (EPOCl)[2]
	17% (EPOCl)[6]
	80% hydrolysable[7]
polarity	60% neutral[8]
	ca. 90% polar[4]
	polar compounds important[9]
acidity	neutral[7]
volatility	10%[7]
	non-volatile[10]
chromatographability	3%[10]
MWD	60% > 300 g mol^{-1} (GPC)[6,8]
Content of elements	no nitrogen, 10-20% sulphur (in cyclohexane)[2]

Estimating the effects of harmful chemicals in the marine ecosystem is an essential task. Knowledge of emissions, total quantities, distribution of compounds and rate of sedimentation are necessary. When this information is combined with information on the bioavailability of the chemicals, their toxicity, rate of uptake and other effects on the biota, a comprehensive picture of consequences of pollution could be achieved. Unfortunately all of this is not usually possible and one must be satisfied with a more restricted approach: almost always there is a lack of data at some of the key points, the amount of samples may be limiting, the behaviour of chemicals in the matrices unknown, etc. This study is no exception. Sediments were the key matrix in the Gulf

of Finland, used first of all to estimate the share of the industrial and natural production, geographical distribution and, secondly, to determine the sources of the observed organohalogen compounds and assess their possible impacts on the Gulf of Finland environment.

2 Review of the literature

This review describes present knowledge on the sources and character of the two main organohalogen groups, the adverse effects of BKME to marine organisms and the methodological differences of the sum parameters used. The main characteristics of the Gulf of Finland are also presented.

2.1 Characteristics of the study area

The Gulf of Finland (30000 km[2]) is a shallow sub-basin (mean depth approx. 38 m) of the Baltic Sea (Fig. 1). Depth in the eastern part is 20-40 m and in the central part 40-60 m. Depth increases to approximately 100 m in the west and the largest depth is 123 m on the Estonian coast. The Gulf area is a direct north-east extension of the Baltic Sea's Gotland Basin, which means there is no hindrance to water flow in and out the Gulf. The surface salinity varies from 0‰ in the east to 6‰ in the west. Most of the fresh water inflow into comes from the Neva River (mean flow 2460 m[3] s^{-1}), which amounts to approximately one fifth of the total riverine flow to the Baltic Sea. The Neva's inflow in the east and the inflow of saline water from the Baltic Proper in the west give rise to the east-west salinity gradient. The vertical salinity stratification of the water-mass is most distinct during the summer, but almost disappears after the autumn storms. The autumn cooling and the consequent mixing brings to the surface the nutrient-rich deep water that provides the means for strong biological production in the spring (Perttilä *et al.* 1995).

There is a general, average, anti-clockwise circulation of water in the Gulf, which means that the northern coast receives most of the impact of the Neva and other rivers in Finland. Estonian waters are affected mainly by the inflow from the waters of the Baltic Proper. Deep water from the Baltic Proper, containing H_2S, may sometimes penetrate into the Gulf of Finland and cause anoxic conditions in the near-bottom water layer (Andersin and Sandler 1991).
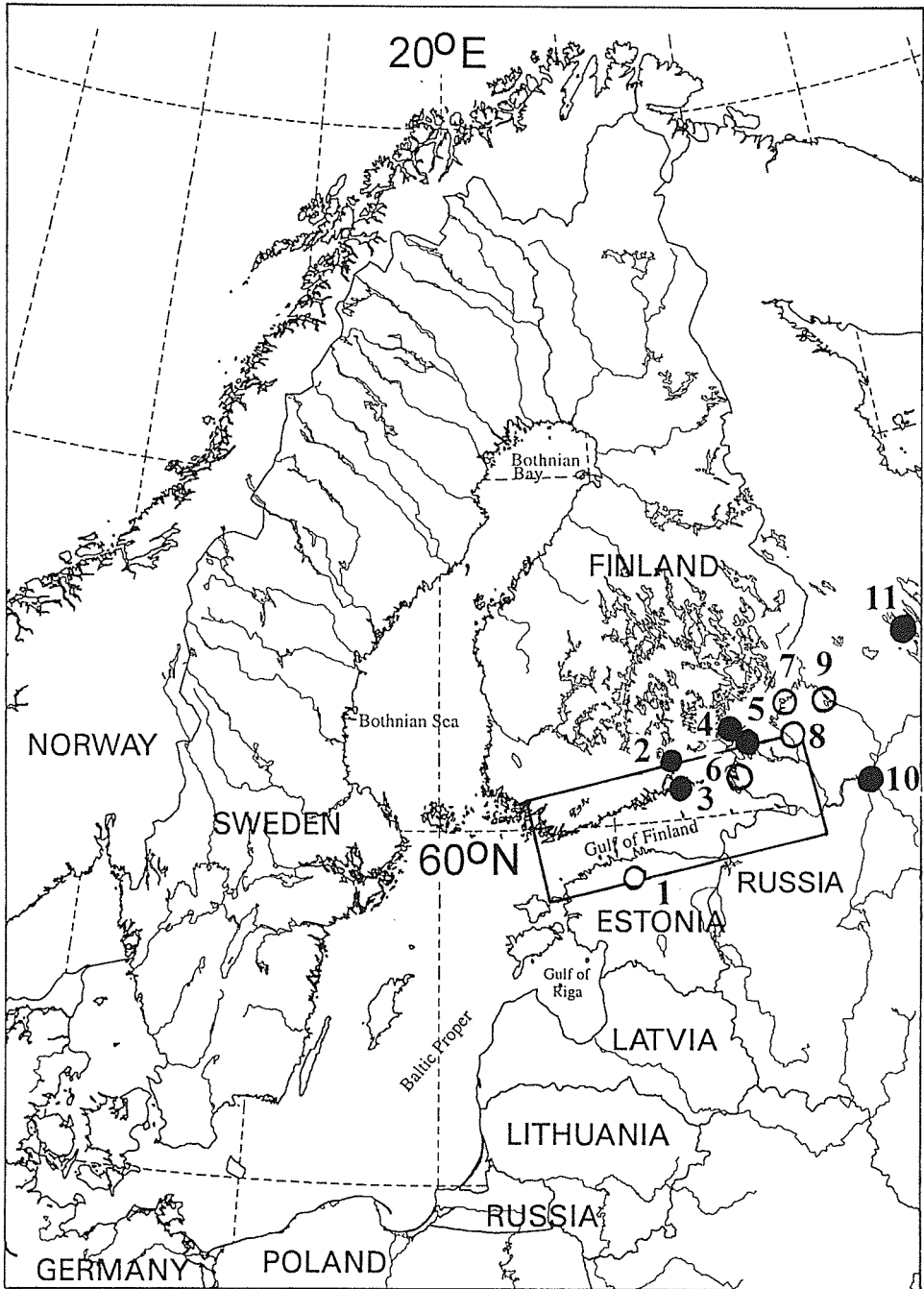
Fig. 1. Location of the study area (frame) and paper and pulp mills affecting the Gulf of Finland or its catchment area. Black circles: pulp mills using chlorine chemicals. Open circles: mills producing unbleached pulp or with unknown situation. 1 = Kehra. 2 = Kuusankoski (UPM Kymmene). 3 = Kotka (Sunila). 4 = Lappeenranta, Joutseno and Imatra. 5 = Svetogorsk. 6 = Sovetskiy. 7 = Lahdenpohja. 8 = Priozersk. 9 = Pitkäranta. 10 = Syasstroy. 11 = Kondopoga.

2.1.1 Characteristics of sedimentation

Sedimentation processes remove large quantities of organic compounds from the water body, and the recent bottom deposits provide an integrated picture of the history of changes in the sedimentation of pollutants. Sedimenting material functions as an adsorbent, trapping chemicals either passively in physical processes or actively through biological uptake, possibly into the lipid fraction of the fresh planktonic material. Pollutants in the sediments may also enter biological cycles through uptake by benthic organisms.

The sedimentation processes are governed by currents, bottom topography, primary production, source of particles (riverine-terrigenous, autochtonous and allochtonous production) and other factors. The origin of the sedimenting material depends mainly on the location: in open sea areas autochtonous and allochtonous materials are dominant, while terrigenous organic material is most prominent in coastal areas (Elmgren 1984, Poutanen 1985). The process of sedimentation, generally described as 'basin-filling' (Winterhalter 1992) in the Gulf, can be compared to snow-fall: descending particles do not fill bottoms evenly. Depending on the conditions, they form sediment packages of varying thickness. The Gulf's bottom structure is complex, especially along the Finnish coastline where areas of rock outcrops alternate with till and clay sediments, which usually fill the deeper parts of the basins. Recent sediment deposits have therefore a patchy distribution (Figs. 2 and 3). The sedimentation basins in the eastern and southern parts of the Gulf are larger than in the north. Typically, sediments in the open sea form pillow-like packages, as exemplified by the transect over stations F41 in the eastern Gulf of Finland and that over LL17c in the Baltic Proper (Fig. 4). Postglacial sediments may reach a thickness of 10-15 m in some places. Figure 4 also illustrates that due to crustal uplift (isostatic rebound) and local currents, the distribution and character of the bottom has changed through time. This has led to local changes in sedimentation, causing shifts in the relation and location of erosion versus sedimentation (Winterhalter, GSF, pers. comm.).

Recent sediments can be dated using radioactive markers (e.g. ^{137}Cs), that have an intermittent supply (e.g. Kyzyurov *et al.* 1994, Robbins *et al.* 1977).

Most of the radioactive contamination in the Gulf of Finland came from the Chernobyl nuclear accident of 1986. Less marked are the traces of the atmospheric nuclear weapon tests in the 1960's and the disharges from the British and French nuclear stations at Sellafield (Windscale) and La Hague respectively. The short-lived radionuclides like ^{134}Cs and ^{121}I have already decayed and the more persistent nuclides ^{137}Cs and ^{90}Sr are now the most abundant in biota and sediments (Baltic Marine Protection Commission 1996).

There are few publications on sedimentation rate values for the Gulf of Finland. Salo *et al.* (1986) reported an average rate of 0.4 cm a^{-1}, using radioisotopes ^{90}Sr and ^{137}Cs, while Perttilä *et al.* (1995) arrived at 0.16 cm a^{-1} by using phosphorus budget calculations. An average rate of 0.74 cm a^{-1} for one station (XV1) was obtained using ^{210}Pb dating, as reported by Voipio (1981). In shallow coastal areas, like Ahvenkoski Bay the west of Kotka, sedimentation rates of 0.43-1.0 cm a^{-1} (0.097-0.14 g cm^{-2} a^{-1}) have been observed using Hg as tracer (Pitkänen 1994). In comparison, Winterhalter *et al.* (1981) reported a mean accumulation rate of approx. 0.1 mm a^{-1} for the whole Baltic Sea, with maximum rates of 0.5-1.5 mm a^{-1}. Boström *et al.* (1981) estimated that recent, soft sediments cover approx. 38% of the Baltic Sea floor and came to a mean accumulation rate of 0.38 mm a^{-1}. It has been suggested that the sedimentation rate has been increasing in the Baltic Sea as a consequence of increased primary production (Jonsson 1992). On the other hand, the decreasing rate of crustal uplift reduces the erosion and sedimentation of minerogenic material from coastal areas.

Accurate deposit maps for the Gulf of Finland area are under preparation (Winterhalter, GSF, pers. comm.), but so far no high-resolution maps depicting recent sediment deposits for the whole Gulf are available. Maps illustrating some of the sub-regions are available, for instance for the Kotka region and eastern Gulf of Finland (Häkkinen and Åker 1991; Winterhalter, Rybalko, Butylin, Spiridonov, unpublished data), as shown in Figures 2 and 3. Due to this lack of comprehensive deposit maps, the estimates on the areal share of the recent sediments are in the range of 25-35% (although 35% was used in paper V and 25% in paper VI, 30% is used in the present study).
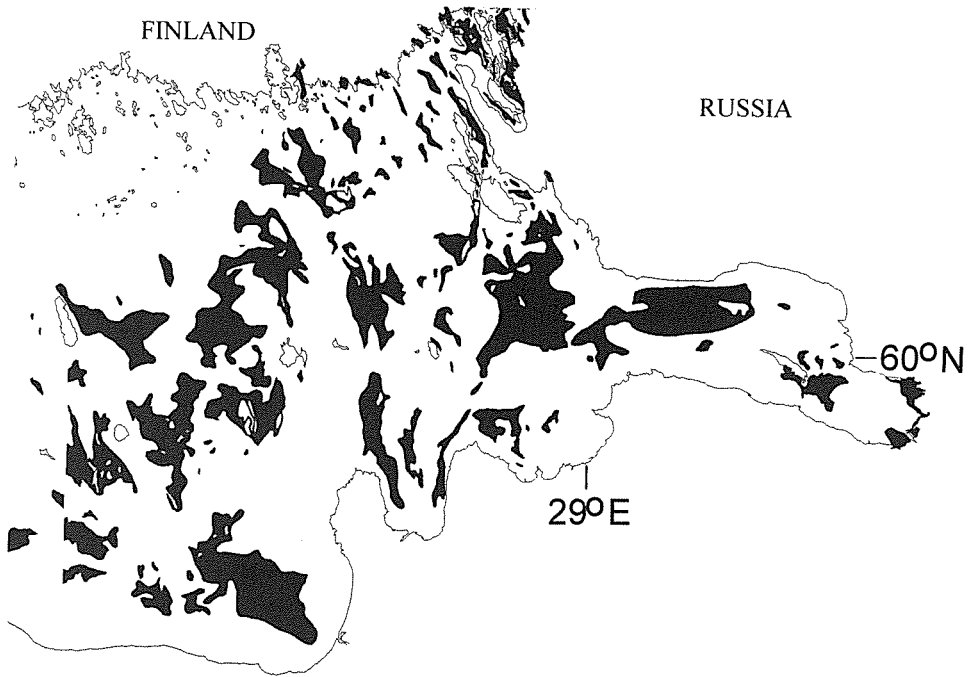
Fig. 2. Recent sediment deposits (black areas) in the eastern Gulf of Finland (Winterhalter, Rybalko, Butylin and Spiridonov, unpublished results).
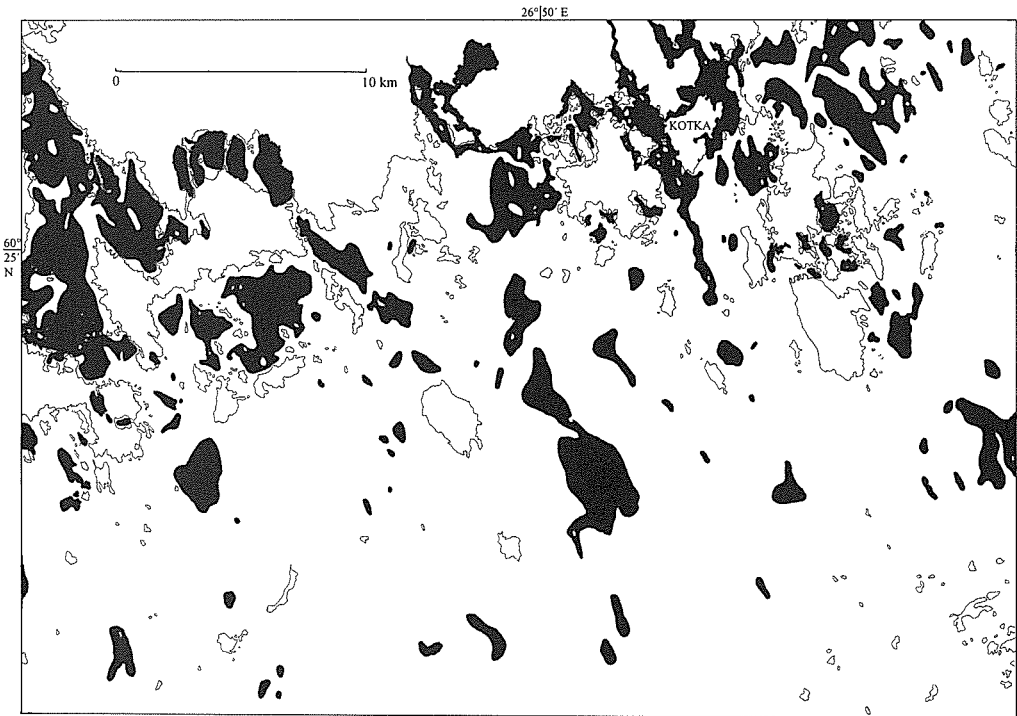
Fig. 3. Distribution of recent sediment deposits (black) in the Kotka area (according to Häkkinen and Åker 1991).
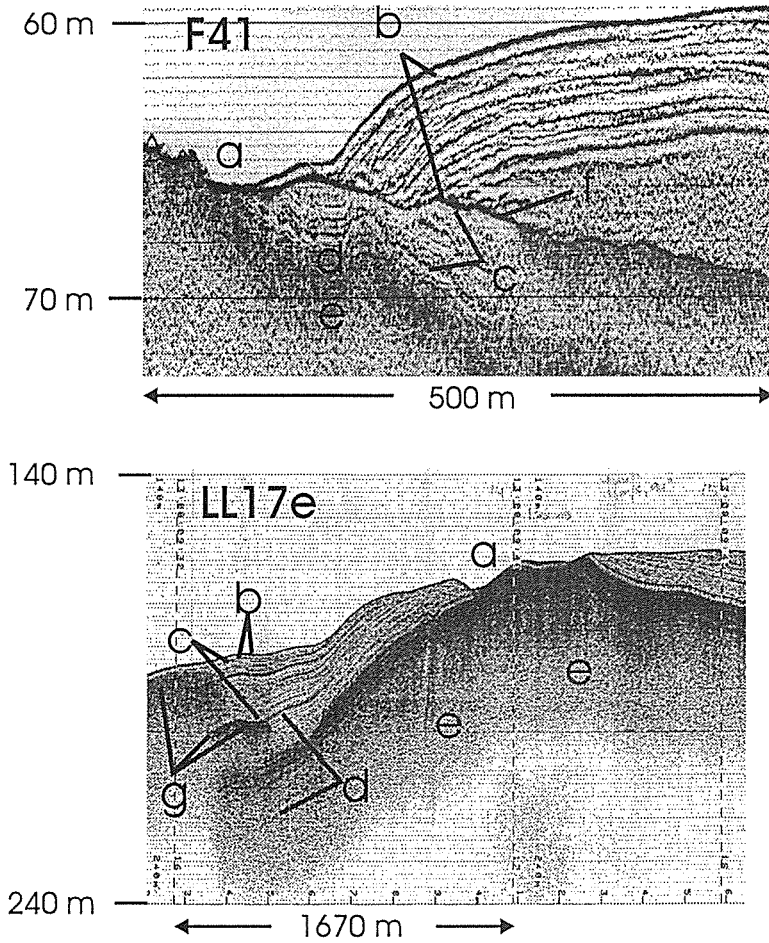
Fig. 4. Example of the seabed structure at stations F41 (eastern Gulf of Finland) and LL17e (the Baltic Proper). a = erosion. b = postglacial and recent sediments (upper line). c = post-glacial clays. d = glacial clays and silts. e = bedrock or till. f = erosional surface forming a hiatus in the deposition. g = gas.

2.2 Pollution in the Gulf of Finland

Pollutants enter the Gulf of Finland from a large catchment area (approx. 420000 km²). Also, the total riverine inflow, 100-125 km³ a⁻¹, from the rivers Neva, Kymi and Narva is large in relation to the Gulf's relatively small water volume, 1100 km³. The Gulf of Finland area receives approximately 180000 t N, 10000 t P and 300000 t of organic matter annually. Most of the nutrient load, approximately 50% N and 60% P, comes from the St. Petersburg area (Pitkänen *et al.* 1993, Pitkänen, FEI, pers. comm.). The extensive nutrient loading has

made the Gulf one of the most eutrophicated areas of the Baltic Sea and the intensity of algal blooming has been increasing. In the spring and summer substantially higher Chl a concentrations have been found in the Gulf of Finland than in the Baltic Proper (Baltic Marine Environment Protection Commission 1996).

Oxygen conditions in the central and eastern Gulf of Finland have been relatively good for the past few decades (1963-1989), but oxygen deficiency in the western part has been more frequent (Andersin and Sandler 1991). In the first quarter of 1995, oxygen

was abundant in the bottom waters of the central (GF2) and western (JML) Gulf, but has thereafter diminished to the low level of approx. 1 ml O_2 l^{-1} in the west and approx. 2 ml O_2 l^{-1} in the central part (Hannu Haahti, FIMR, pers. comm.). In summer 1997 the situation became worse along the whole Gulf of Finland (FIMR monitoring data).

Excepting nutrients, the harmful substances threatening the Gulf of Finland are anthropogenic organic compounds, trace metals, radioactive elements, and natural toxins. Organic contaminants continue to enter the Gulf of Finland environment as atmospheric deposition (PAHs, DDTs, HCHs, HCB, and toxaphene residues), as diffuse loadings, and as point pollution from industrial and municipal outlets. There are two main problem areas in the Gulf of Finland created by the industrial and municipal load of organic pollutants from the St. Petersburg-Neva River and from the Kymi River-Kotka town. The data on the loading of organic pollutants from the St.Petersburg area is still very limited.

After the collapse of the Soviet Union, it has been possible to organise several joint expeditions to study the easternmost Gulf of Finland. Pollution studies have concentrated mainly on trace metals and nutrients. There are very few Russian publications on organic compounds in the eastern Gulf, but high levels of benzo[a]pyrene and oil products have been reported in both water and sediment (Grigori Frumin, Russian Academy of Sciences, pers. comm.). From the Gulf of Finland harmful substances have been analysed in algae, benthic animals, mussels, water, fish, and sediments (Roots 1996). According to HELCOM recommendations, PCBs, DDTs, some OCPs and trace metals are constantly monitored in two-year-old herring, but organic compounds in sediments are not monitored.

2.2.1 Anthropogenic organochlorines

The chlorinated compounds that need most attention are the PCBs, DDTs, chlorinated pesticides (OCPs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and complex pulp mill effluents. These harmful organic compounds originate from incomplete combustion (dioxins), disposal and disintegration of old electrical equipment (PCBs), or as the side-products of chemical processes (e.g. furans from the production of wood preservatives and pulp bleaching). Extremely high concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans have been found in Kymi River sediments (Koistinen *et al.* 1995). These highly toxic compounds originate from the use of the wood preservative Ky-5, 24000 tons of which were produced by a

factory in Kuusankoski (Fig. 1) between 1940-1984 (Koistinen *et al.* 1995, Palm 1995) and, to a lesser extent, from pulp bleaching.

The ban of PCBs and DDTs resulted in reduced levels in fish. In the Gulf of Finland, concentrations in herring are down from peak values in the late 1970's to a steady low level of approx. 10 ng g^{-1} of PCBs (7 HELCOM congeners) and 5 ng g^{-1} for DDTs (FIMR HELCOM monitoring data, Haahti 1995), also in other parts of the Baltic Sea (e.g. Baltic Marine Environment Protection Commission 1996). Although PCB and DDT levels in herring caught in the Gulf have shown a steady decline, the concentrations have started to level-out. This may be because past emissions are being mobilised, or due to wearing-off of the effects of the bans. Levels in Gulf of Finland surface sediments in 1983 were approx. 60 ng PCB g^{-1} dw (Aroclor equivalents) and 15 ng DDTs g^{-1} dw (Perttilä and Haahti 1986).

The modern kraft process dominates today's pulp industry because it provides possibilities to recover and recycle chemicals and minimise discharges (Owens 1991). Nevertheless, none of the kraft pulp mills in the area have yet achieved a complete 100% efficiency in recycling and recovery of wastes. In addition to the monitoring of the effluents, permit holders (i.e. mill owners) must monitor the effects of their effluents on fish, fishing and benthic communities in the surrounding sea, but monitoring of the levels of organochlorine compounds in benthic animals and sediments in receiving waters is not obligatory.

In 1993 it was estimated that, in the Baltic, the greatest part of total organic halogens (>70%) originated from pulp mills in the Baltic Region (Wulff *et al.* 1993). Today, while pulp production has increased significantly, the output of waste-waters from the Finnish pulp mills has decreased to a fraction of what it was ten years ago. Oxygen delignification is now commonly applied after the cooking of wood material and the mills are moving from Cl_2 and ClO_2 bleaching to totally chlorine-free bleaching with e.g. ozone and peroxides. Thus the AOX load has been cut down from typical values of 5-6 kg Cl t^{-1} pulp to approx. 0.3 kg Cl t^{-1} pulp (1995), as illustrated by the over 80% decrease (Fig. 5) for the UPM Kymmene pulp mill in Kuusankoski and the Sunila pulp mill in Kotka (Timo Jouttijärvi, FEI, pers. comm.). The amount of solids and the values of chemical oxygen demand (COD) and biological oxygen demand (BOD) in effluents have also decreased (Saunamäki 1997). The UPM and Sunila mills continue to have a negative impact to the Ahvenkonski-Kotka area and still emit most of the industrial organic chlorine that enters the Gulf of Finland. Today the Sunila mill produces ECF and TCF

pulp, and the UPM mill only ECF pulp. Discharges from the ECF mills in the towns of Lappeenranta, Joutseno and Imatra in the southern Lake Saimaa may also enter the Gulf of Finland through the Saimaa Canal. Also, some effluent may be transported to Lake Ladoga via the Vuoksi River (Jokela *et al.* 1992).
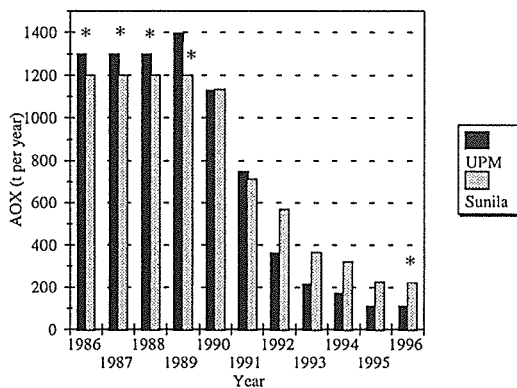

Fig. 5. Production of AOX at the Sunila and UPM Kymmene (Kuusankoski) pulp mills in 1986-1996. * = estimate.

In Russia there is a recommendation to reduce the AOX load to 1.4 kg Cl t^{-1} pulp and to reduce discharge of chlorinated compounds by 50% from the present level (Anonymous 1996). The reduction in pulp production that followed the collapse of the USSR has already produced an approx. 50% reduction in discharge (Anonymous 1996). For instance, the output of AOX from Pitkäranta pulp mill (northern Lake Ladoga) was reduced from 480 t Cl a^{-1} in 1987 to 48.5 t Cl a^{-1} in 1994. In 1987 the pulp mills in Kondopoga, Lake Onega, and Syasstroy, southern Lake Ladoga, produced 480 t and 7667 t of Cl, respectively (Anonymous 1996). The Sovetskiy pulp mill is located in the Vyborg Bay, but does not produce bleached pulp. An operational Estonian pulp and paper mill is located in Kehra (19500 t paper and 21000 t pulp in 1996), but does not use chlorine chemicals for bleaching (Suursaar, EMI, pers. comm.) See Figure 1 for the location of pulp mills around the Gulf of Finland catchment area.

Atmospheric deposition of chlorine in DDTs, PCBs, lindane, and other OCPs is negligible compared to the emissions from the pulp mills (Baltscheffsky 1997, Pacyna *et al.* 1994, Pacyna *et al.* 1996, Roots 1996). In Finland chlorine disinfection has been estimated to produce a total amount of about 20 t of AOX a^{-1} (Jokela *et al.* 1992) and

atmospheric deposition of AOX on land in Finland has been estimated at 3.6-4.8 mg Cl m^{-2} a^{-1} in 1989-1990 (Jokela *et al.* 1992). When these figures for atmospheric deposition are extrapolated over the whole Gulf of Finland, the figures for wet precipitation for the Gulf are 110-140 t AOX a^{-1} or 0.6-4 t EOX a^{-1} (using 0.5-3% EOX/AOX, Berry *et al.* 1991, Martinsen *et al.* 1992). Wulff *et al.* (1993) estimated 0.38-0.42 kg Cl km^{-2} a^{-1} wet precipitation for the Bothnian Bay, Bothnian Sea and the Baltic Proper, which would yield 11-13 t a^{-1} EOCl precipitation over the Gulf of Finland.

2.2.1.1 Chemical character of BKME

The reaction of lignin with bleaching agents produces the BKME components, of which more than 400 have been identified (Palm 1995). A brief review of the compounds and compound classes typically found in BKME from bleaching with chlorine chemicals is given in Table 2. Chemically, pulp mill effluents are challenging mixtures, containing a large amount of unknown components and only a fraction of the chlorinated compounds from chlorine bleaching has been characterized. The complexity of BKME arises from the presence of lignin-derived compounds of various molecular weight (e.g. Higashi *et al.* 1992, Jokela *et al.* 1993) that cannot be assigned to any exact structures. Both LMW- and HMW-material is produced in the bleaching process. The LMW fraction consists mainly of largely unidentified chlorophenolics, the HMW (>1000 g mol^{-1}) fraction of mainly polar, hydrophilic breakdown products of lignin and polysaccharides (Kringstad and Lindström 1984). Chlorolignin also contains fragments that do not bioaccumulate (Pellinen *et al.* 1994) and a multitude of non-chlorinated compounds, for instance aromatic compounds from perchymatous fiber in raw wood. Juuti *et al.* (1996a, 1996b) also found that ClO$_2$ bleaching produces chlorinated compounds.

A common analytical approach used for characterising the HMW fraction in lignin and humic material is to first degrade the polymeric compounds with oxidants, derivate the product and subject the derivatives to chromatographic analysis using universal or chlorine-sensitive detectors (Dahlman *et al.* 1993, Dahlman *et al.* 1994, deSousa 1988). This approach provides possibilities to trace the presence of certain anthropogenic marker compounds (4-ethoxybenzoic acid derivatives, Table 2), but a draw-back of this method is that only compounds that can be extracted with alkaline solutions can be included in the analysis.

Table 2. Characteristics of lignin-derived organic material from BKME and sediments from pulp mill recipients. [1] Jokela *et al.* 1993. [2] de Sousa *et al.* 1988. [3] Paasivirta *et al.* 1988a. [4] Paasivirta *et al.* 1988b. [5] Voss *et al.* 1980, [6] Jonsson *et al.* 1993. [7] Tavendale *et al.* 1995. [8] Martinsen *et al.* 1992. [9] Hyötyläinen *et al.* 1995. [10] Dahlman *et al.* 1994. [11] Dahlman *et al.* 1993. [12] Grimvall *et al.* 1995. [13] Rantio 1992. [14] Koistinen *et al.* 1994a. [15] Remberger *et al.* 1990. [16] Koistinen *et al.* 1994b. [17] Jonsson 1992. [18] Koistinen *et al.* 1995. [19] Juuti *et al.* 1996a and b.

	BKME	SEDIMENT
MWD (g mol^{-1})	Cl (AOX) to recipient: range 50-4000, peak 100-500 (1000, one observation). 5-40 mg Cl l^{-1} non-adsorbable to AC[1].	most HMW compounds from lignin and natural humic acids[2]
Identified compounds	chlorophenols[3,4] chloroguaicols, catechols, syringyls[3,4,5]	chlorophenolics[3,4,6,7], chlorophenolics <1% of EOCl[8]
	chlorinated benzaldehydes, vanillins, syringaldehydes, protocatechaldehydes, syringols, acetosyringones[5,9], chlorovanillic acids[9]	6-chlorovanillic acid, chloroacetovanillone, 6-chlorovanillin, 2-chloro-syringaldehyde[9], chloro- and bromovanillins, chlorodihydroxybenzoic acids[2]
	oxidation: 6-chloro-4-ethoxy-3-methoxy benzoic acid[10], 6-chloro-4-ethoxy-3,5-dimethoxy benzoic acid[11]	oxidation: mono- and dichlorinated 4-ethoxy-3-methoxy- and 3,4-diethoxy benzoic acids[12]
	cymenes[13], chlorophenantrenes, alkylchlorophenantrenes, alkylchloronaphtalenes[14]	dehydroabietin, resin acids, seco-1-dehydroabietic acid, dehydroabietic acid[7], chlorinated alkanoic acids, chlorinated resin acids, terpenes, plant sterols[15]
	chlorofluorenes, alkylchlorofluorenes[16]	PCDDs, PCDFs[6,17,18]
	chloroform, dichloroacetic acid methyl ester, dichloro-thiophene[19]	

2.2.2 Natural organohalogens in the marine environment

Marine algae have been reported to contain up to 19.8 µg g^{-1} ww of chlorometabolites and 19.3 µg g^{-1} ww of bromometabolites (Neidelman and Geigert 1986) and the highest chemical diversity of halogenated metabolites, e.g. acyclic compounds including volatile haloalkanes, monoterpenes, sesquiterpenes, diterpenes, phenols, indoles, acetylenes and complex macromolecules (Faulkner 1993, Gribble 1994, Neidelman and Geigert 1986). Also, synthesis of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tet-rachlorodibenzofuran has been observed (Gribble 1994). On average 20% of the compounds extractable from marine algae contain halogen atoms (Hager 1982, Neidelman and Geigert 1986). Bacteria may also be contributing to the synthesis of organohalogens in the marine environment (Neidelman and Geigert 1986).

Biogenic halogenation of organic material by haloperoxidases is one of the possible mechanisms by which natural organohalogens are formed in the marine environment, and may take place according to a general reaction in which hydrogen peroxide is reduced and halide oxidized:

$$\text{ORG-H} + \text{H}_2\text{O}_2 + \text{X}^- + \text{H}^+ \xrightarrow{\text{haloperoxidase}} \text{ORG-X} + 2\,\text{H}_2\text{O}$$

pH <8
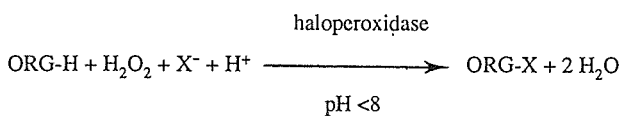
where the ORG is an organic molecule that can be a substrate to the enzyme. The oxidation-reduction potentials for the half-reactions for the reduction of H_2O_2 (+1.77 V) and oxidation of X^- (F^-, -3.06 V; Cl^-, -1.36 V; Br^-, -1.07 V; I^-, -0.54 V) mean that the oxidation of fluoride by haloperoxidases using H_2O_2 is not possible. The biological halogenation of aromatic compounds in natural environments is generally kinetically not thermodynamically controlled, and the reactions of, for example, aromatic compounds have ΔG values of -200 to -100 kJ and equilibrium constants of 10^{23} to 10^{27} (Dolfing and Salomons 1995). Enzymatic halogenation may also take place via a carbocation route (Wuosmaa and Hager 1990).

The haloperoxidase enzymes have been isolated and they are characterised as often containing a ferriprotoporphyrin IX (a heme) prosthetic group, but the exact reaction pathway is not certain. The reaction proceeds with ping-pong kinetics and may either involve a hypohalous acid (HOX) intermediate or an enzyme-bound halogen intermediate (Neidelman and Geigert 1986). In the final stage of the reaction, one or other intermediate halogenates the organic substrate. Chemically, the haloperoxidases catalyse the addition of halides to carbon-carbon double-bonds. Also large organic molecules like steroids and bicyclic compounds are readily halogenated (Neidelman and Geigert 1986). In the presence of sufficient OH^- concentration, $\alpha\beta$-halohydrins are formed. The halogenation reaction is feasible also with alkynes, cyclopropanes, aromatic compounds, β-ketoacids, amines and thiols. Another compound that may be very significant to the natural organohalogen budget is chlorinated chlorophyll RC I (13^2-hydroxy-20-chloro-chlorophyll a), which is an essential part of the photosynthetic system of algae and occurs in appreciable concentrations, 1:87-1:86 Chl RC I: Chl a in algae of the genera Anacystis and Anabaena (Dörnemann and Senger 1982, Dörnemann and Senger 1986, Katoh *et al.* 1985).

The presence in terrestrial environments of large quantities of halogenated humic and fulvic acids and other halogenated humic compounds has been described, and characterised using oxidative degradation techniques (Asplund *et al.* 1989, Asplund and Grimvall 1991, Dahlman *et al.* 1993, Dahlman *et al.* 1994). The halogenated humics have also been found in the marine environment (Grimvall *et al.* 1995, Johansson *et al.* 1995). In the River Rhine 30-70% of the total AOX has been estimated as natural (Hoekstra and de Leer 1994). Arctic and Antarctic macroalgae produce volatile halogenated organics and represent a global example of natural production (Laturnus *et al.* 1996, Mehrtens 1994). Some typical halogenated molecules produced by algae and molecules found in unpolluted humic waters are illustrated in Figure 6.

2.3 Use of sum parameters in the Baltic Sea

The sum parameters AOX, EOX, EOCl, AOCl etc. are used to estimate the total content of halogens in samples. Sum parameters for measuring total amounts of organohalogens have been developed on the basis of elemental halogen content analogous to the nitrogen Kjeldahl analysis, and bear resemblance to COD and BOD. The EOX or EOCl are both ecologically meaningful since they are considered to express the fraction of bioaccumulable compounds in samples. AOX and TOX more or less express the total amount of non-bioavailable organohalogens.

The sum parameters have the natural draw-back of not being able to give information about the specific compounds present in the samples. Most of the individual compounds included in the total halogen content remain unidentified (Table 1). Chromatographic and other analytical techniques must be applied when information on the character of specific compounds is needed. Maximal information of the organohalogens can be obtained by combining the use of sum parameters and specific analytical techniques. If toxicity tests are also included an even better picture of the nature of organohalogens in environmental samples can be obtained.

The method of extracting or adsorbing the compounds from sediment, and the type of detection used are critical aspects of the use of sum parameters. Several combinations of solvents, detection systems and normalisation parameters have been used and, due to the different techniques, results by different researchers are often difficult to compare. Possible positive interferences in analysing organohalogen compounds may arise from the presence of chloride (NAA and microcoulometry), sulphide (microcoulometry, Grøn and Dybdahl 1996), and manganese (NAA). Nitrate may cause negative bias if it enters the microcoulometer titration cell.

Although it is possible to measure the content of specific halogens in the sample with NAA, the microcoulometric determination is easier to perform and more suitable for routine analysis. With microcoulometric detection only the sum of chlorine and bromine is obtained, and reported as chlorine equivalents. Based on empirical results, X = Cl + 0.3 Br. Some of the most common solvents used for extraction of EOX or EOCl/Br are cyclohexane/2-propanol (Martinsen *et al.* 1988), cyclohexane (with 2-propanol treated sediment; Wulff *et al.* 1993), n-pentane (Østfeldt *et al.* 1994) and petroleum ether - ace-
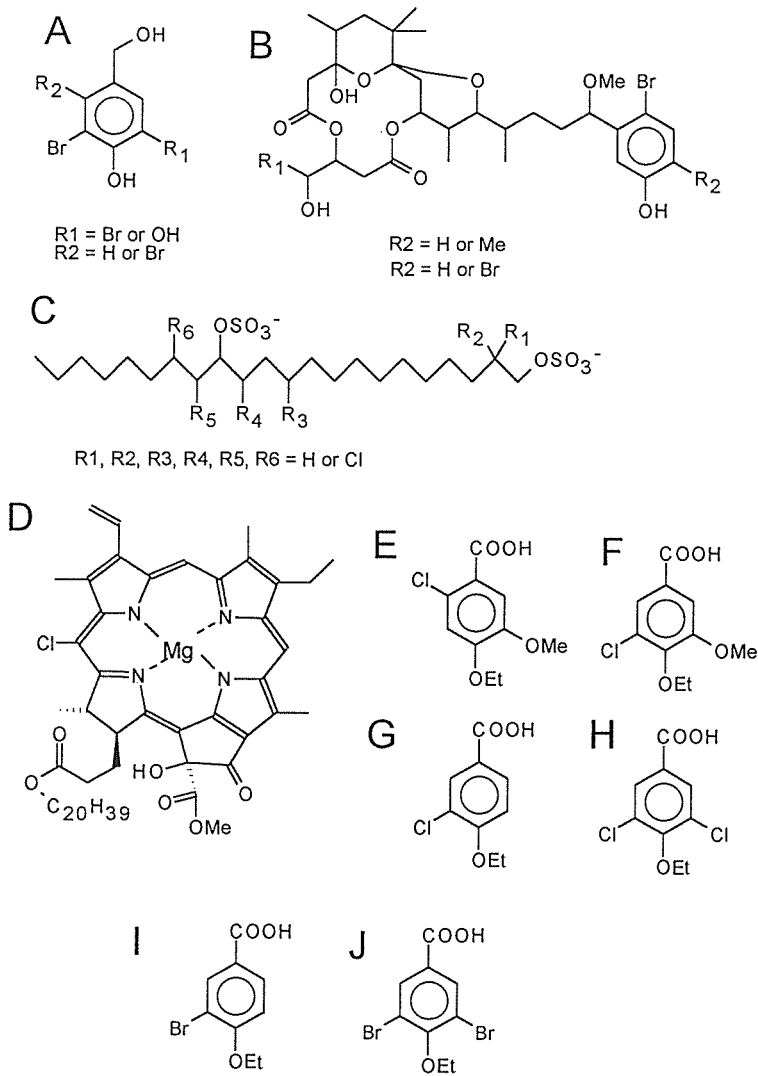
Fig. 6. Examples of halogenated molecules produced by marine algae and those found in non-polluted water environments. A-C from algae *Calothrix brevissima, Oscillatoria nigroviridis* and *Ochromonas danica* respectively (Neidelman and Geigert 1986). D from algae *Scenedesmus obliquus, Anabaena variabilis,* and *Anacystis nidulans* and from spinach (*Spinacia oleracia*) leaves (Katoh *et al.* 1985, Dörnemann and Senger 1986). E-F from fulvic acid preparations (Dahlman *et al.* 1994). G-J from Gotland Deep sediment (Grimvall *et al.* 1995).

tone (Palm and Lammi 1995). For inorganic halide removal, both pre- and post-treatment (relative to extraction) with nitrate solution have been used (Martinsen *et al.* 1988, Martinsen *et al.* 1994), but washing after extraction is most common. A special sum parameter, sediment total organic halogen (SOX) is based on KOH-methanol extraction followed by activated carbon adsorption (Pellinen and Soimasuo 1993). AOX methods for sediment analysis are still the exception, but Manninen (1990) has

described a procedure for extraction with alkaline propanone and water dilution followed by activated carbon adsorption. Extraction with aqueous methanol together with activated carbon adsorption has also been used (Palm and Lammi 1995). An activated carbon-based AOX method resembling that described in the present study (I) has been reported by Hoffmann *et al.* (1988) for sludges and sediments.

The AOX, EOCl or EOX results are usually normalised to either dry weight, total carbon or loss on ignition (LOI). In the Baltic Sea, LOI-normalisation is usual (Håkanson *et al.* 1988, Södergren *et al.* 1993, Østfeldt *et al.* 1994). Near pulp mills, EOCl levels up to 1100 μg Cl g^{-1} dw and 6270 μg Cl g^{-1} LOI (Martinsen *et al.* 1994, Södergren *et al.* 1993), EOX levels up to 70 μg Cl g^{-1} dw and AOX up to 230 μg Cl g^{-1} dw (Palm and Lammi 1995) have been reported. At a distance of 29 km off a pulp mill 26 μg Cl g^{-1} (EOCl) was found (Martinsen *et al.* 1994). Usually the background EOCl level has been estimated at 5-10 μg Cl g^{-1} dw (Håkanson *et al.* 1988, Martinsen *et al.* 1994).

2.4 Harmful effects of pulp mill effluents to marine organisms

In effluent discharge from pulping there are three conventional pollutant factors causing adverse environmental impact, 1) fibers and suspended solids, 2) colour and turbidity and 3) organic and nutrient enrichment (Owens 1991). Significant organic and nutrient loads can be discharged by pulp and paper mills, readily altering or degrading local habitats (Hutchins 1979). Increased loading can lead to bottom anoxia, inducing changes in benthic populations. Eutrophication can stimulate the growth of phytoplankton. This is a complex question, since phytoplankton growth may be limited by reduced transparency caused by the discharge of particulate material, but early data from the Baltic Sea indicated that plankton biomass and chlorophyll concentrations did not decline due to utilization by the phytoplankton of the organic material in the effluents, which compensated photosynthetic losses (Lyden and Landner 1979). A review of the different adverse effects of BKME has been given by Södergren *et al.* (1993) for the Bothnian Sea area. Effluents from Swedish pulp mills using chlorine chemicals were reported to cause deformations in pike, reduced gonad growth, disappearance of benthic animals and reduced density of macroalgae (Södergren *et al.* 1993).

Correlation between halogen concentration (EOX, AOX) and toxicity is not well established, and is often totally missing (e.g. Ahokas *et al.* 1994, Craig *et al.* 1990). In addition, there are no direct comparisons of short- and long-term effects of pulp and paper mill effluents. Södergren *et al.* (1993) reported that unbleached kraft mill effluent caused considerably smaller effects on fish than BKME. On the other hand, Haley *et al.* (1995) found that the reduction of chloro-organics in effluents after in-creased substitution of Cl$_2$ by ClO$_2$ was probably not responsible for biota responses. Moreover, the overall changes in mill-process on experimental stream biota were minor (Haley *et al.* 1995). It is probable that a large part of the physiological effects of pulp and paper effluents may be related to nonchlorinated substances, which in some cases have been found to be more toxic than the chlorinated ones, e.g. according to 7-ethoxyresorufin-o-deethylase (EROD) activity in Rainbow trout (*Oncorhynchus mykiss*) hepatocytes (Pesonen and Andersson 1992).

Although it is possible to show that specific organochlorine compounds and BKME are toxic to many organisms, in general the effects of BKME remain controversial, and both the acute and chronic effects of BKME on fish, mussels and benthic animals must be considered (for a review, see Owens 1991). Typical effects of BKME are increased liver EROD activity (e.g. Balk *et al.* 1993, Förlin *et al.* 1995, Haley *et al.* 1995), expression of multi-function oxygenase (MFO) enzymes (e.g. Larsson *et al.* 1988, Munkittrick *et al.* 1992), alterations in gonad size, changes in number of lymphocytes, changes in carbohydrate metabolites, disturbances in plasma ion composition (Förlin *et al.* 1995) and decreased survival of larvae (e.g. Pellinen and Soimasuo 1993). Increased activity of uridine diphosphoglucuronyl transferases (UDPGTs), which facilitate the operation of the cytochrome P450 monooxygenase system, was reported by, for example, Förlin *et al.* (1995). Induction of UDPGT activity is indicative of exposure to xenobiotics. BKME and the polar fraction of BKME was mutagenic according to the Ames bacterial test and SOS Chromotest, and the polar fraction toxic to *Daphnia magna* and luminescent bacteria (Microtox) (Rao *et al.* 1994). The Microtox (*Photobacterium phosphoreum*) test was found to be a sensitive indicator of BKME toxicity (Oanh and Bengtsson 1995).

Over large areas fish populations may suffer from BKME exposure (e.g. Sandström and Thoresson 1988, Förlin *et al.* 1995). The area of BKME influence may extent 8-10 km (Larsson *et al.* 1988) or even 20-40 km (Balk *et al.* 1993) from a pulp mill. Using a flow-through mesocosm, accumulation of low-molecular-weight EOX in the mussel *Anodonta anatina* L. was observed, but EOX accumulation in the mussels and in the fish *Salmo salar* L. was not observed in waters near a pulp mill (Pellinen *et al.* 1993). Higashi *et al.* (1992) demonstrated that polar, high-molecular-weight material from BKME was acutely toxic to salmonid fish. BKME exposure adversely affected reproduction, growth, survival and histopathology of Rainbow trout (Haley *et al.* 1995). Minnows (*Pimephales promelas*) were not

significantly affected by chlorine-bleached BKME from Canada (Kovacs *et al.* 1995). Similarly, Pellinen and Soimasuo (1993) reported that exposure to BKME-polluted sediment from Lake Saimaa did not increase mortality or deformities in midges (*Chironomus riparius* Meigen).

Because benthic animals bioturbate sediments and use organic matter from sediments as their primary food, they are subject to sedimented pollutants. The benthic animals mainly responsible for bioturbating sediments in the Gulf of Finland are the amphipods *Monoporeia* (formerly *Pontoporeia*) *affinis* and *Saduria entomon*, and the mollusc *Macoma balthica*. These species have been increasing in number since the middle 1980's (Andersin and Sandler 1991). Through bioturbation they mix the vertical distribution of chemicals in sediments. *M. affinis* is one of the most important organisms in Baltic foodchains and an important food source for the Baltic herring (*Clupea harengus*), especially during the maturation period of male *M. affinis* individuals (e.g. Flinkman *et al.* 1991, Flinkman, FIMR, pers. comm.).

Changes in behaviour of benthic species during exposure to xenobiotics under laboratory conditions can also be monitored: Lindström and Lindström (1980) and Lindström (1992) studied the effects of phenols and chlorophenols on the nocturnal swimming activity of *M. affinis* Lindström, and showed that animals avoided elevated phenol levels in water by diminishing their swimming activity. Sundelin (1988) observed increased, long-term mortality (disturbed embryogenesis) of *M. affinis* and other macro- and meiofauna when exposed to sediment contaminated with sulphate mill effluent. Both unbleached and bleached effluents were toxic, but bleached effluent significantly more so. In contrast, Haynes *et al.* (1995) did not observe bioaccumulation of EOX from pulp mills in *Mytilus edulis*, nor any adverse effects. Similarly, Mäkelä *et al.* (1992) found no clear dependence between EOCl in mussels and distance to pulp mill.

3 Aims of the study

The present work was designed to improve the knowledge on the amounts, distribution and sources of organohalogens in the Gulf of Finland area. The following multidisciplinary aims were set:
1) to estimate the usefulness and applicability of AOX and EOX methods to the study of marine sediments

2) to determine the suitability of chemical characterization methods for total organohalogen preparations and to characterise the organic halogen material in Gulf of Finland sediments
3) to evaluate the background organohalogen concentrations in sediments and algae, the horizontal (spacial) and vertical (temporal) distribution of total organohalogens in sediments, and to locate polluted areas
4) to estimate total organohalogen quantities in sediments, fluxes of organohalogen material and also the contribution of anthropogenic and natural organohalogen sources to the total budget of the study area
5) to evaluate some of the possible ecological consequences of BKME material discharge and the need for monitoring sediments for halogenated compounds.

4 Materials and methods

4.1 Collection of material

The location of sediment sampling stations together with their basic characteristics are listed in Appendix 1.

4.1.1 Positioning accuracy, ship stability and co-ordinates

The positioning accuracy of the R/V Aranda is ±5 m using differential global positioning system (DGPS) navigation, and approx. ±30 m with global positioning system (GPS). Most of the sampling took place using DGPS. The positioning during sampling from other vessels and platforms was usually GPS or less accurate (see Appendix 1 for the navigation systems and accuracies). The R/V Aranda can stay within an approx. 20 x 20 m area during sampling in good weather (Bruun and Kankaanpää 1996 and unpublished results). The co-ordinate system is either the Finnish 'karttakoordinaattijärjestelmä' (KKJ) or the international WGS-84, also indicated in Appendix 1. Within the Gulf of Finland interconversion between the two systems can be made using the formulas 1 and 2:

(1) $LAT(WGS\text{-}84) = LAT(KKJ) + 0.00017°$

(2) $LON(WGS\text{-}84) = LON(KKJ) - 0.00317°$

4.1.2 Baltic sediment and marine fauna

Sediment sampling for paper I was carried out during the cruise of the Finnish R/V Aranda to the Bay of Bothnia in September 1990 using a gravity corer with diameter 50 mm (Niemistö 1974). The samples were collected a few hundred meters from the Veitsiluoto pulp mill. In papers II and III samples from the open Gulf of Finland were collected from R/V Aranda using a larger gravity corer of $\varnothing$ 80 mm (Gemini corer) in February 1993. In paper III the Neva Bay 0-2 cm sediment samples (R/V Raduga, box corer) and 0-2 cm samples from Kotka area (motorboat, using a gravity corer of $\varnothing$ 50 mm) were collected in August and September 1993, respectively. For paper IV sediment from the Bothnian Sea was collected from R/V Aranda using a van Veen grab sampler in June 1994. *Monoporeia affinis* individuals were collected from the sediment by sieving and stored (+ 4°C) in darkness.

Sediment samples for paper V, covering areas in Finnish, Estonian and Russian waters, were collected from R/V Aranda (using a gravity corer of $\varnothing$ 80 mm) and a motorboat (Kotka and Sovetskiy coastal areas using a gravity corer of $\varnothing$ 50 mm) in June 1994. Sediment samples from the Luzhskaya-Koporskaya region in August 1994 were obtained during the cruise of the Russian R/V Persey and from Lake Saimaa in July 1994 from the Finnish R/V Muikku using a $\varnothing$ 50 mm gravity corer. Samples from the Kymi River were taken from a motorboat and from piers with a $\varnothing$ 50 mm gravity corer in September 1994.

Additional sediments (Kankaanpää 1996) were collected during the ICES-HELCOM Sediment Baseline Study from R/V Aranda in June 1993, using a gravity corer of $\varnothing$ 80 mm. Sediments for the trap study (paper V) were collected from station GF2 (central Gulf of Finland, see Appendix 1) using R/V Aranda in May-September 1995 with an $\varnothing$ 80 mm gravity corer. In August 1996 a single 0-5 cm box core sample for characterization studies was taken from the same station.

4.1.3 Settling material

The system for collection of settling particulate material consisted of a conical sediment trap with a collection area of 1.0 m² and aspect ratio 1.6 (Technicap P.P.S. 5/2, France), which was equipped with 24 250-ml receiving cups (polypropylene). The trap was moored at station GF2 at 64 m and at 20 m above bottom. The trap was operated between May 17 and September 22, 1995, and between April 25 and October 20, 1996. The cups were prefilled with 5% (v/v) formalin solution (Merck, p.a.) containing 10 g l^{-1} NaCl (Merck, suprapur). Each cup was programmed to collect for exactly 3 days.

The material from the automatic trap was in both cases combined to form 9 consecutive samples that were then subjected to the analyses. The combined samples represented time intervals of May 17-29, May 29-June 10, July 7-16, July 16-28, August 8-20, August 20-September 1, September 1-10, and September 10-21, 1995, and in the second case study April 25-May 16, May 16-25, May 25-June 6, June 6-27, June 27-July 18, July 18-August 15, August 15-September 14, September 14-26, and September 26-October 20, 1996.

4.1.4 Antarctic sediments, plankton and fauna

All the samples were collected during the FINNARP 95/96 cruise to the Weddell Sea with the R/V Aranda in February 1996. Ice, containing plankton, was collected from an ice floe (74.0170° S, 35.8078° W), placed in plastic baskets and melted in the laboratory. Ice algae were allowed to attach to the walls of the baskets and were subsequently sucked to polyethylene bottles. The frozen samples were stored (-20 °C) for two months and transferred to FIMR for analysis.

Sediment was collected near the Riiser-Larsen Ice Shelf (72.5157° S, 16.5330° W) from a depth of 205 m, using a box corer and stored at -20 °C for two months. The sediment was clayey and sandy with an over 2 cm thick surface layer of corals, brittle-stars and small tube-like animals with a siliceous core. Before pre-treatment in the laboratory, the organic surface was removed. An unknown species of sponge was collected from the Weddell Sea (72.2453° S, 15.6000° W, depth 365 m) and stored frozen (-20 °C) for two months.

4.1.5 Collection of water samples and BKME

In the Kotka area and in Russian and Estonian waters, water samples of 500 ml were collected from above the sediment core to polyethylene bottles. The water was frozen (-20 °C) and melted before analysis for AOX. A total of 60 l of BKME was collected from the Sunila pulp mill in Kotka, in May 1994. During the collection time the mill used both Cl$_2$ and ClO$_2$ for bleaching. The samples were stored at -20 °C and brought to room temperature prior to the experiment. Sea water was collected from the Tvärminne area (western Gulf of Finland). Before the test, the BKME solution was vacuum filtered through a Whatman no.1 filter and diluted 1:2 with the sea water.

4.1.6 Other material used for chemical analyses

The algal cultures of *Anabaena lemmermannii* and *Nodularia spumigena* were kindly prepared by Dr Kaarina Sivonen, University of Helsinki. Commercial chlorophyll a (Sigma chemicals C6144, isolated from *Anacystis nidulans* algae), spruce (*Picea abies*) needles and spinach (*Spinacia oleracea*) were also used.

4.2 Pre-treatment of sediments

4.2.1 Determination of <63 μm fraction

A representative portion of each wet sediment sample analysed was sieved, under a water flow, through a 63 μm cut-off sieve (Fritsch, Germany). The material left on the sieve was weighed after drying at 60 °C for 48 h. The weight of the fine-grained material passed through the sieve was used to calculate normalised EOX and AOX concentrations.

4.2.2 Drying and homogenisation

Analysis of ^{137}Cs was carried out from wet sediment either onboard or before pre-treatment in the laboratory. For chemical analyses the frozen sediment sub-samples were lyophilized using an Edwards Super Modulyo freeze-dryer (-20 °C, 24-48 hours), and homogenised either manually or using a planetary mill (Fritsch pulverisette 5).

4.3 Aquarium system for investigating effects of BKME on *M. affinis*

The detailed construction is given in paper IV. Briefly, two control and four test aquaria (L 33 x W 6 x H 35 cm) were filled with brackish sea-water (6-7‰), 40 randomly selected animals were placed in each aquarium, and the bottoms covered with sediment from the area where the animals were sampled. Sea water (control aquaria) or sea-water mixed with BKME (test aquaria) was allowed to flow through the aquaria at 12 ml min^{-1}. A 12:12 hour light-dark cycle was used and the swimming activity of animals was recorded during the adaptation period (12 days, without BKME), control period (7 days, without BKME), test period (7 days, with BKME) and recovery period (12 days, without BKME). The activity was recorded with four IR photocell pairs.

Water samples for AOX were collected from seawater and from the BKME stock solution before the test, and from the aquaria during the test period. An aliquot of bottom sediment from each aquaria was collected before and after the experiment, and the EOX concentration and number of surviving animals was counted after the recovery period. The statistical treatment of the raw activity data was carried out using one-way ANOVA with an SAS programme. The obtained p values were used to estimate whether the swimming activities during the C, T and R periods deviated significantly from each other.

4.4 Chemical analyses

4.4.1 The AOX sediment procedure and its validation

For each analysis, 50 mg of pre-treated sediment was suspended in 9 ml of dilute acid (pH 2, set with HNO_3, Merck, p.a.) in a test tube, to which 1 ml of 1M $NaNO_3$ was added. The suspension was sonicated (Branson 3200 ultrasonicator) for 30 minutes and then shaken vigorously for 30 minutes in a vertical rotator (Braun Certomat) at ambient temperature. The suspension was then centrifuged at 3000 rpm (Heraeus Megafuge 2.0R) for 30 min. The supernatant was removed and placed in another test tube. After addition of 200 μl of 0.1M $AgNO_3$ (Fluka, p.a.) the tube was shaken for 10 minutes in darkness. Precipitated silver salts were removed by filtration onto a Schleicher & Schuell FP 050 NLGF 0.45 μm filter and the filtrate was transferred back to the solid sediment phase. 100 mg of activated carbon (Euroglas, maximum Cl content 15 μg g^{-1}) was added and the solution was again agitated in a vertical rotator for 16 hours. The solid phase was then filtered on a polycarbonate filter (Euroglas) and washed with 10 ml of 1 M $NaNO_3$ (Merck, p.a.). Blank samples were prepared similarly, without the sediment.

Accuracy and precision of the method were estimated by preparing four o-chlorobenzoic acid (Merck, p.a.) solutions of 2000, 1000, 500 and 0 μg Cl l^{-1} (Millipore mQ deionized water). To check the possible interference by silver ion or the silver halide precipitate formed, five further solutions were prepared with the same Cl content but with $AgNO_3$ concentrations of 1.0, 0.5, 0.2, 0.1 and 0 mM. These solutions were then analysed for AOX according to the ISO 9562 standard (ISO 1989; see below).

Possible loss of the model compound, o-chlorobenzoic acid, was investigated by preparing six du-

plicate sample solutions of 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 mM of the acid. The pH of the solutions was adjusted to 2.0 with HNO_3. Two additional solutions, also in duplicate, having 1.0 mM and 4.0 mM of the acid and 5 g l^{-1} of NaCl were prepared. Deionized mQ water was used for every solution. Absorbance of the solutions was measured at 273 nm (see below). An aliquot of 5 ml of each sample was treated with 240 µl of 2.0 M $AgNO_3$ and stirred for 30 min in darkness before the precipitate was filtered off. Finally, the absorbance (at 273 nm) of the solutions was measured again.

To estimate possible interference to the AOX analyses from inorganic chloride in the sediments, the salinity of leachate from sediment samples was analysed and possible correlation with AOX was examined. The leachate was prepared from 500 mg of homogenised sediment from the KEMI 17 station (Appendix 1). Sediments were suspended in 3 ml of deionised water, ultrasonicated (Branson 3200) for 30 minutes and shaken in a vertical rotator for 30 minutes, both at 23 °C. The suspension was centrifuged and the salinity of the supernatant measured with a Beckman Solu Bridge RB-5 salinometer with CEL G-20 electrode. Interference by high H^+ concentrations was excluded since the pH of the leachates was over 4 and did not increase conductance during salinity measurements.

4.4.2 Preparation of water samples for AOX determination

The water samples taken from above the sediment surface, from the sea surface in Kotka and from the test aquaria were analysed. An aliquot of 100 ml was taken and adjusted to pH 2 with HNO_3, after which 5 ml of 0.2 M KNO_3 and 100 mg of activated carbon (Merck or Euroglas) were added. The mixture was agitated for at least 16 h and then filtered onto a polycarbonate filter (Euroglas). The filter and activated carbon were subsequently washed twice with 20 ml of 0.01 M KNO_3 (pH 2) and twice with 20 ml of deionized water.

4.4.3 EOX extraction and method validation

The method was a modification of a procedure by Martinsen *et al.* (1988). In brief, 0.08-10 g of pretreated sediment, seston, algae, or sponge was extracted by sonication (2h) in 75 ml of cyclohexane/2-propanol (4:1, v/v), followed by strong agitation in a vertical rotator (16 h). Solid material and solution were separated by centrifuging. Supernatants were

washed twice with 25 ml of 0.2 M KNO_3 (pH 2) solution to remove inorganic halogens. Possible cloudiness was removed by adding a small amount of 2-propanol. The extracts were concentrated to 2-5 ml with a rotary evaporator and then to 0.5-2 ml under a nitrogen flow. Precipitate, when it did form, was observed to contain negligible amounts of EOX and was removed by centrifuging.

The detection limit was calculated using the formula:

$$(3) \qquad DL = 2 \times \sqrt{2} \times t_{0.05} \times s_w$$

where $t_{0.05}$ is the tabulated value of the Student's t-test (single-sided) at 95% probability and s_w is the within-batch standard deviation of duplicated blank samples determined during 7 days. Linearity was measured using standard solutions of 4-chlorophenol, injected over a range of 2-35 µg Cl per injection. The injection repeatability was calculated by injecting four different standard solutions and one extract of a contaminated sample 10 times consecutively. Injection reproducibility was measured by injecting three standard solutions per day over a period of 9 days. The repeatability of the EOX method was measured using sediments from stations KY2, KY3 and S2 and by conducting from one to four EOX measurements per sample per day for 3 days. EOX method reproducibility was measured over a period of ten days using sample KY3. In the interlaboratory comparison test, made by the Finnish Institute of Marine Research and the Finnish Environment Institute, five different sediment samples (stations S1-S5) were analysed in duplicate or triplicate in both laboratories and the results were processed with the Student's t-test. During the analyses, daily control of the microcoulometric measurement analyses was carried out by injecting a 4-chlorophenol (Fluka, p.a.) control solution of 13.8 (±2%) µg Cl ml^{-1} into the system. Blank solvent samples were analysed daily in the same way and the blank value was subtracted.

Two tests were carried out to check possible interference from inorganic halides. In the first test an aliquot of the sediment extract was placed in a ceramic crucible, evaporated to dry and kept at 550 °C for 2 hours to remove organic material. The cooled, colourless precipitate was then dissolved with 100 µl of deionized water (mQ). The final volume was set to 500 µl with methanol, and 100 µl of the solution was burned in the analyser. In the second test 100 µl of the extract was injected directly to the coulometer cell. To exclude the interference of any other compounds in the microcoulometric detection of the halogens, two sediment extracts and one standard solution were analysed with microcoulometry and NAA.

4.4.4 Microcoulometric detection of halogens

The halogen content was determined using an Euro-glas ECS 2000 halogen analyser (Euroglas BV, Delft, the Netherlands). The extracts or filters containing solid material (two or three replicates) were combusted in O_2 at 850 °C (EOX) or 1050 °C (AOX). The halogen content was expressed in chlorine equivalents.

4.4.5 NAA detection of halogens

For comparison and further validation of the EOX method three samples were also analysed with NAA. The analyses were carried out in the Reactor Laboratory of the Technical Research Centre of Finland, Espoo, Finland. The extracts or 4-chlorophenol were placed in a 0.5 ml polyethylene capsule and frozen in liquid nitrogen. A standard was made by dissolving KBr and KCl in water and 5 µg of Br and 50 µg of Cl was weighed into a capsule.

The standard and samples were analyzed by irradiating for 5 min in a Triga MkII research reactor and neutron flux of 4 x 10 s^{-1} cm^{-2} using a pneumatic sample transfer system. The sample capsule was opened and the solution weighed into a new capsule to minimize the risk of contamination. After a decay time of 10 minutes, the sample was measured for 5 min using a γ-spectrometer equipped with a 25% Ge(Li) detector. The 616.3 keV (^{80}Br) and 1642.7 keV (^{38}Cl) energies were used for quantification. Concentration was calculated by comparing the photopeak count rate of the sample with the corresponding count rate of the standard. Because equal irradiation, decay and counting times were used, no decay correction was needed. The standard deviations of the Br and Cl measurements were better than 5% with a detection limit of 0.2-0.8 µg Cl g^{-1} and 0.03-0.05 µg Br g^{-1}.

4.4.6 Determination of chlorophenolics, PCBs and OCPs

Analyses of chlorophenolics (PCPs, PCGs and PCCs) in sedimenting material were carried out at the National Public Health Institute, Kuopio, Finland. Free and bound chlorophenolics were analysed together. Internal standards (3,5-dichlorophenol and 2,3,6-trichlorophenol) were added to the pre-treated sediment, which was then extracted with 6M NaOH and cleaned with hexane. The water phase was

acidified with 2M H_2SO_4 and then extracted with diethylether three times. The ether phases were combined and dried with activated Na_2SO_4. The ether phases were then filtered and evaporated to dry, and finally acetylated with acetic anhydride and 0.1M K_2CO_3. The acetylated chlorophenolics were back-extracted to hexane and determined with an HP5890II gas chromatograph with an HP-5 capillary column (25 m x 0.2 mm), using a temperature program of 60°C (1 min), 20 °C min^{-1} to 140.°C, 4 °C min^{-1} to 240 °C. The sum of the chlorophenolics (ΣPCP) was calculated. All reagents and solvents were p.a. grade.

PCBs and OCPs in sedimenting material were analysed at the Finnish Environment Institute, Helsinki, Finland. Sedimenting material was 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 3000 rpm for 7 minutes (Heraeus Megafuge 1.0). The extracts were combined and the solvent was evaporated almost to dryness in a rotavapor (Büchi RE-121) and redissolved in iso-octane. The internal standard 1,2,3,4-tetrachloronaphtalene (Ultra Scientific) was added and the sample was purified with concentrated H_2SO_4 until the solvent phase was colourless. Additionally, the elemental sulphur in sediment extracts was removed with copper chips. The sample was concentrated to a final volume of approximately 0.5 ml with nitrogen flow. All the solvents and reagents were of p.a. grade.

Organochlorine compound analysis was performed on an HP5890II gas chromatograph equipped with two ^{63}Ni ECDs, two capillary columns HP-1701 and HP-5 (60 m x 0.25 mm i.d., film thickness 0.25 µm) and an HP7673 automatic sampler. Helium was the carrier gas with argon-methane as the detector make-up gas. The injector and detector temperatures were 270 °C and 300 °C respectively. The oven temperature program was 90 °C for 3 min, 30 °C min^{-1} to 215 °C for 42 min and 5 °C min^{-1} to 270 °C for 10 min. Compounds were identified from both columns by comparing the retention times with known compounds, 1,2,3,4-tetrachloronaphtalene was used as an internal standard. Quantification was based on a standard mixture prepared by weighing neat crystals (Dr Ehrensdorfer, Germany), dissolving them individually in iso-octane and then mixing them together to make up the final solution in iso-octane. The total concentration of the 7 CBs analysed (CB28, CB52, CB101, CB118, CB138, CB153 and CB180) was calculated.

4.4.7 Determination of TC

Two to three weighed subsamples of the pretreated sediments were analysed by combustion in pure oxygen at 900-950 °C and the CO_2 produced was measured. Oxalic acid or glucose was used as standard. The instruments used were UNICARBO IV, Shimadzu TOC-5000 and Heraeus CHN-O-RAPID.

4.4.8 Recording of UV-VIS spectra

For acquiring the spectra and absorbances of unwashed EOX solutions a Perkin-Elmer Lambda 2 spectrophotometer was used. The spectra of the solutions (in a 1 cm quartz cuvette) were between 190 and 600 nm. In paper I, absorbances between 240 and 300 nm and at 273 nm were recorded before and after the addition of the silver nitrate solution used to estimate possible loss of the 4-chlorophenol being used as a model compound.

4.4.9 RP-HPLC analysis

EOX extracts from sediment and sedimenting material at station GF2 were filtered through a 0.45 μm PVDF/PE filter (Millipore, USA). An aliquot of 100-150 μl of the filtrate was injected (Rheodyne 7125) to the HPLC system consisting of Waters M-45 and 510 pumps, μBondapak C18 pre-column, a preparative Nova-Pak C18 column (7.8 x 300 mm), and a Perkin-Elmer LS-5B Luminescence Spectrometer (fluorescence mode, excitation 420 nm, emission 650 nm, slits 5 nm). The extracts were fractioned into 5 or 7 fractions (see results), which were then subjected to EOX, MS, HPLC-SEC and MS analyses.

4.4.10 SEC-HPLC analysis

EOX extracts from sediment samples from the open sea, Kotka area and Neva Bay, as well as RP-HPLC fractioned samples, were filtered through a 0.45 μm PVDF/PE filter (Millipore, USA) and 50-100 μl of the filtrate was injected into the HPLC system using a Rheodyne 7125 injector. The instrument used consisted of a Waters M-45 pump with a UV-VIS detector (Waters 490) operating at 254 nm and one or two consecutive 300 x 7.6 mm PL-gel 3μ Mixed-E columns (Polymer Laboratories, MA, USA) with a short pre-column of the same material. THF was used as eluent using a flow rate of 0.5 ml min⁻¹ (isocratic). The system was calibrated using a mixture of toluene and polystyrenes with molecular weights of 162, 266, 370, 474, 580, 1680, 3250, 5050, 7000, 11600 and 22000 g mol⁻¹. The samples were fractioned into 6 or 12 fractions of known MWD (see results), each fraction was evaporated to dry and finally redissolved in 100-150 μl of cyclohexane/2-propanol (80:20 v/v). The fractions were then subjected to microcoulometric measurement.

4.4.11 TLC separation

An amount of 1-3 μl of EOX solution (final concentrate) was applied to a fluorescent silica TLC plate (Merck 5554 Kieselgel 60 F_{254}, 20 x 20 cm). The separation was carried out using petroleum ether: 2-propanol: H_2O (100:10:0.25 v/v/v) as eluent, and the plates were developed twice with the eluent. The fluorescent spots were detected by illumination with a 366 nm UV-lamp (UVL-21, Ultra-Violet Prod. Inc., CA, USA) and photographed (Nikon F801 camera with a 35 mm macro objective) on colour film (Agfa Ultra 50 ASA). The colour films were subsequently recorded with a photoscanner and processed.

4.4.12 Mass spectrometric methods

The RP-HPLC fractions were analysed with mass spectrometry at the State Technical Research Centre, Espoo, Finland. The mass spectrometer was a Quattro II tandem quadrupole mass spectrometer (Micromass, Altringham, UK) with a Micromass MassLynx data system. The electrospray (ES) interface was a standard Micromass pneumatically assisted ESI source operating with a capillary voltage of 3.2 kV and temperature of 70 °C. Spectra of the fragment ions were recorded using a cone voltage of 60 eV. The mass spectrometer was operated in negative ion mode. Tandem mass spectra were recorded with collision energy of 30 eV using argon as a collision gas (pressure of 5 x 10⁻⁴ mbar).

For the matrix assisted laser desorption (MALD) ionization, samples were prepared using the dried drop method in which the matrix (α-cyanocinnamic acid) was evaporated from acetone solution to a sample plate, to which the sample was added. Polar molecules in the samples were desorbed using a laser pulse and then accelerated in an electric field of 10-18 kV cm⁻¹. The mass of the molecules was calculated from the time of flight (TOF) to the mass detector or ion mirror. Chl a was used as a reference compound. From each sample 25 spectra were measured and added together.

4.4.13 NMR analyses

Aliquots of 5 ml of the EOX extracts of sediment and sedimenting material were lyophilized. The dried material was dissolved in d_6-acetone (CIL, Andover, MA, USA) and filtered through glass wool into NMR tubes. A few drops of tetramethylsilane (CIL) were added to serve as reference. The spectra were recorded at the Department of Polymer Chemistry, University of Helsinki, using a Gemini-200 NMR spectrometer. The ^{1}H spectra were measured at 200 MHz with a 1 s relaxation time, 45.5° pulse, 3.744 s acquisition time, 3000 Hz bandwidth and by adding 128 spectra. The conditions for the ^{13}C (50 MHz, ^{1}H decoupled at 200 MHz) measurements were: 1 s relaxation time, 43.7° pulse, 1.498 s acquisition time, 15000 Hz bandwidth; the total number of spectra added was 1024 (sedimenting material) or 13264 (sediment).

4.5 Estimation of rate of sedimentation

4.5.1 Detection of ^{137}Cs and calculation of sedimentation rates

The gamma-spectra of the sediment samples were measured with an UMKA spectrometer manufactured by the Radiochemical Laboratory of the Krylov Shipbuilding Institute, St. Petersburg, Russia. The measurement takes place in 2π geometry using 1024-channel NaI/Tl scintillation detectors of 80 x 80 mm and 150 x 100 mm. Spectra were acquired for 10-30 minutes and the obtained peaks were integrated with a PC program. The system was calibrated with a ^{137}Cs standard with initial 20.20 Bq g^{-1} activity; background activity was subtracted from sample activity. Finally, the activity of ^{137}Cs was plotted against sediment depth so that the 1986 fallout maximum could be located.

The average linear sedimentation rate (v'; cm a^{-1}) was calculated as:

(4) $v' = z\, t^{-1}$

where z is the depth of the radiocaesium maximum (cm) and t is time (a) between sampling (June 1994) and May 1st 1986. As sediment compaction was not taken into account, the v' value expresses the average rate for the whole post-Chernobyl layer. The average dry matter accumulation rate S was calculated as:

(5) $S = m\, A^{-1}\, t^{-1}$

where m is the cumulative dry-mass over and including the maximum activity layer (g) and A is the sectional area of the corer (cm^2).

4.5.2 Sedimentation rates from sediment trap experiments

The fluxes were calculated as:

(6) $F_{comp} = m\, c_{comp}\, t^{-1}\, A^{-1}$

where F_{comp} is the flux of the compound in question, m is the total accumulated dry-weight during a given time period, c_{comp} is the concentration (per dw) of the compound during the time period, t is the time of collection (days) and A is the collecting area of the sediment trap (m^2).

4.5.3 Calculation of total EOX for the Gulf of Finland

The total recent accumulation of organohalogen material was calculated for the 0-1 cm sediment layer for both the Kotka area (polluted sediments) and the non-polluted sediments. The average chlorine content (in µg) in the surface layer was calculated and extrapolated to include all Gulf of Finland recent sediments according to:

(7) $m_{tot,surf} = m_{av,\ surf}\, A_{region} \times 0.3$

where $m_{tot,surf}$ is the average content of Cl in surface sediments in the area in question, $m_{av,\ surf}$ is the average content of Cl in surface sediments from the area, A_{region} is the area (2.86×10^{10} m^2 for the Gulf of Finland and 1.4×10^9 m^2 for the Kotka area), and 0.3 (30%) is the areal share of accumulation bottoms. A value of 35% was used in the original publication V, but was changed to 30% to accord with latest information (Winterhalter, GSF and Spiridonov, VSEGEI, pers. comm.)

An integrated value of the sedimentation of EOX was obtained by using the depth of the Chernobyl fall-out maximum (^{137}Cs) in sediments and by calculating the total chlorine content in the 1 cm sediment layers from 1986 to 1994 (sampling time). This was calculated as:

(8) $m_{tot} = \sum\limits_{i=1}^{n} c_i\, m_i$

where m_{tot} is the total halogen content (Cl equivalents) in the 1986-1994 sediment layer (Kotka area and other locations), n is the depth of the ^{137}Cs activity maximum, c_i is Cl concentration (EOX) in

each 1 cm sediment layer, and m_i is the dry mass of the sediment layer.

For the studied compounds, the average fluxes ($F_{comp,av}$) for the whole experimental period (May 17-September 22, 1995 and April 25-October 20, 1996) were calculated. Extrapolated annual sedimentation for all Gulf of Finland accumulation areas was calculated as:

(9) $ACC_{tot,comp} = F_{comp,av}$ x 365 d x
        3×10^{10} m^2 x 0.3,

where $ACC_{tot,comp}$ is the total sedimentation of the compound in question, and 3×10^{10} m^2 is the total area of the Gulf of Finland.

5 Results

5.1 Validity of results

The AOX and EOX methods were validated and results are shown in Table 3. The recoveries and repeatabilities of the methods were good, and the intercalibration with another equivalent coulometric system and NAA confirmed that the method is reliable. Interference from inorganic halides was minor (<10%). In 10 cases out of 13 the fractionation of halogenated material with SEC was successful and the calculated sum total of the EOX fractions was in agreement with the total EOX values from the original, unfractionated samples.

Table 3. Validation and characteristics of the AOX and EOX methods. r = correlation coefficient. N.D. = not detected. RSD = relative standard deviation. σ = standard deviation. * = GF2 sediment, sedimenting material and Weddell Sea algae. **= to compare, NAA results were converted to X using formula X = 0.3 Br + Cl.

PARAMETER	VALUE
AOX	
recovery from solution	88-98% (500-2000 µg Cl l^{-1})
loss of chlorinated model compound with Ag^+ treatment	N.D.
Reproducibility	2-5% (n = 30)
Correlation (r) with leachable halides	0.73 (paper I), 0.22 (paper II)
EOX	
content of extractable material in final concentrate	4-33 g l^{-1}
Amount (v/v) of X in extractable material*	0.11-0.21%
content of X in possible precipitate	1-2%
detection limit	0.18 µg Cl g^{-1}
recovery	> 92%
linearity	0.9986
injection repeatability	RSD < 2%
reproducibility	RSD < 6%
method repeatability	5% < RSD < 17%
reproducibility	RSD < 7%
intercalibration (coulometry)	RSD < 8% (> 50 µg Cl g^{-1})
	RSD < 25% (≈ 2 µg Cl g^{-1})
	r = 0.982
intercalibration with NAA**	difference -7.5...+14.0% (4.3-97 µg Cl ml^{-1})
	r = 1.000
contribution of halides	5-11% (washing-burning)
	av. 8% (σ = 4.7%, SEC-HPLC < 90 g mol^{-1}),
	0.5-0.6% (injection to coulometer cell)
EOX:AOX	0.3-7.8% (av. 3.4%, open sea)
	r = 0.67 (open sea)
	2.3-9.4% (av. 5.6%, Kotka area)
	r = 0.92 (Kotka area)

5.2 EOX concentrations in different matrices

All analysed matrices (sediment, algal, plant and other) contained detectable amounts of organic halogens (Table 4). Especially the pure algal cultures (4.8-11.9 μg Cl g^{-1}) and trap material from the spring accumulation maximum (14.9-19.1 μg Cl g^{-1}) contained high levels of EOX. The lowest EOX levels were found in clayey sediments, e.g. in the one from the Weddell Sea, and in sediments collected in winter time.

Table 4. Levels of EOX in marine and terrestrial origin samples in this study.

SAMPLE	EOX (μg Cl g^{-1} dw)	REMARKS
surface sediments from the open Gulf of Finland		Kotka area and stations T2 and T3 are excluded.
February-April 1993	0.5-6.0 (av. 2.5, σ =1.7, n = 16)	
June-August 1994	1.2-13 (av. 5.5, σ = 2.7, n = 38)	
Sediment trap material May 17- September 22, 1995	4.0-19.1 (av. 10.5, σ = 5.0, n = 9)	Main species: *Achnanthes taeniata, Thalassosira baltica baltica, Skeletonema costatum, Chaetoceros wighamii Aphanizomenon* sp.
Sediment trap material, April 25 - October 20, 1996	2.7-14.9 (av. 7.6, σ = 4.5, n = 9)	Main species: *Achnanthes taeniata, Chaetoceros* spp., *Diatoma tenuis, Skeletonema costatum Aphanizomenon flos-aquae*
Anabaena lemmermannii	4.8 (n = 1)	cyanobacteria, lab. culture
Aphanizomenon flos-aquae	11.9 (n = 1)	cyanobacteria, lab. culture
Ice algae from the Weddell Sea	64, 82 (n = 2)	Main species: *Phaeocystis pouchetii, Nitzschia cylindrus, Nitzschia cf. closterium, Fragilaria striatula, Dactyliosolen antarcticus* (diatoms)
Sponge from the Weddell Sea	13.3 (n = 1)	Unidentified yellowish-brown sponge, length ca. 15 cm.
Weddell Sea sediment	0.2, 0.6 (n = 2)	clayey, low TC content
chlorophyll a (Sigma chemicals C6144)	below detection limit	prepared from *Anacystis nidulans*
Needles of *Picea abies*	0.5 (n = 1)	forest, Vihti, Southern Finland
Spinach (*Spinacia oleracea*)	5.5 (n = 1)	commercial food product

5.3 Areal distribution of AOX and EOX

In 1990, AOX pollution in surface sediments near the Veitsiluoto Pulp Mill on the Bothnian Bay was up to 590 µg Cl g^{-1} dw (Appendix 1). AOX and EOX results from 1993 and 1994 clearly showed the pollution from pulp mills in the Kotka area (Figs. 7-9, Table 5), where the sediments were systematically contaminated and where contamination had spread at least 30 km from Kotka to stations K22 and K23 (XV1) in the open sea, with the deeper sediments at the stations containing more than 5 µg Cl g^{-1} dw (EOX). In the Kotka area the total organochlorine content per core in the 1986-1994 sediment layers was also substantially high (Fig. 8, Table 6). All muddy sediments around Kotka (K1-K9, KO1-KO9) contained over 15 and usually over 20 µg Cl g^{-1} dw (EOX), and the highest surface concentrations reached 65 µg Cl g^{-1} dw. Levels of up to 116 µg Cl g^{-1} dw were observed (at station K15) further out to the sea. In the western Kotka area pollution was evident in the mouth of the Ahvenkoski Bay (up to 38 µg Cl g^{-1} dw). The total EOX content in the surface sediments collected from the Kotka area in 1994 was estimated at 8 t (Table 6). However, in the EOX levels from the Kotka area, the contribution from natural, background EOX was not subtracted, and total anthropogenic EOX in the Kotka area is less.

Fig. 7. EOX (µg Cl g^{-1} dw) in surface (0-1 and 0-2 cm) sediments from the Gulf of Finland (A) and the Kotka area (B) in 1993-1994.

Fig. 8. Total EOX storages (µg Cl) in sediment core layers from May 1986 - June 1994. A = Open Gulf of Finland. B = Kotka area.

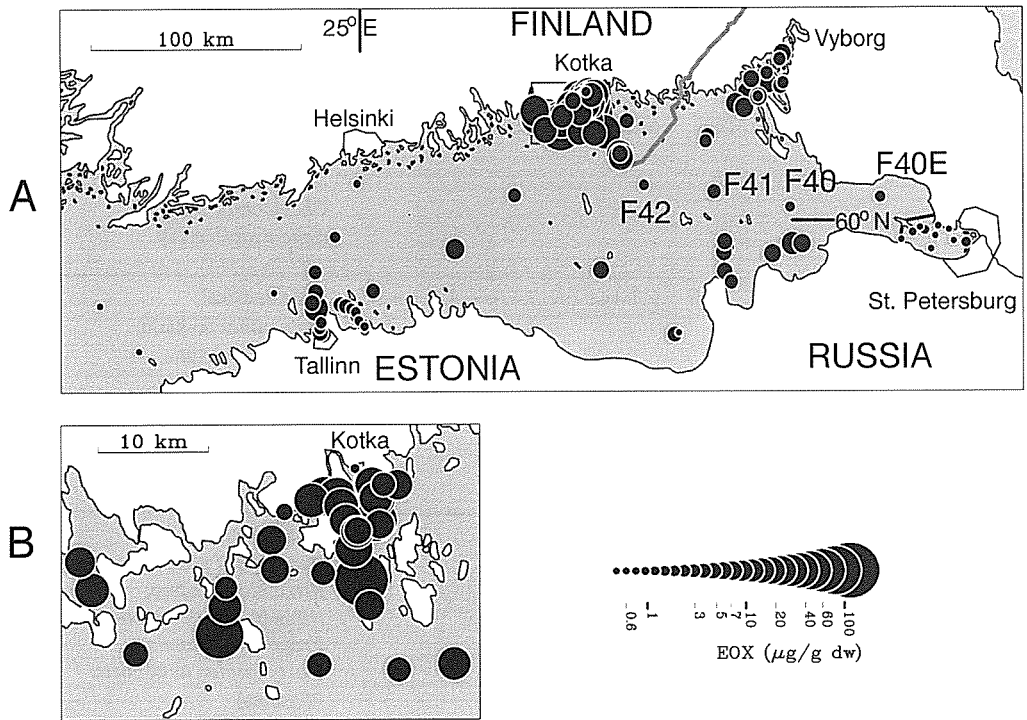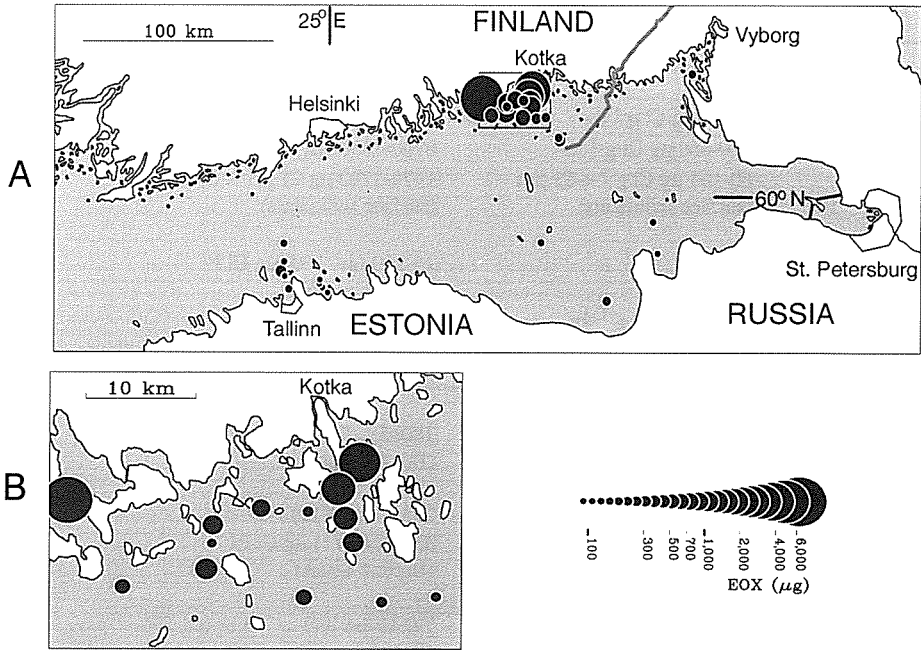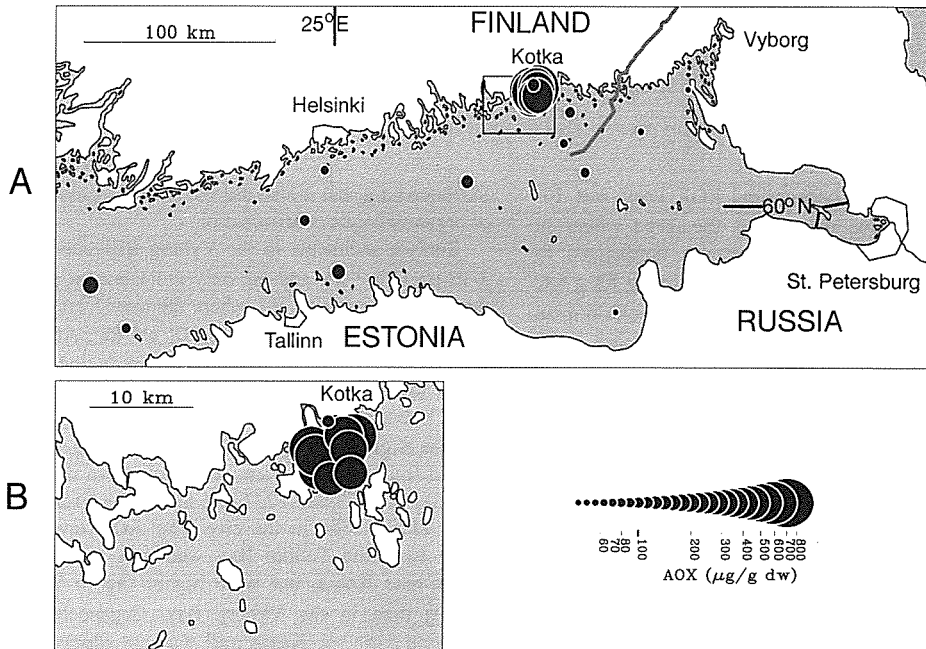**Fig. 9.** AOX (µg Cl g^{-1} dw) in surface (0-1 and 0-2 cm) sediments from the Gulf of Finland (A) and the Kotka area (B) in 1993-1994.

Table 5. Concentrations of EOX and AOX in polluted sediments and of AOX in water from the Gulf of Finland.

AREA	EOX	AOX
Kotka 1993	15-70 μg Cl g^{-1} dw 220-660 μg Cl g^{-1} C 60-155 μg Cl g^{-1} < 63 μm (surface sediments)	420-620 μg Cl g^{-1} dw 6700-10300 μg Cl g^{-1} C 1470-2700 μg Cl g^{-1} < 63 μm (surface sediments) 25-200 (av. 100) μg Cl l^{-1} (Bottom water)
Kotka 1994	13-120 μg Cl g^{-1} dw 160-920 μg Cl g^{-1} C (surface sediments)	3000 μg Cl l^{-1} (500 m north of st. KO2, surface water)
Vyborg Bay, Sovetskiy 1994	19 μg Cl g^{-1} dw, 220 μg Cl g^{-1} C (3-4 cm sediment)	180±5 ... 240±40 μg Cl l^{-1} (Bottom water)
Vyborg Bay 1994		26±10 (st. V12) - 55±2 (st. V1) μg Cl l^{-1} (Bottom water)
Tallinn Bay 1994	10.0 μg Cl g^{-1} dw, 300 μg Cl g^{-1} C (st. T2) (1-2 cm sediment) 17.1 μg Cl g^{-1} dw, 310 μg Cl g^{-1} C (st. T3) (surface sediment) 220 μg Cl g^{-1} C (st. T7) (surface sediment)	27±10 (st. T7) ... 75±18 (st. T5) (Bottom water)

The maximum background EOX level was 10-13 μg Cl g^{-1} dw. Apart from the listed values in Table 5, background EOX values normalised to carbon and fine particles were 15-115 μg Cl g^{-1} C and 1.7-16.3 μg Cl g^{-1} <63 μm respectively in open sea sediments in February 1993. In Summer 1994, the non-polluted sediments contained 30-190 μg Cl g^{-1} C. The corresponding AOX levels were 50-180 μg Cl g^{-1} dw, 1000-4000 μg Cl g^{-1} C and 70-460 μg Cl g^{-1} <63 μm in February 1993. These values represent the background levels before the sedimentation of the spring bloom material.

Organohalogen pollution in the Neva Bay and the open sea was not observed. In the Neva Bay surface sediments contained EOX levels comparable to other non-polluted sediments in the open sea: <0.1-1.7 μg Cl g^{-1} dw, 15-140 μg Cl g^{-1} C and <0.1-4.7 μg Cl g^{-1} <63 μm in August 1993. The highest concentration of 1.7 μg Cl g^{-1} dw was found near the harbour of St. Petersburg, but it also did not show any evidence of organohalogen contamination.

Surface sediments in the Vyborg Bay contained 3-10 μg Cl g^{-1} dw and the only indication of pollution was from station V4, where the over 3 cm sediment layers contained 7-19 μg Cl g^{-1} dw. Also, at V4 vertical EOX distribution showed reducing EOX levels toward core top, which was not observed at other Vyborg Bay stations.

The slightly elevated EOX (max. 17 μg Cl g^{-1} dw) in some of the 1-2 cm sediments from the Tallinn Bay (T2, T3 and T7, Table 5) may be a result of water chlorination in the city. The AOX levels in water from the Tallinn Bay were not as high as found near Kotka, but were higher (up to 75 μg Cl l^{-1}) than in the Vyborg Bay. Organochlorine pollution from the Kehra mill was not observed in sediments from Ihasalu Bay, where EOX was 1-4 μg Cl g^{-1} dw.

Table 6. Summary of sedimentation rates and total EOX quantities in the Gulf of Finland. * = UPM: pre-1989 EOX using 1989 production values, Sunila: pre-1990 EOX estimated from 1990 production values. ** = estimated from 1995 production. TOTAL = extrapolated total sedimentation in accumulation areas in the Kotka area and in the remaining part of the Gulf of Finland.

PARAMETER	RANGE	AV.	STD	n	TOTAL (t)
Average linear sedimentation rate in 1986-1994 (cm a^{-1})	0.05-1.94	0.60	0.39	91	
Average dry-matter sedimentation rate in 1986-1994 (g m^{-2} d^{-1})	0.27-8.2	4.1	1.9	44	1.3×10^7
EOX in open sea surface sediments (50 cm^3) in 1994 (μg)	6-83	42	18	39	72±31
EOX in open sea sediments from 1986-1994 (μg)	100-390	160	80	11	270±140
EOX in Kotka area surface sediments (50 cm^3) in 1994 (μg)	28-336	96	58	24	8±5
EOX in Kotka area sediments from 1986-1994 (μg)	210-5600	1330	1500	14	110±130
Dry-matter sedimentation rate at station GF2 in 1995 (g m^{-2} d^{-1})	0.75-4.1	1.5	1.1	9	4.9×10^6
Sedimentation of EOX at station GF 2 in 1995 (μg Cl m^{-2} d^{-1})	7.5-29	16.8		9	56
Sedimentation of chlorophenolics at station GF2 in 1995 (μg m^{-2} d^{-1})	<0.5-0.7			2	<3
Dry-matter sedimentation rate at station GF2 in 1996 (g m^{-2} d^{-1})	0.50-1.6	0.85	0.38	9	2.8×10^6
Sedimentation of EOX at station GF2 in 1996 (μg Cl m^{-2} d^{-1}).	1.4-21.6	6.1		9	20
Sedimentation of Cl as specific compounds at station GF2 in 1996 (μg Cl m^{-2} d^{-1}).				9	0.042
EOX output from mills a) 1992-1993 b) 1986-1994* c) Oct. 1994 - Oct. 1995 d) Oct. 1995 - Oct. 1996**					23 440 1.8 1.7

The chlorine levels in polluted sediments from Gulf of Finland studies of 1993-1994 are presented in Table 5. Results from non-contaminated sediments are summarised in Table 4. The non-contaminated recent surface sediments over the whole Gulf of Finland were calculated to contain 72 t Cl (as EOX, Table 6).

5.4 Vertical distribution of EOX

Examples of vertical EOX distribution in cores are presented in Figure 10. In Appendix 2 there is a complete presentation of all vertical EOX profiles. Open sea sediments showed higher EOX levels in the surface layer than in the deeper sediments and

the concentration increased toward the top of the cores. In the surface layer maximum concentrations were 10-13 μg Cl g^{-1} dw and in deeper layers under 5 μg Cl g^{-1} dw.

In polluted sediments from Kotka area decreased, constant and increased EOX sedimentation was ob-

served. Muddy surface sediments contained 13-116 μg Cl g^{-1} dw (Fig. 7, Appendix 2). The stations of increased EOX sedimentation were located in the outer Kotka area. Reduction in EOX sedimentation was observed at a few stations in the inner area.
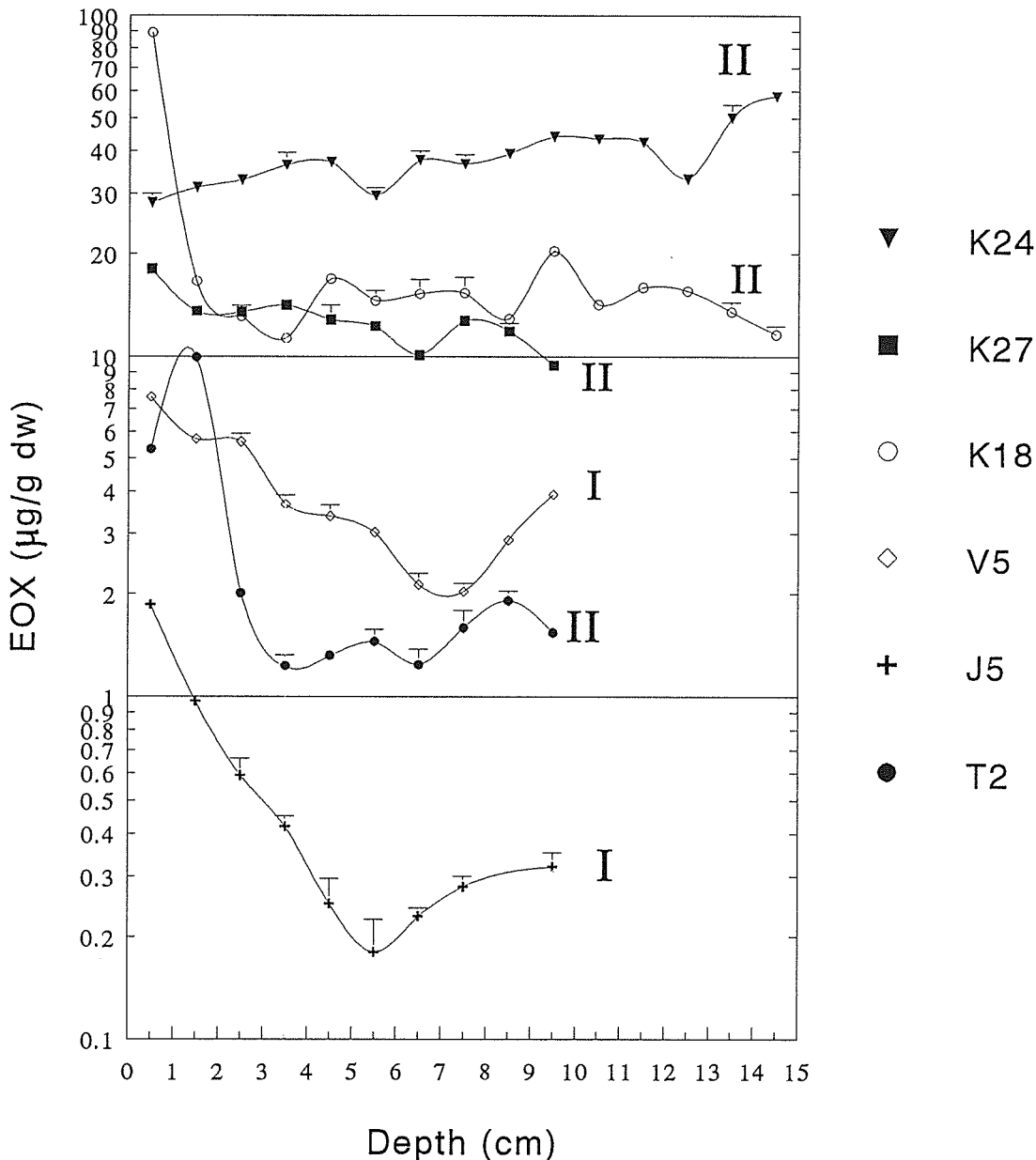
Fig. 10. Examples of vertical EOX distribution in cores from the polluted area (II; K18, K24, K27 and possibly T2) and non-polluted area (I; V5, J5 and T2). Error bars (+σ) are not shown when smaller than symbols.

5.5 Sedimentation according to sediment trap studies and the ^{137}Cs method

The flux of specific organochlorines was very small compared to the EOX flux (Table 6) and equal to only 0.2% of the EOX flux. In 1996, PCBs were the most abundant type of organochlorines in the Gulf of Finland with total PCB sedimentation at about 60 kg (VII). Other compounds were estimated as follows: 20.6 kg of DDTs, 10.9 kg of HCHs, 1.6 kg of HCB, 1.5 kg of chlordanes, and 0.51 kg of trans-nonachlor annually (VII).

The 1995 sediment trap study showed that chlorophenolic compounds were present in extremely low concentrations. Sedimentation of EOX was strongly dependent on the sedimentation of particulate material. Most EOX accumulated during April-May (Fig. 11), with a small peak in the autumn. Sedimentation fluxes were smaller in 1996 than in 1995. Total sedimentation of EOX and dry-matter to Gulf of Finland accumulation areas (i.e. 30% of total area) are given in Table 6. According to ^{137}Cs measurements, the average sedimentation rates for 1986-1994 in the Gulf of Finland varied between 0.05-1.94 cm a^{-1} and 0.27-8.2 g m^{-2} d^{-1} (Table 6). The 1986-1994 sediment layers were calculated as containing 110 t of Cl (EOX) in the Kotka area and 290 t of Cl (EOX) in other parts of the Gulf of Finland.
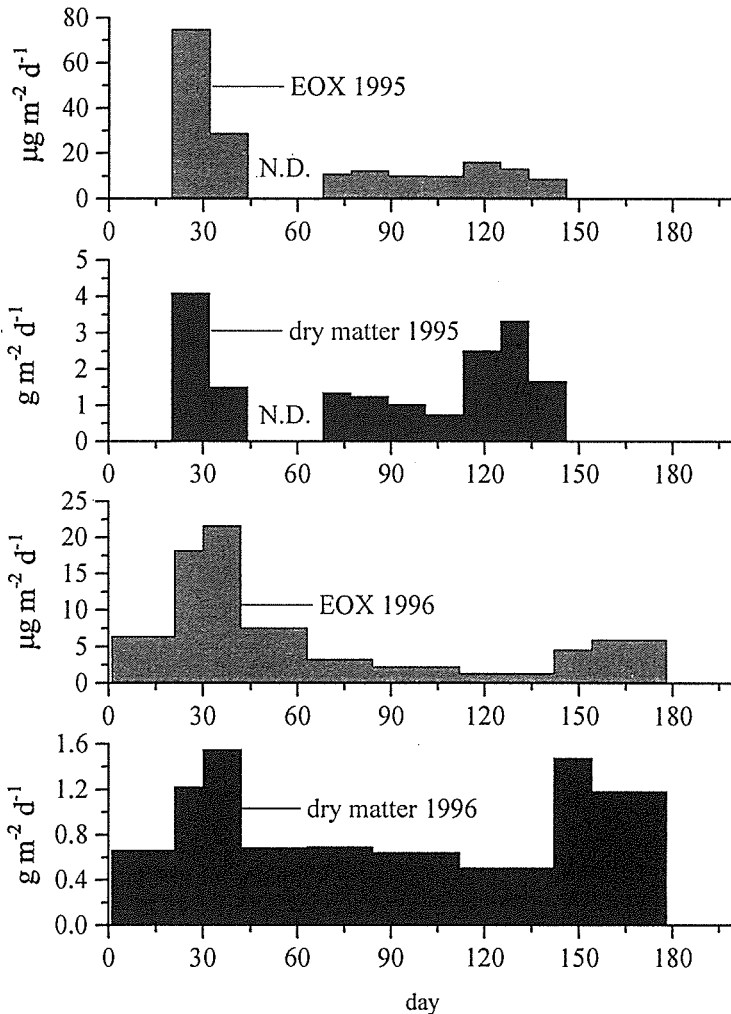
Fig. 11. Sedimentation of EOX (μg Cl m^{-2} d^{-1}, gray bars) and dry-matter (g m^{-2} d^{-1}, black bars) in 1995 and 1996. Day 0 corresponds to April 25. N.D. = not determined.
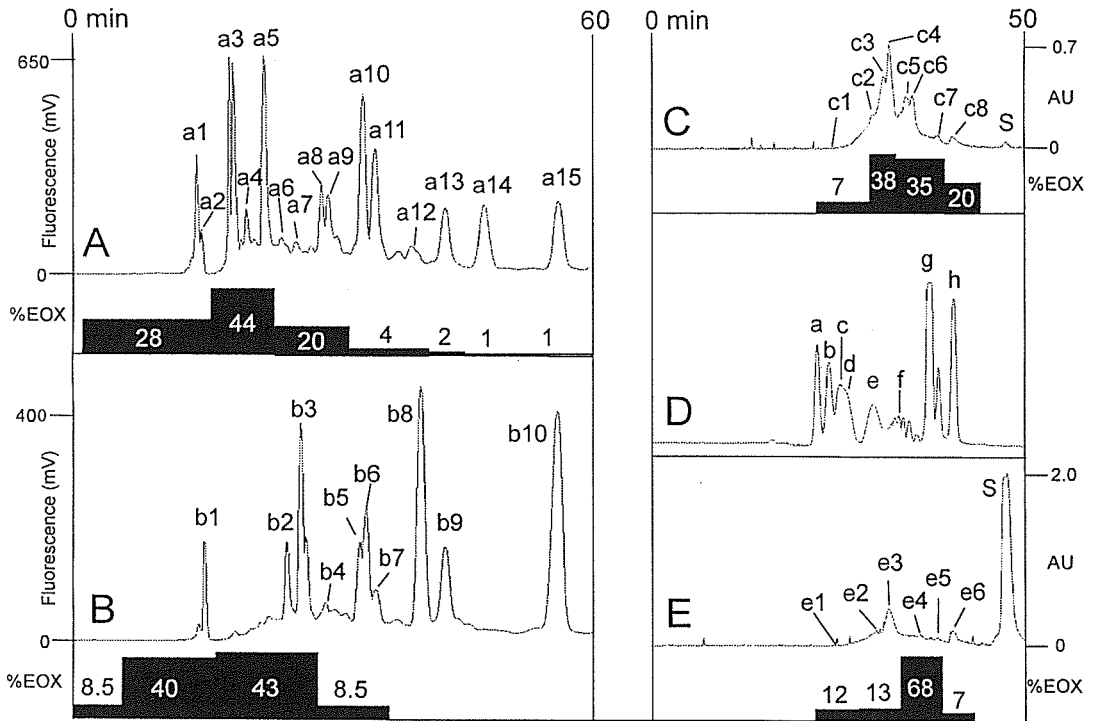
Fig. 12. RP-HPLC (A and B) and SEC-HPLC (C-E) chromatograms and distribution of EOX (black bars, %) in the extracts of sediment and sedimenting material from station GF2 (unpublished results). A, C = sedimenting material. B, E = sediment (0-5 cm). D = polystyrene standard. a1-a15 and b1-b10 unidentified fluorescent material (pigments). In the RP chromatograms peak a2 = b1, a6 = b2, a7 = b3, a8 = b4, a10 = b6, a13 = b9 and a15 = b10. In chromatogram C, c1 - c8, e1 - e6 are calculated MW peaks (see text). S = sulphur. a-h standard peaks of 11600, 7000, 5050, 3250, 1680, 580, 162 and 92 g mol^{-1} respectively. AU = absorbance units.

5.6 Chemical characterizations

The summarised results are presented in Table 7. The MWD (Fig. 12) in sediment trap extract was calibrated using polystyrenes, and the UV-absorbing material was found at approx. 100-12000 (Fig. 12, c1) g mol^{-1}, with peaks (Fig. 12, c2-c8) at 2500, 1100, 900, 450, 320, 130 and ~100 g mol^{-1}. Most of the EOX was found in between 780-2560 g mol^{-1} (38%) and 130-780 g mol^{-1} (35%). In 0-5 cm sediment extract the MWD range was narrower, approx.

100-7000 g mol^{-1} with peaks (Fig. 12, e2-e6) at 1300, 900, 240, 130 and ~100 g mol^{-1}. The molecular weight range of EOX was 130-780 g mol^{-1} (68%), lower than in the trap sample. The last peak, eluting at <100 g mol^{-1} (48 minutes), is probably from elemental sulphur, which was apparently more abundant in the partly anoxic sediment sample. Typical SEC profiles for Gulf of Finland sediments (II, III) are presented in Figure 13 and show similar MWDs in both non-polluted (station F55) and polluted sediments (KO2).
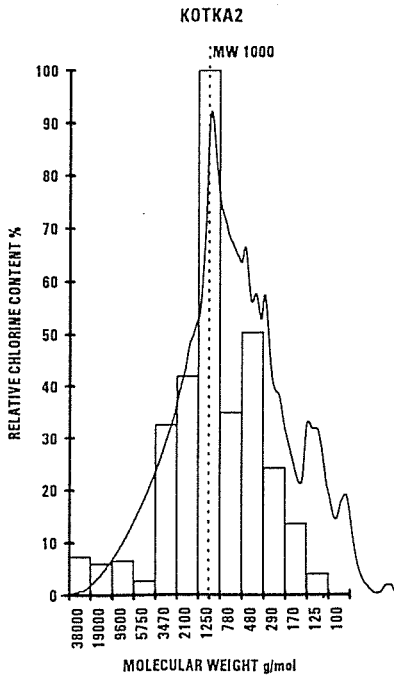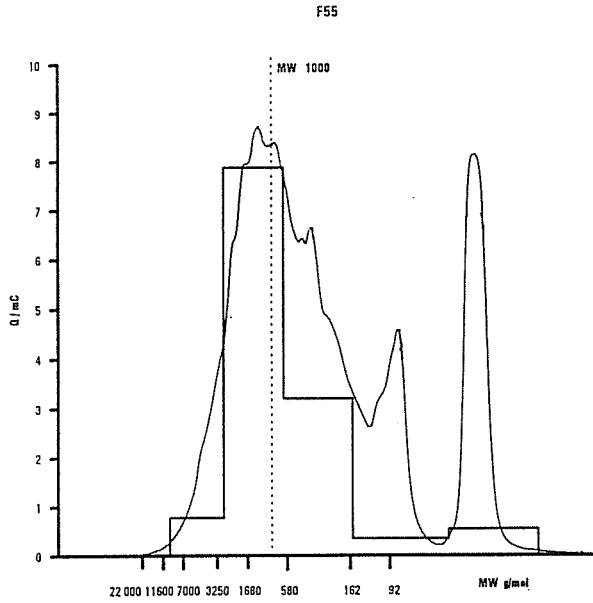
Fig. 13. Examples of molecular weight distribution (line) of UV-absorbing compounds and EOX (bars) in sediment extracts from stations F55 (open sea) and Kotka2 (KO2, Kotka area). MW 1000 = location of 1000 g mol^{-1} in the chromatogram. Y axis is millicoulombs in the upper and % in the lower picture.

Table 7. The chemical character and uniformity of the sediment extracts. [1]paper II. [2]paper III. [3]unpublished results. [a]Gulf of Finland sediments. [b]sediment trap material. *see Fig. 12. M_n = number-average molecular weight.

PARAMETER	VALUE, INTERPRETATION
MWD (254 nm)[a]	80-20000 g mol^{-1}, 63% <1000 g mol^{-1} (n=13)[1], <100-20000 g mol^{-1} (n=6)[2]
Typical peaks (approx.)[a]	140-150 g mol^{-1} (n=9), 400 g mol^{-1} (n=5), 500 g mol^{-1} (n=7), 800-1100 g mol^{-1} (n=9), 1300-1500 g mol^{-1} (n=2), 1700 g mol^{-1} (n=11), 2500 g mol^{-1} (n=6), 4500 g mol^{-1} (n=5)[1] 90, 130, 220, 400 and 900 g mol^{-1} (n=6)[2]
MW maximum (EOX)[a]	500-1700 g mol^{-1} (n=3), 600-2900 g mol^{-1} (n=7)[1], 1250 g mol^{-1} (n=4), 2100 g mol^{-1} (n=2)[2] 55% of EOX in range 700-2300 g mol^{-1} (n=7)[1]
M_n (254 nm)[a]	650-1210 g mol^{-1} (n=6)[2]
M_n (EOX)[a]	870-1550 g mol^{-1} (n=6)[2]
UV-VIS maxima[a]	205 nm (n=13), 260-265 nm (n=13), 277 nm (n=8) and 411-416 nm (n=12)[1]. Chlorophylls and pheophytins.
Br:Cl (NAA)	1:6.86 (n=1)[3,a] 1:15.6 (n=1)[3,b]
TLC[a]	R_f 0.96 (blue), 0.93 (dark, 254 nm excitation), 0.91 (blue), 0.82 (red), 0.79 (red), 0.71 (red), 0.68 (red), 0.64 (red), 0.62 (red), 0.59 (red), 0.57 (red) and 0.44 (red) (n=10)[3]. Fluorescent algal pigments.
^{1}H NMR, ^{13}C NMR[a,b]	dominantly aliphatic compounds with (conjugated) C=C bonds (δ_H 6.56-6.57), CH_x-O- (x = 1-3, δ_H 3.54-3.68, 4.1-4.4, δ_C 62.79), possibly aromatic structures (δ_H 6.83, 6.96 and 7.85, δ_C 130.6), but in low quantities according to ^{1}H spectra.[3]
ES-MS[b] HPLC fractions 1-3*	no positively charged organic ions. Negatively charged ions from aliphatic saturated and unsaturated hydrocarbons and also Cl and Br compounds, mainly m/z <400, maximum at m/z 250-270.
MALD-MS[b]	molecules of <600 m/z. No chlorophyll structures.
MS-MS[b] HPLC fraction 1*	fragment m/z 35 from parent ion m/z 267: possibly Cl. No Br.
HPLC fraction 2*	fraction contains Cl. Parent ions m/z 253 and 283 contain no Br or Cl. m/z 235 may be from a carboxylic acid.
HPLC fraction 3*	fraction contains Cl, and possibly Br. Parent ion m/z 281 does not contain Cl.

The broad maximum at 410-415 nm in the UV/VIS spectra (Table 7) suggests that chlorophylls or pheophytins are present in the EOX extracts. The spectra from all samples were very similar. The fluorescent peaks detected indicated that the sediment trap samples contained more pigment material. Polar and semi-polar halogenated molecules were dominant in both trap material and bottom sediment. In the bottom sediment sample there were more polar EOX molecules than in the trap sample (Fig. 12).

According to the RP-HPLC most of UV-absorbing material eluted in the semi-polar to non-polar region of the chromatogram, while most EOX eluted in the polar region.

The TLC separation of organic material in sediments produced several characteristic fluorescent spots (Fig. 14) between R_f values 0.44 and 0.96. At R_f 0.93 a dark band (between A and B in Fig. 14) was observed with 254 nm excitation. Most fluorescent material was observed at $R_f > 0.6$ and was thus dominantly semi-polar - non-polar. The extracts from more clayey, organic material-depleted sediments J7, T1 and V3 contained less fluorescent ma-

terial than the extracts from muddy sediments. TLC showed that the pigment composition of the sediments is very uniform.

No clear resonances from chlorophyll compounds were observed in the NMR spectra (Fig. 15). Most (240 units) of the ^1H resonances came from aliphatic compounds, less (max. 7 units) from aromatic compounds. No resonances can be attributed to halogenated compounds although they are present according to the EOX measurement. Possible resonances from halogenated compounds may be obscured by the strong signals from non-halogenated material.
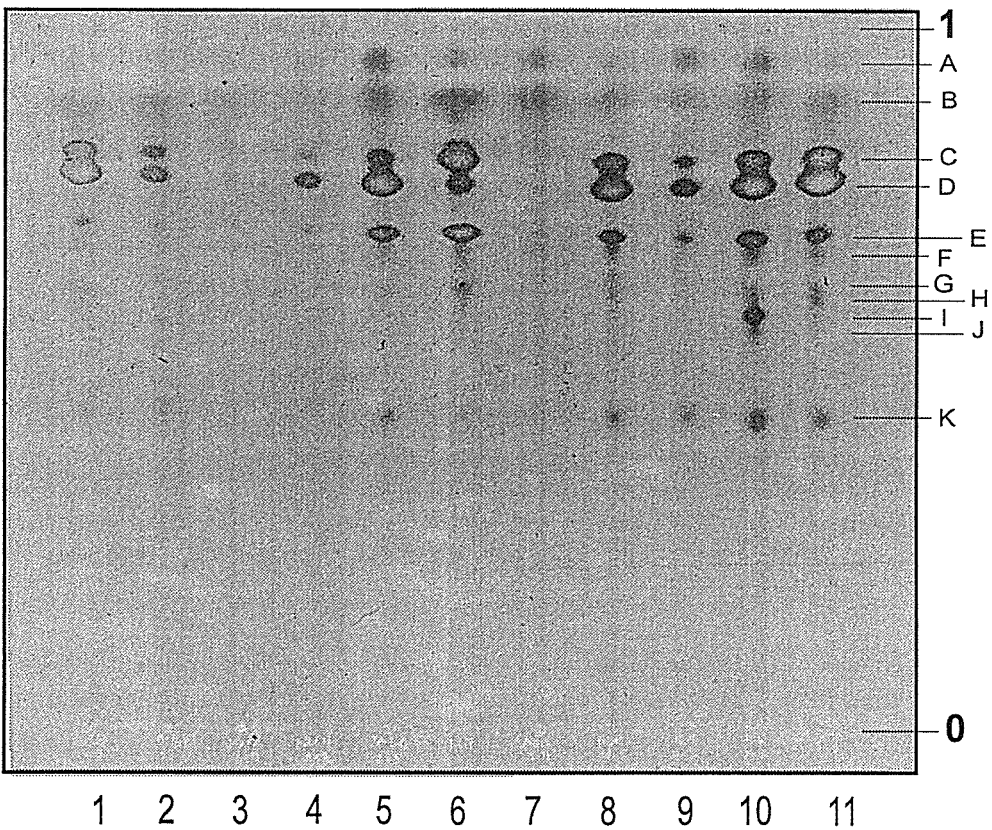
Fig. 14. TLC chromatograms of EOX preparations from Gulf of Finland sediments showing uniform composition of fluorescent material. Plate illuminated with 366 nm light. 1, 11 = st. V1 1-2 cm. 2 = st. V6 2-3 cm. 3 = st. V3 3-4 cm. 4 = st. J7 2-3 cm. 5 = st. T3 2-3 cm. 6 = st. LL7 0-1 cm. 7 = st. T1 3-4 cm. 8 = st. K26 4-5 cm. 9 = st. K1 4-5 cm. 10 = st. K8 1-2 cm. 0 = start-line. 1 = eluent front. A-K observed individual spots.
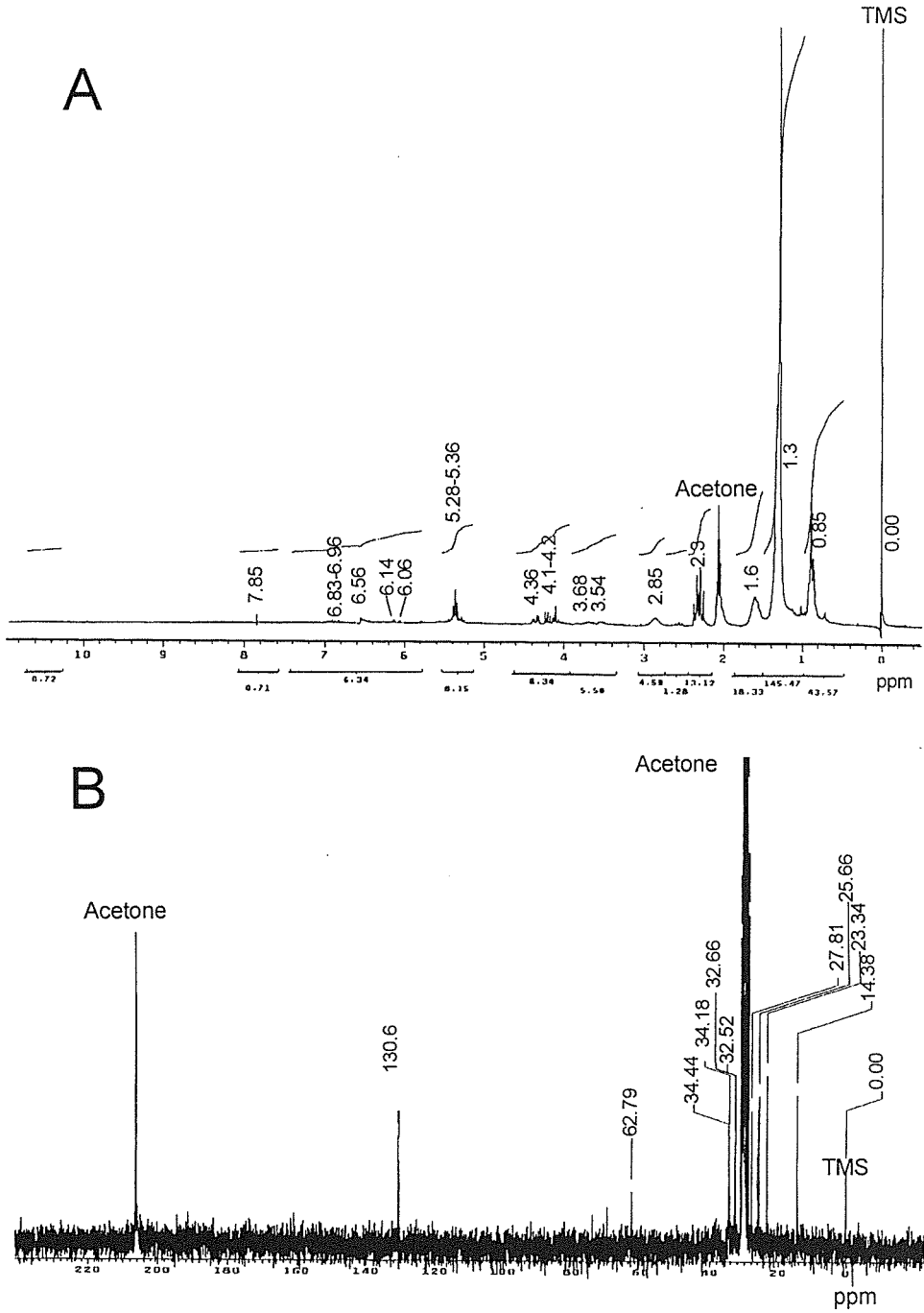
Fig. 15. [1]H (A) and ^{13}C (proton decoupled, B) NMR spectra of sediment extract from station GF2. The main resonances (ppm) are indicated. TMS = tetramethylsilane.

As in NMR, the non-halogenated mass peaks may mask the possible halogenated peaks in the ES-MS spectra (Fig. 16), and no mass peaks resembling those of chlorophylls (Dörnemann and Senger 1986) were observed. Molecular weights of 300-600 and 850-1400 g mol^{-1} (not shown) were detected in the HPLC fraction 2 (A in Fig. 16) using SEC, but the latter ones were not observed in the ES-MS or MALD-MS spectra. This may indicate that the heavier molecules were somehow lost in the preparation of MS samples or in the MS analysis itself.
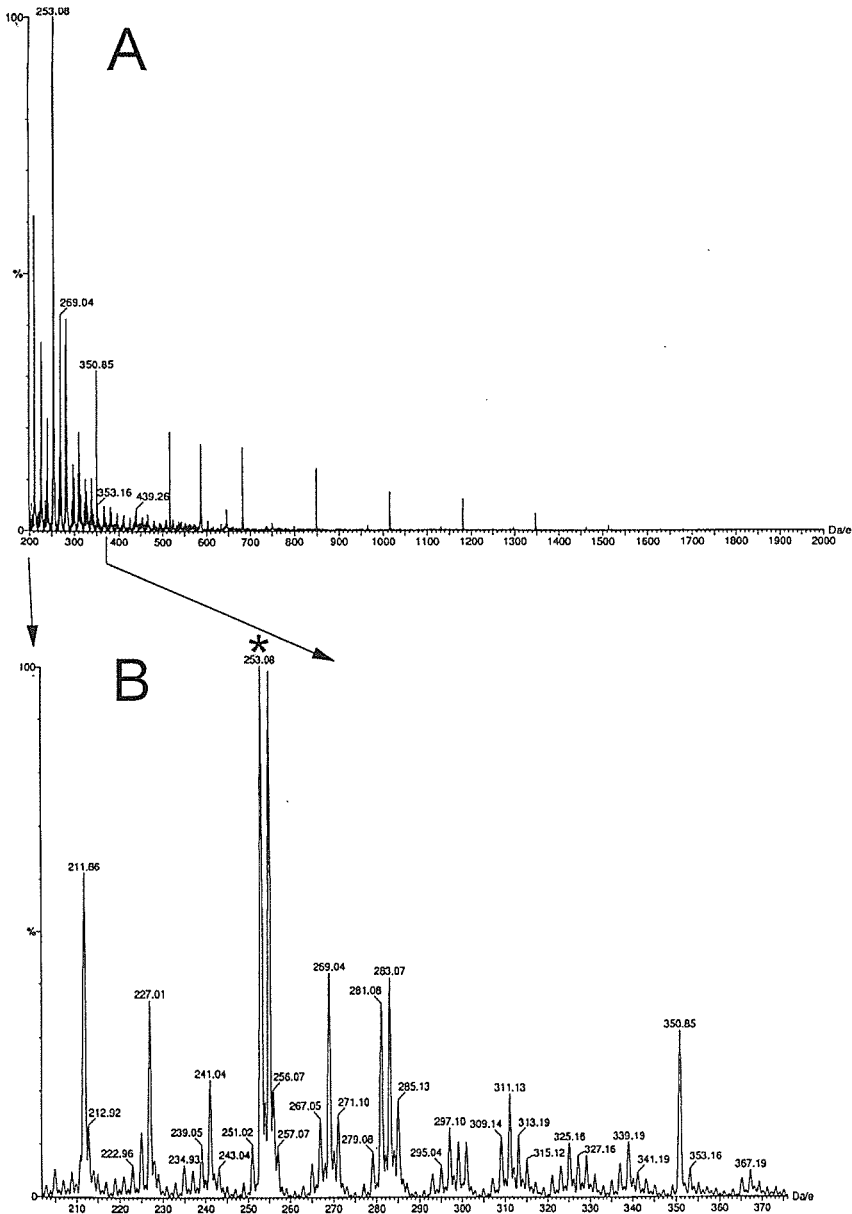
Fig. 16. An ES/MS spectrum of EOX preparation of sedimenting material from station GF2. A = whole spectrum. B = magnification of the m/z 200-375 region. * = peak analysed using MS/MS later.

The ions with the highest intensity in HPLC fraction 1 had m/z values of 267 and 269. Around the peak of intensity fragments with m/z 14 intervals were observed. The main peaks can be identified as originating from norphytene, from 6,10,14-trimethylpentadecan-2-one and from pristane, all degradation products of phytol (296 g mol⁻¹). In fraction 2 (Fig. 16) the main ions were m/z 255 (2,6,10-trimethylpentadecane) and 253 (6,10,14-trimethylpentadec-1-ene), also degradation of phytol.

5.7 Aquarium experiments and effects of BKME on *M. affinis*

The sediments in aquaria contained only 0.10-0.76 µg Cl g⁻¹ dw after one-week of exposure to diluted BKME containing 2500-2700 µg Cl l⁻¹. Irreversible adsorption of EOX to sediments did not occur during this short-term exposure and from this it seems likely that EOX transport mediated by sedimenting particles is the dominant process in pulp mill recipients. ANOVA showed (p ≤ 0.0063) that, in three cases out of four, introduction of BKME reduced the nocturnal swimming activity of *M. affinis* (Fig. 17) which retreated to the sediment. The BKME exposure did not affect diurnal rhythms. The adverse effects are not irreversible since the animals almost recovered their original nocturnal swimming activity.

6 Discussion

6.1 Applicability and reliability of the methods

Since interference by inorganic halides was ruled out by the validation (Table 3) and by using a method similar to the original that was validated by Martinsen *et al.* (1988), analytical artefacts in the EOX method can be excluded. The sum parameter methods used were reproducible and the microcoulometric detection compared well with the NAA. In EOX analysis interference from halides and sulphides was insignificant (Table 3) indicating that the results were truly representative of the organic compounds present, but in AOX the contribution of halides or sulphides could not be totally excluded. The low correlation coefficient for AOX and chloride in open sea sediments suggests that there is no interference.

The AOX results from the open sea and polluted area sediments are comparable with results obtained using a similar AOX method for sludges (200-400 and >1000 mg Cl kg⁻¹ dw) and sediments (10-160 mg Cl kg⁻¹ dw) (Hoffmann *et al.* 1988). Correlation of AOX with EOX was good (r=0.92) in the Kotka area sediments, but not so good (r=0.67) in the open sea sediments (Table 3). This supports the theory that the two parameters are not directly comparable (e.g. Wulff *et al.* 1993). Nevertheless, the AOX method for sediments can be used to distinguish between polluted and non-polluted areas. With the EOX method larger variability in halogen concentration was observed than with the AOX method. For instance, in the Kotka region in 1993 the difference between the largest and smallest AOX value from muddy sediments was 1.5-1.8 fold, but with EOX it was 3-4.7 fold. Normalisation to dry weight produced the largest variability.

In most cases the non-polluted sediments analysed had an oxidised surface and obviously contained more sulphide (as H₂S) in the deeper layers, which may interfere with AOX measurements (Grøn and Dybdahl 1996). During the sediment lyophilisation and homogenisation, the sulphides are mostly oxidised to sulphates. Thus the theoretical bias from sulphides to EOX and AOX values should produce profiles with increasing halogen concentrations toward the deep layers, but this was not observed. It is unlikely that sulphides interfere in the microcoulometric detection, which was, furthermore, reliable according to the NAA inter-comparison. Interference from other sulphur compounds would also have been detected in the HPLC-SEC fractionation, where low-molecular-weight inorganic compounds elute last, but this last fraction represented only a small contribution of the total EOX. Organic sulphur and nitrogen compounds may also interfere with the microcoulometric detection, but combustion of approx. 0.5 mg of sulphur or nitrogen compounds does not interfere with the detection (Grøn 1990). Using cyclohexane/2-propanol extraction Remberger *et al.* (1990) found that nitrogen was absent and that sulphur accounted for 10-20% of Baltic sediment extracts. The content of nitrogen and sulphur compounds in the AOX and EOX preparations of the present study is unknown, but, then again, the successful NAA inter-comparison excludes such interference.

Chloride from plant cells may cause positive bias to AOX measurement when measuring plants, but its effect in sediments has been reported negligible due to the relatively small amount of the cells (Nkusi and Müller 1995). Inorganic chloride in soil and microorganisms has not been found to disturb analysis of leachable organic halogens (Asplund *et al.* 1994). In EOX measurements the bias from chloride with similar samples was small, as demonstrated by the
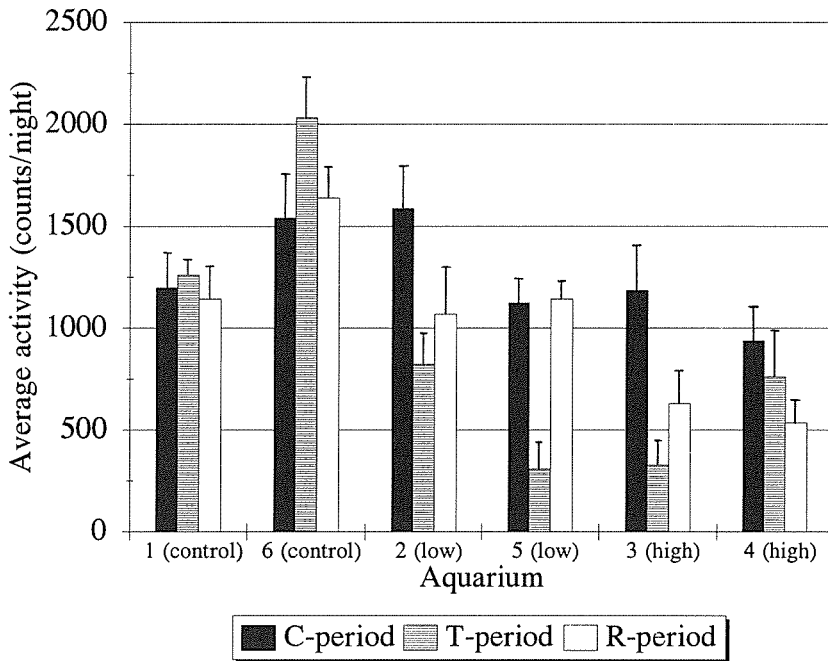
Fig. 17. Changes in the swimming activity of *M. affinis* in the test (2-5) and control aquaria (1 and 6). Aquaria 2 and 5 contained low concentration of AOX, aquaria 3 and 4 higher concentration. C-period = control period. T-period = test period with 1994 BKME from Sunila pulp mill. R = recovery period. Error bars = standard deviation.

EOX validation (Table 3). The zero result from the measurement of the Chl a sample showed that the microcoulometric instrument is not affected by Mg in samples. Obviously the commercial Chl a preparation is also free of Chl RC I.

The use of the Chernobyl fall-out as a time marker is comparable to the use of, for example, Hg by Pitkänen in the Ahvenkoskenlahti Bay (Pitkänen 1994). The reliability of such methods is dependent on the firm sorption of the marker to material in the sediment column. The majority of the ^{137}Cs has been reported in an immobile form, with only 10-20% in a mobile form (Crusius and Anderson 1995). In consequence, the position of the radioactivity maximum will tend to stay in the original sediment layer, but the peaks will spread. Bioturbation also affects the vertical distribution of radiocaesium. The result of these phenomena can be seen in the ^{137}Cs profiles presented in paper VI, where the peaks were spread more toward the core top than downward, but had well-defined ^{137}Cs maxima.

The ^{137}Cs dating of sediments yielded sedimentation rates comparable to the values from the sediment trap studies. The sedimentation rate for station GF2 was 1.4 g m^{-2} d^{-1} during 1986-1994 according to ^{137}Cs and 0.85-1.5 g m^{-2} d^{-1} in 1995 and 1996 according to the trap results. Recent comparisons with Gulf of Finland sediments showed that the ^{137}Cs method produces results that compare well with ^{210}Pb dating (Ilus *et al.* 1997). Also, in many cases, ^{210}Pb results have been confirmed using ^{137}Cs distribution (e.g. Pempkowiak 1991).

Total EOX sedimentation from 1986-1994 is only an approximation, because the exact time gap between the atmospheric fall-out and maximum sedimentation of ^{137}Cs on the sea-bed is not known well enough. The data from the Finnish Centre for Radiation and Nuclear Safety (Ilus *et al.* 1993) suggests that it may have taken 1-2 years for all the Chernobyl fall-out to sediment. However the maximum sedimentation should have taken place directly after the accident on April 25, 1986, which was just before the spring bloom in the Gulf of Finland. In 1994, the main bottom sediment sampling took place in June, i.e. when only part of the sedimentation had reached the sea-floor. According to the 1995 results (V), it takes approximately one month before EOX material reaches the bottom, which means that the extrapolated, surface EOX values for 1994 may be an underestimation.

Due to uncertainty with the areal share of soft, recent deposits in the Gulf of Finland, the extrapolations of total EOX and dry-matter sedimentation are not more than estimates. It must also be remembered that the trap results are only from one location and show rather high year-to-year variability. The extrapolation is not as accurate as if several trap locations had been used.

6.2 Polluted areas and transport of pollutants

Although the Neva estuary is known to be heavily polluted by metals and hydrocarbons, the low concentrations of EOX in the inner Neva Bay and outside the flood protection barrier indicated no organochlorine pollution from the city of St. Petersburg and Lake Ladoga. This is important since it outrules any idea that open sea sediments in the Gulf of Finland are being contaminated by a large-scale source in the east.

In the Neva Estuary, none of the surface sediment concentrations exceeded 1.7 μg Cl g^{-1} dw and there were no clear patterns or gradients of EOX or AOX along the transect F42-F40E - Neva Bay (Fig. 7, Appendix 1). The sediments from this area were of low carbon content and probably represented mainly areas of transportation. Even so, the surface sediments would have shown some indication of pollution if sources were present.

Pollution from the Kymi River and Kotka town extends south-east to at least 30 km out into the open sea (south-east), to where in 1994 EOX in the surface sediment was still 17 μg Cl g^{-1} (Fig. 7). Similarly, Martinsen *et al.* (1994) found that there was EOCl up to 26 μg Cl g^{-1} dw in surface sediments 29 km off the Iggesund area in Sweden.

6.2.1 The Kotka-Kymi river area

Looking at the overall AOX and EOX results in Figures 7-9 and Table 5, the impact of the mills along the Kymi River and in the Kotka area is evident. Concentrations of EOX were up to 10 times greater than the maximum concentrations of 10-13 μg Cl g^{-1} dw and 150-200 μg Cl g^{-1} C in non-polluted sediments. Maatela (1995) reported total organochlorine levels near pulp mills in central and western Finland up to 40-fold higher than in reference areas. In the present study, the corresponding maximum value was of the same magnitude, 20-30 fold, when compared with the non-polluted summer sediment samples with their average EOX values at approx. 5 μg Cl g^{-1} dw. The

total amount of Cl in sediment layers from 1986-1994 showed the clearest difference between the Kotka area (210-5600 μg Cl per core) and the non-polluted Gulf of Finland (100-240 μg Cl per core, Fig. 8). It is probable that most of the EOX from pulp mills is deposited already in the Kotka area, where sedimentation rates are high, frequently over 1 cm a^{-1} (Appendix 1).

It is not known how much further from the core sites in the Kotka area the polluted sediments can be found. Within 30 km from Kotka all the sediments were polluted and thus at least within this range, about 1400 km^2 of seabed are polluted by the pulp mills. Outside the known polluted area EOX will eventually reach its background level, and pollution cannot be distinguished. Vartiainen *et al.* (1997) analysed the distribution of PCDD/Fs near the marine dumping site of Neste oil refinery at Sköldvik, northern Gulf coast, and observed that natural background of PCDD/Fs was achieved after only a few kilometers from the source. The organochlorine pollution in Kotka area is local, but not as localised as that in the Sköldvik area.

Due to the average currents in the northern Gulf of Finland, BKME is expected to flow westward and not to Vyborg Bay and even less likely to Neva Bay or to the south. EOX levels in all samples east of the Kotka area were infact low (Fig 7). Most of the pollution in the Ahvenkoski Bay probably comes from the pulp mill in Kuusankoski. To a large extent material from the UPM mill is deposited within 30 km downstream of the mill (V). The EOX that reaches the western river branch is effectively deposited in the Ahvenkoski Bay, where sedimentation rates reach 1.9 cm a^{-1} (VI) and EOX was up to 38 μg Cl g^{-1} dw, which is comparable to the EOX observations from the Gulf of Bothnia (Palm and Lammi 1995).

In the Kotka area the complex nature of the seabed (Fig. 3) and the varying transport and accumulation conditions all affect the distribution of EOX. Vertical EOX distribution in sediment cores from the outer Kotka area indicated increased deposition of EOX, while opposite trends were observed in the inner Kotka area (V). Reductions in the use of chlorine at the mills in Kotka and Kuusankoski was not clearly reflected in the vertical EOX distribution in sediment cores. In case of stations K2, K4, K5, K7, K8, K11, K12, K24 and K26, where the recent EOX concentrations are down from previous levels, only K2, K5 and K7 showed a distinct decrease (Appendix 2). The rest of the stations in the Kotka area showed constant or even increasing EOX sedimentation, which is evidence that secondary sedimentation processes, e.g. lateral transport, are contributing to EOX sedimentation in this area.

Organic chlorine compounds from industrial sources began to enter the Baltic Sea in the 1940's (Wulff *et al.* 1993). In the cores from the Kotka area the deepest layers (not dated) were probably not older than the mid-1940's, and did not represent the correct vertical EOX background value. In contrast, in non-polluted areas of low linear accumulation rates, the deepest sediments reflect more closely natural background values.

Maximum sedimentation of total PCDD/Fs (reflecting both Ky-5 and pulp mill emissions) in the Ahvenkoski Bay occurred in 1960 (Verta, FEI, pers. comm.). In this study cores were only dated from 1986, so that the 1960 sediment layer was not located in any of the samples. Thus it is possible that the vertical profiles (Appendix 2) for the polluted sediments analysed in this study do not show the possible maximum EOX levels.

At stations K3, K15, K17, K18, K21, K22 and K23 the abrupt (by 20-80 µg Cl g^{-1} dw) elevation of EOX values in the polluted surface sediments may not be explained solely by the appearance of the fresh planktonic cover, but rather by recent, lateral transport of sediments. All these stations, except K3 and K17, represent areas of high sedimentation rates (approx. 0.6-1.6 cm a^{-1}), and are situated in the outer Kotka area, south of the town. The abrupt increase in the outer area may be due to recent remobilisation of polluted sediments close to the town. Sedimentation of EOX in the Kotka area was not depth-dependent, in contrast to, for example, trace metals in the Gulf of Bothnia (Leivuori and Niemistö 1995).

In comparing the results from the Kotka area in September 1993 with summer 1994 it can be seen that the results from around the Kotka island are of the same order in the both cases, except for station KO9 (K9 in 1994), where the surface concentrations were 24 and 65 µg Cl g^{-1} respectively. The bottom variability (Fig. 3) may in part explain the difference, since the distance between stations K9 and KO9 was only about 500 m. Accordingly, the pollution load around Kotka island did not change between 1993-1994, which also agrees with the calculated, rather constant, EOX output from the mills during the same period (Table 6, Fig. 5).

Threshold concentrations to distinguish between polluted and non-polluted surface sediments can be drawn from the non-polluted sediment and Kotka area results. For EOX the threshold values are approximately 10-13 µg Cl g^{-1} dw, 200 µg Cl g^{-1} C and 30 µg Cl g^{-1} <63 µm. For AOX the threshold values are approximately 250 µg Cl g^{-1} dw, 5000 µg Cl g^{-1} C and 1400 µg Cl g^{-1} <63 µm. Also the Cl:C ratio can be used to distinguish of polluted sediments; ratios over ~1:5000 (EOX) indicate an-

thropogenic pollution while values of ~1:26000 indicate natural organohalogens.

Palm and Lammi (1995) have reported that EOX fluxes have reduced markedly in a pulp mill recipient area in the Gulf of Bothnia after construction of a secondary activated sludge plant. The reduced flux was reflected in the sediment cores, in which, in two cases out of three, EOX (petroleum ether extraction) levels decreased from up to ~70 to ~10-20 µg Cl g^{-1} dw. In the third polluted core they found rather constant vertical EOX levels in the 0-12 cm sediment layer, resembling the profiles obtained for many Kotka stations in the present study.

The decrease in output of EOX from the mills between 1992-1994 (Fig. 5) may prove to constitute a time marker that may be used analogously with ^{137}Cs or Hg measurements (Pitkänen 1994), although in 1994 no sudden EOX decrease in Kotka area sediments had been observed. Today the surface sediments may be already reflecting the changes in EOX output.

Transport of AOX from the Saimaa mills to Lake Ladoga has been demonstrated (Jokela *et al.* 1992), but no trace of pulp mill effluents from Lake Saimaa was observed in Vyborg Bay sediments (Fig. 7). The AOX concentrations in bottom water were higher in the northern (55 µg Cl l^{-1}) than in the southern part of Vyborg Bay (26 µg Cl l^{-1}), which may be due to the waste waters from Sovetskiy. The water from Lake Saimaa is humic rich and may contain natural AOX, as described by Grimvall and Asplund (1991), and may thus be contributing to the AOX distribution in Vyborg Bay. Chlorination of municipal water in the town of Sovetskiy may explain the observed high AOX levels in the water of the easternmost part of the Bay and the high EOX level in the deep sediment at station V4.

The slightly elevated EOX (max. 17 µg Cl g^{-1} dw) in some of the Tallinn Bay sediments (Table 5) may result from chlorination of the city water supply. The AOX levels in water from the Tallinn Bay were not as high as those found near Kotka, but were on average higher (up to 75 µg Cl l^{-1} at station T5) than in the Vyborg Bay. Organochlorine pollution from the Kehra mill was not observed in sediments from the Ihasalu Bay, where EOX levels were only 1-4 µg Cl g^{-1} dw. Results indicated that the use of chlorine chemicals has been low.

6.2.1.1 Adverse effects of pulp mill effluents

Both past and present organochlorine pollution from the pulp and paper industry was clearly seen in the Kotka area and along the Kymi River in 1994. In general, the old discharges are being rapidly covered

by new sediment layers, especially in near coast areas with high sedimentation rates, but the old deposits could still cause problems if the bottom is disturbed by some episodic events. In 1994, however, EOX concentrations in the surface sediments were still high. It may thus be that the benthic fauna will be subjected to chlorinated compounds from the mills at many locations for many years to come.

HMW organochlorines from bleaching are considered non-toxic (Paasivirta *et al.* 1997). In the sediments analysed in the present study, the amount of <1000 g mol^{-1} EOX material was substantial, usually over 50% according to the SEC analyses. It is thus possible that the bioavailability of EOX in polluted sediments from Kotka is relatively high, at least in the uppermost sediment layers. On the other hand, natural production forms a significant contribution to the LMW material (Fig 13, II).

The adverse effects of BKME on *Monoporeia affinis* (Fig. 17) may be due to the predominant non-halogenated compounds, which also have been demonstrated as harmful (Sundelin 1988, Pesonen and Andersson 1992, Tana *et al.* 1994). In the exposure test, the BKME from the Sunila mill, produced during chlorine/chlorine dioxide bleaching, had not been subjected to secondary-activated sludge treatment. Also Cl/ClO$_2$ bleaching seems to produce relatively high AOX concentrations (~8000 µg Cl l^{-1}) in BKME.

Xenobiotic molecules may be released from sediment if the concentration of the xenobiotics decrease in the water column (Kukkonen 1992). Adsorption by sediments of chlorolignin compounds from pulp mill effluents is strong, but not irreversible. Desorption from Baltic sediments occurs more readily than from fresh water sediments (Pellinen 1994). Thus, in areas of lower sedimentation rates or lateral sediment transport within the impact area of the Kotka pulp mills, the organochlorine material in surface sediments may be bioavailable for several years.

6.3 Evidence of extensive natural organohalogen production

The distribution pattern of EOCl, EOX and EOCl/EOBr (Østfeldt *et al.* 1994) gave evidence that open sea sediments in the Gulf of Bothnia were affected by industrial organochlorines, but, alone, long-range transport of pulp mill effluents cannot explain the presence of organohalogens in the open sea. Jonsson *et al.* (1993) reported that levels of trichloroguaiacols correlated with levels of EOCl in sediments from areas polluted by pulp mills. In the present study, there was no indication of chlorophe-

nolic compounds in the open sea samples, and the EOX is probably therefore not from pulp bleaching. As chloride and bromide are readily available as substrates in the marine environment, the abundance of natural organohalogens in the sea is not surprising. The key observations that support the hypothesis of significant contribution from natural organohalogen production by algae are:

1) organohalogen levels appear uniform in non-polluted Gulf of Finland sediments
2) EOX was detected in all analysed marine and terrestrial samples, including samples not affected by pollution
3) EOX concentrations in different matrices decreased in the order: algae, sedimenting material, summer sediments, winter sediments
4) there was a seasonal variation in EOX sedimentation, connected with algal blooming
5) the EOX output from pulp mills was much lower than the total amount of EOX sedimenting or in surface sediments
6) the analysed specific organochlorines occurred in very low levels in sedimenting material
7) EOX concentration increased toward the top of the sediment cores, although the output from the mills has decreased markedly.

These points will be discussed in detail below.

6.3.1 Presence of halogens in all matrices

EOX was observed in all samples, which indicates that the natural organohalogens are present in a large variety of organisms, including marine samples, the samples from the pristine Weddell Sea and the terrestrial samples of spruce and spinach (Table 4). Levels of EOX in non-polluted surface sediments from the Gulf of Finland were uniform, within 0.5-13 µg Cl g^{-1} dw.

EOX levels in the marine samples decreased in the order: algae > trap material from a warm summer > trap material from a cold summer > summer sediments > winter sediments (Table 4). This order is apparently caused by the proceeding degradation of EOX-rich algal material. Winter sediments are subjected to the degradation of organic material for the longest time and thus contain the lowest EOX levels.

The presence of EOX in spinach demonstrated that EOX may arise from the presence of the Chl RC I found in spinach by Dörnemann and Senger (1982), and that the Chl RC I is readily detected by the EOX method used. Altogether, the marine and terrestrial samples supported the theory of a global presence of natural organohalogens. This theory was first put forward in study of soils by Asplund and Grimvall (1991).

6.3.2 Seasonal sedimentation of EOX

Sediment from winter 1993 contained less EOX than sediment from summer 1994. For instance, at stations F38 and XV1 EOX concentrations in 1993 were 2.2 and 6.0 µg Cl g^{-1} dw respectively, while the corresponding values in 1994 were 6.7 and 17.5-20.8 µg Cl g^{-1} dw respectively. This time-dependence is probably caused by the degradation of EOX material after autumn, and the subsequent deposition of EOX-rich material in spring-summer. Bottom sediments reflected the sedimentation of EOX-containing material. At station GF2 the surface sediments contained 4-5 µg Cl g^{-1} dw before the spring bloom and 12 µg Cl g^{-1} dw after the spring maximum, thus the sedimentation of the organohalogens from diatoms (VII) thus took approximately one month to reach the sea-floor (V).

Weather conditions affected the seasonal production of EOX at station GF2. In the warm summer of 1995, the dry-matter and EOX sedimentation were effective, whilst in the cold summer of 1996 the both fluxes were low. This phenomenon probably is due to weather-dependent algal growth.

6.3.3 Sedimentation and total quantities of organic halogen in sediments

According to the ^{137}Cs dating, the calculated sedimentation of dry-matter in the active sedimentation areas for the 1986-1994 period was 0.60±0.39 cm a^{-1} and 4.1±1.9 g m^{-2} d^{-1} (Table 6), or 0.18±0.11 cm a^{-1} and 1.2±0.6 g m^{-2} d^{-1} for the whole Gulf of Finland. The average sedimentation in the sediment traps at station GF2 was on 0.85-1.5 g m^{-2} d^{-1}. The average, linear sedimentation rates are close to estimates of 0.16 cm a^{-1} (Perttilä *et al.* 1995) and 0.4 cm a^{-1} (Salo *et al.* 1986) for the whole Gulf of Finland.

Natural sources are mainly responsible for the present flow of EOX in the Gulf of Finland. The anthropogenic EOX from pulp mills, atmosphere, and diffuse sources have only a minor contribution to the total budget. The mass-balances of EOCl reported by Wulff *et al.* (1993) indicated that pulp mills were the main source of organochlorine compounds to the Bothnian Sea and Baltic Proper in 1988-1989. However, Wulff *et al.* (1993) did not take into account the natural EOCl component in their calculations, although they recognised that it is of potential importance.

For the calculations in the present study, EOX/AOX relations of 0.5-3% (Berry *et al.* 1991, Martinsen *et al.* 1992) were used, depending on the bleaching process, to estimate the EOX output from

the pulp mills (Table 6). The amount of chlorinated compounds from the UPM Kymmene pulp mill in Kuusankoski retained in Kymi River sediments is not known. It is however certain that an appreciable fraction of the EOX from the mill is deposited in the river and the inner Ahvenkoski Bay (V). Therefore, the actual total output of EOX material from the mills to the Gulf of Finland is lower than the calculated value given in Table 6. The integrated content of EOX in sediments between 1986-1994 indicates that, proportionally, pulp mill-derived material forms a greater fraction of the total EOX than the surface sediments, but the large variance in total EOX in the cores from the Kotka area (Fig. 8, Table 6) makes calculation of exact relations difficult.

The trap results from 1995-1996 showed that deposition of specific organochlorines was negligible compared to the total EOX sedimentation (Table 6). The highest EOX concentrations and fluxes were observed in spring when diatoms were the most abundant algal species. Dominant species during the spring bloom in 1995 and 1996 were *Achnanthes taeniata*, *Chaetoceros* spp. and *Skeletonema costatum*, and it would be of interest to analyse pure cultures of these diatoms in the future.

According to the trap results, the EOX output from the mills was only 4-10% of the extrapolated EOX sedimentation over the whole Gulf of Finland. The difference between the extrapolated sedimentation of EOX in 1995 and 1996 was probably due to different amounts of primary production during those years. The differences cannot be explained by changes in output from the pulp mills. Using the values of wet precipitation of EOX (Jokela *et al.* 1992, Wulff *et al.* 1993), the Gulf of Finland should receive approx. 1-13 t of EOCl from the atmosphere annually. Chlorine disinfection of water as an EOX source is negligible (Jokela *et al.* 1992). In order to obtain a comprehensive picture of the flow and mass-balance of chlorine in the Gulf of Finland, data on concentrations of total organohalogens and specific compounds in water, air, biota and sediment should be available. Unfortunately such comprehensive data is not available, but, by using the data from the present study and the above-mentioned works, the sources and sediment stores of EOX in the Gulf of Finland may be illustrated schematically (Fig. 18).

By using the EOX fluxes of 1995, when the dry matter flux was closer to the average sedimentation of 1986-1994 (Table 6), the contribution of natural production to the present total EOX sedimentation would be 70-90%. According to the surface sediment EOX content (Table 6), the polluted sediments in the Kotka area comprised, on average, only approx. 10% of the total EOX in Gulf of Finland sediments. This
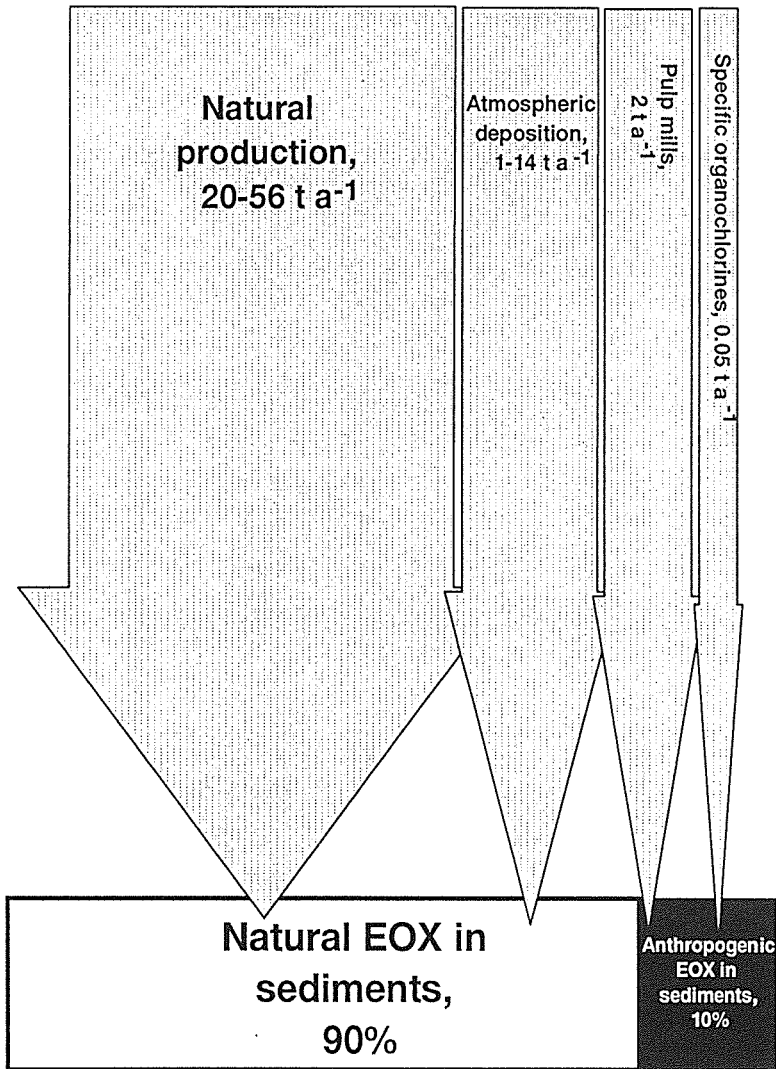
Fig. 18. Schematic representation of the EOX balance in the Gulf of Finland today.

is in accordance with observations of Hoekstra and de Leer (1994), who reported that 30-70% of the total AOX in the River Rhein was natural.

6.3.4 Possible causes of vertical EOX distribution in non-polluted sediments

Although EOX output from the mills has decreased, all the surface sediments from areas other than Kotka contain more EOX in the surface sediment than in the lower layers (Fig. 10, Appendix 2). This cannot be explained in any other way than by natural

EOX production. Palm and Lammi (1995) found a similar surface EOX increase in a non-polluted core from the coastal Bothnian Sea. The vertical EOX concentrations in non-polluted cores also resemble the profiles reported by Håkanson et al. (1988) for the open Bothnian sea sediments, where the EOCl increased upward in the sediment cores and the maximum natural EOCl concentrations were approx. 10 µg Cl g^{-1} dw. This is close to the EOX threshold level for polluted and natural sediments used in the present study. EOCl and EOX are not exactly equivalent because EOX may have a contribution from brominated compounds, but the results of NAA

showed that the bromine content was almost insignificant compared to the content of chlorine in sediments from station GF2. It seems that EOX results in this study may be comparable to the EOCl analysed in earlier studies (e.g. Jonsson 1992, Södergren *et al.* 1993). Håkanson *et al.* (1988) also recognised the contribution of natural EOCl in surface sediments and attributed the shape of the EOCl profile in the cores to sediment compaction, downward increase in organic material degradation and upward mobility of EOCl-containing material.

In the non-polluted sediments, the vertical distribution of EOX is less influenced by sedimentation of pulp-mill-derived material or terrestrial humic organohalogens (Asplund *et al.* 1989, Asplund and Grimvall 1991), than it is by the halogenation-dehalogenation reactions of the deposited organic material. For example, chlorophenols and chlorocatechlos are dechlorinated into phenols and chloride by microbes in anoxic sediments (Abrahamsson and Klick 1991, Liu *et al.* 1996, Neilson *et al.* 1990), and by bacteria of the genera *Rhodococcus* (Apajalahti and Salkinoja-Salonen 1987). Remberger *et al.* (1986) reported the anoxic dechlorination of chloroguiacols and chloroveratrols in brackish water sediments. Although chlorophenolic compounds seem not to be important in the open sea, analogous reactions may take place. In anoxic conditions halogenated organic matter (AOX) may be dechlorinated and release halides into sediment interstitial water (Müller *et al.* 1996). In a study with anaerobic river sediments, Song and Müller (1993) found that bromide is released from organic matter during early diagenesis, indicating the presence of brominated compounds in the sediments.

In oxic sediment surfaces, biotic exoenzymatic halogenation of recently deposited organic matter may take place (Müller *et al.* 1996), which may in part explain the presence of observed EOX in the non-polluted surface sediments during the present study. Oxic conditions are essential for the formation of H_2O_2 from partial oxidation of O_2, which may happen by respiration or photosynthetic water oxidation. H_2O_2 is then available for the enzymatic halogenation of the organic material (Neidelman and Geigert 1986). Biotic halogenation activity seems to decrease in the deeper sediments with decreasing O_2 content.

6.3.5 The chemical character of EOX

Results from chemical characterisations gave new information on molecular weight distribution, spectral characteristics, and polarity distribution of EOX material in sediments. Additionally, NMR and MS spectra were used to characterise the organic matter in the extracts.

Volatile organohalogens are lost during the lyophilisation of the sediment material and EOX consists of non-volatile compounds. The MWD of the extracts showed distinct peaks around 1000 g mol^{-1}, which is close to the molecular weight of chlorophylls and pheophytins. The MWD maximum was observed for both the halogen content and the coloured, UV-absorbing, organic material (Figs. 12 and 13, Table 7). This observation supports the hypothesis of

the presence of halogen-containing chlorophylls (e.g. Chl RC I), which would explain, to a large extent, the EOX levels observed in the sediment extracts. The possible role of the Chl RC I will be discussed in the next section.

The shape of the MWD profile of UV absorbing material from sediments resembles the shape of MWD profiles of humic material from raw and drinking water samples (Vartiainen *et al.* 1987, Miettinen *et al.* 1994). However, the main peaks that Vartiainen *et al.* and Miettinen *et al.* observed occurred at 50000-100000 g mol^{-1}, while the main peaks in the present study were near 1000 g mol^{-1}. Accordingly, the molecular weight of the extracted material is clearly much smaller than that of the humic materials in aqueous medium analysed with aqueous SEC.

It is possible that chemically the polystyrenes (see chapter 4.4.10) used for SEC calibration differ too much from the analysed extractable material and may not provide correct MWD values. This incompatibility can cause small shifts in the peak positions, but the shifts cannot be orders of magnitude. Moreover, chlorophyll a eluted at 900 g mol^{-1} (result not shown), suggesting that the molecular weight of chlorophyll pigments can be measured reliably.

The non-polluted and polluted sediments showed similar MWDs (Fig. 13, Table 7) and molecular weight could not be used to indicate the presence of BKME material in sediments.

The incorporation of organohalogens to sediments has been demonstrated to occur by binding to humic material (Bollag and Dec 1995). In sediments with high organic carbon content this mechanism may be important, but the MWDs of EOX and organic material from both unpolluted and polluted sediments resemble each other to a great extent. The MWD suggests that the organic material in unpolluted sediments is the chemical backbone, which incorporates organochlorines from the BKME, and it is for this reason that MWDs in the two cases are so similar.

The molecular weight distribution of the BKME that reaches the recipients is 50-4000, with a peak at

100-500 g mol^{-1} (Jokela *et al.* 1993). This distribution was determined using aqueous SEC, but those of the present study with non-aqueous SEC. The results therefore may not be directly comparable, but would suggest that the MWDs of sediment extracts from both polluted and non-polluted areas are different to the MWD of BKME.

Within the polluted area, HMW chlorolignins have been found to be the main source of organohalogen material (Remberger *et al.* 1990). The results of the present study support to some extent the observation of Remberger *et al.*, since no significant increase of LMW compounds was seen in sediments from the Kotka area (III). However, no change in the MWD toward HMW was observed either. The humic HMW compounds present in sediments (Poutanen 1985) or the large chlorinated lignin polymers from BKME apparently are not extractable with the neutral, organic solvents used. Consequently, the contribution of the halogenated humic structures reported by Dahlman *et al.* (1993, 1994) to total EOX should be negligible. In the 0-5 cm sediment from station GF2 the observed shift toward lower molecular weights (Fig. 12) probably arises from the degradation of organic material in the deeper sediments. The sample from station GF2 was a 0-5 cm section representing at least a 10 year interval.

Organohalogens in sediment from the Gotland deep were studied by S. Jonsson *et al.* (1995). According to their data, observed lignin-derived structures, of primarily natural origin, showed large-scale bromination. In the samples of the present study, bromine was more abundant in bottom sediment than in sedimentating material, but still had only a minor contribution to the EOX in both matrices. The process of biohalogenation in the Gulf of Finland seems to be producing mainly chlorinated compounds.

The polarity range of the EOX material varied from semi-polar to polar according to the RP-HPLC analyses (Fig. 12). The TLC analyses revealed in turn that the extracted material was very uniform (Fig. 14) and had the spectral characteristics of chlorophylls and other pigments. Similarly, Reemtsma and Jekel (1996) found that polar constitutents are important fractions in sediments, and that n-hexane was able to extract only a small amount of the organohalogens. The polarity range of the observed fluorescent material in TLC was in accord with the RP-HPLC (254 nm) chromatograms, but the polarity distribution of EOX cannot be compared because EOX was not determined from the TLC plate.

According to the NMR analyses, most of the extracted material consisted of aliphatic compounds, possibly with C=C bonds (Fig. 15, Table 7). The absence of resonances typical to Chl a and RC I

(Dörnemann and Senger 1986) indicated that the porphyrins were present in low quantities compared to other compounds. That humic substances are to some extent contributing to the EOX mixture in the analysed sediments cannot be totally excluded. Virkki (1993) reported that aquatic humic substances had a high content of oxygen-bearing aliphatic groups, which were found abundant also in the EOX preparations from the present study. However, in general, the ^{1}H NMR spectra of aquatic humics (Poutanen 1985, Virkki 1993) differ markedly from the spectra of this study.

Most MALD and ES ions had molecular weights less than 500-600 g mol^{-1}, (Fig. 16, A) which could be explained by the presence of carotenoids, pheophytins or their fragments. This observation did not in accord with the SEC results and may be due to the incomplete or non-existent introduction of heavier molecules into the MS equipment, or because of the molecules having charges greater than one unit. The absence of the heavier molecules (~800-1000 g mol^{-1}) would suggest that no chlorophylls were present in the analysed sample. Chlorine was detected in the HPLC fractions exposed to high cone voltage (ES analysis), but the presence of chlorine or bromine in the fragment ions (<300 g mol^{-1}) taken to MS/MS analysis was uncertain. These fragments were all under 300 g mol^{-1}.

In comparison with the MS spectra of Chl RC I (Dörneman and Senger 1986), no similar molecule peaks were observed. The molecular ions in the ES spectra (Fig. 16, B) from fractions 1 and 2 clearly showed that the MS samples contained mainly phytol derivatives, not pheophytins or other porphyrins. This is in contradiction with the UV/VIS and SEC-HPLC analyses which indicated that coloured, relatively HMW algal pigment material was present.

Mass spectrometry and NMR obviously are not sufficiently able to characterise the single molecules present in the EOX preparations. However, Virkki (1993) reported that the most abundant functional groups in polydisperse material can be characterised with NMR. For individual compound identification, the fractionation of the samples prior to analysis needs to be better accomplished. With this achieved, the use of techniques like capillary electrophoresis / MS could be useful. Gas chromatographic techniques are not suitable for the underivated preparations with large molecules. However, MS and NMR analyses did reveal that most unhalogenated material was probably from degraded of chlorophylls, which also suggests that break-down products of Chl RC I may have an important contribution.

6.3.6 Role of chlorophyll RC I

The chlorophylls and their degradation products (pheophytins, etc.) are readily extracted from plant material with polar solvents such as 2-propanol, and identifiable through the greenish-yellow colour of the extract. There was a positive dependence between colour intensity and EOX concentration in the samples and, according to the MWD, material with same molecular weight as chlorophylls (approx. 1000 g mol^{-1}) is also present.

Chlorophyll RC I is a part of photosystem I in all aerobic photosynthetic organisms (Katoh *et al.* 1985). If Chl RC I is present in the algal material deposited to sediments, it is also bound to be present in the extracts because Chl RC I is also readily dissolved by the 2-propanol used in the EOX extraction (Katoh *et al.* 1985). Dörneman and Senger (1981) have reported Chl a : Chl RC I ratios of 1:400-1:28 in extracts of alga *Scenedesmus obliquus*. Since Cl represents 3.76% by weight of Chl RC I, 100-1300 µg Cl g^{-1} Chl a was present in those samples. In the alga *Anabaena lemmermannii* the Chl RC I : Chl a ratio was 1:87-1:86, or 430-440 µg Cl g^{-1} Chl a. The amount of Chl a in algae from the Northern Baltic Sea is generally about 2.5% by dry weight (Heiskanen, FEI, pers. comm.). According to these values, the algae could contain 60-900 µg Chl RC I g^{-1} dw, or 2-30 µg Cl g^{-1} dw, which is of the same order as the maximum EOX concentrations observed in sedimenting material and algae (Table 4).

The molecular mass of Chl RC I is 943 and that of Chl a 894 g mol^{-1}. The observed SEC-HPLC chromatograms showed that most of UV-adsorbing material and EOX elutes close to 1000 g mol^{-1}. This would suggest that chlorophylls, pheophytins and pheophorbides may be the dominant molecules contributing to the SEC profile. Changes produced in chlorophyll a during attack by microorganisms involves loss of Mg to form pheophytin a, and then the loss of the phytol group to form pheophorbide a. In sediments the latter is transformed to a variety of porphyrin-type compounds (Stevenson 1982). The degradation of Chl RC I in sediments has not been described, but degradation of Chl a first generates phytol (M = 296) and pheophytin a (M=871), which is later converted to pheophorbide a (M = 615). Smaller degradation products are produced later. Chl RC I probably behaves similarly and may be first converted to pheophytin RC I (M = 919), pheophorbide RC I (M = 641), and chlorinated porphyrins (M < 600).

6.3.7 Other possible explanations?

It has been suggested that the increased primary production due to eutrophication has increased sedimentation, the sequestering of pollutants in sediments and also the observed temporal reduction of contaminants in biota (Gunnarsson *et al.* 1995, Jonsson 1992). Furthermore, according to Jonsson (1992), increased sequestering of anthropogenic organochlorines is also seen in relation to estimated loading from pulp mills, through the vertical EOCl sediment content. To further extend the Jonsson's hypothesis, it is possible to suggest that the two phenomena (increased sequestering of BKME material and natural production) work together and explain the formation of the observed sediment profiles.

In non-polluted areas, where EOX concentrations can be explained solely by natural production, the vertical profile is most probably caused by remineralisation of the EOX material. In non-polluted areas, although the sequestering of natural material may increase, the sequestering of anthropogenic chlorine (or halogen) may not.

Explanations for the overall uniformity of EOX levels in the open Gulf of Finland like long-range transport of pulp-mill derived material are unlikely. Although industrial EOX material could form a part of the spring sedimentation of EOX, it is difficult to imagine that the pollutants would reach all the studied areas in the rather uniform manner that is observed. Water from the eastern Baltic Proper enters the Gulf of Finland, but the effect of the Swedish or Russian (Kaliningrad region) pulp mills on this water is surely very small.

Long-range transport of BKME from the Bothnian Sea and Baltic Proper to the Gulf of Finland has been not studied, but is unlikely. The Narva, Koporskaya and Luzhskaya Bays are wide with sill-free connection to the open Gulf of Finland and the Neva Estuary. In contrast, the Vyborg Bay is semi-enclosed and thus the entering of water-masses from the open Gulf or the Kotka area is substantially restricted. The atmospheric deposition of EOX to the Gulf of Finland has not been measured directly, but it can be responsible for only a small part of the total sedimentation of EOX.

6.4 Monitoring and recommendations

Hazard assessment of pulp mill effluents is a difficult task and requires multidisciplinary efforts that must integrate chemical, toxicological and biological data at several organizational levels.

EOX gives basic information on the presence of the organochlorine pollutants within the impact area, but on the outskirts of the impact zone it is difficult to distinguish between the natural and anthropogenic contribution. If high concentrations of total organohalogens are found, the EOX may indicate that toxic groups of organochlorines are also present, especially the chlorophenolic compounds like PCGs, PCCs and PCPs from the pulp and paper industry. The old emissions of the wood preservative Ky-5 and of pulp mill effluent along the Kymi River mean that, in the studied area, the extremely toxic PCDDs, PCDEs and PCDFs are also of concern.

Monitoring of sediments using EOX (and possibly AOX) in the Kotka area is recommended because sediments may remain toxic to the biota for several years. The monitoring could be arranged by FIMR and FEI, e.g. every five-ten years. Three-five active sediment basins could be selected for this purpose. According to sedimentation rates and vertical EOX profiles in sediments from the Kotka area, stations K8, K11, K12, K24 and K26 are suitable for chronological monitoring. At all of these stations the reduction in the EOX output from the mills is observable. It would be interesting to take further cores also from, for instance, station K9 or K15 where the uppermost layer contained high levels of EOX compared to the deeper layers. When considering vertical history, the formerly polluted areas can be distinguished by the presence of >10-13 µg Cl g⁻¹ dw (EOX), or >150-200 µg Cl g⁻¹ dw (AOX) in surface sediments. In keeping with Håkanson *et al.* (1988), concentrations of over 5 µg Cl g⁻¹ dw (EOX) in sediments deeper than 3-4 cm indicate anthropogenic pollution. Using Cl:C ratios to detect polluted sediments is also feasible. Values higher than 1:5000-1:3000 indicate certainly pollution from anthropogenic sources. Monitoring should be carried out preferably in February-May, to minimize the contribution of natural compounds and provide better estimates of the concentration levels of the more permanent anthropogenic fractions of EOX.

Mussels and other benthic animals from the area should be analysed for EOX and chlorophenolics. Monitoring of responses in biota would be relevant even if and when the use of chlorine chemicals is completely stopped. Pellinen *et al.* (1994) considered that the natural EOX background in mussels may be 330-360 µg Cl g⁻¹ lipid (digestive gland). As with sediment, in mussels the natural EOX background value should be subtracted from the total EOX value. The effects of the pulp mill effluents on benthic communities in the Kotka area could be studied also with other bioindicators, for instance *M. affinis*. Even with further reductions in the use of chlorine chemicals at the pulp mills, the effects of the non-chlorinated chemicals need to be assessed. Transport of organochlorine pollutants from the Russian pulp mills in Lake Ladoga to the Gulf of Finland should be studied jointly by Finnish and Russian institutions.

Due to the small size of the active sediment basins in the Kotka area and the unhomogeneous character of recent sediments (Vallius *et al.* 1996, 1997), attention should be given to the quality of the sediment sampling. This can be improved with accurate positioning of the ship sampling platform with DGPS systems. Precise selection, location and repetition of sediment coring is essential, as is study of the variability of pollutant concentrations within the active sediment basins.

The chemical character of the natural organohalogens needs to be evaluated more accurately. Techniques that may help provide more insight could be capillary electrophoresis (CE)-MS and use of Cl-selective detectors with CE or HPLC. To better understand how much different algal species contribute to the natural EOX, more pure, algal cultures should be analysed. Future analyses could also include isolating the Chl RC I molecule from algae to estimate the contribution of the molecule to the total EOX.

7 Conclusions

The AOX and EOX methods applied were suitable for the study of organohalogens in sediments. Chemical characterisations showed that the sediment material analysed is very uniform and that algal pigments may be important components of the natural EOX. The presence of Chl RC I in algae is probable, and this presence alone may explain the high EOX concentrations in algae and in sedimenting material. The characterisation and fractionation of the EOX material is difficult. NMR and MS techniques for the HPLC-fractionated and unfractionated EOX solutions proved inadequate. More effective methods should be used. Although the exact chemical structures of natural organic halogen compounds remains to be determined, the quantity of these compounds is obviously substantial.

Background organohalogen concentrations were studied and sediments with background EOX levels were found to be of special significance. Natural

organohalogen production seems to be the major source of the EOX sedimenting in the Gulf of Finland. At present specific organochlorines and pulp mill effluents are responsible for only a minor part of the total EOX. EOX is produced predominantly during the spring diatom bloom. As anthropogenic input decreases, the share of natural production in the total EOX budget will increase, and this must be taken into account when calculating the organohalogen budget of different sea areas.

Organochlorine pollution from the pulp and paper industry in the Gulf of Finland area seems to be limited to the pollution of the Kotka area, where, still in the summer of 1994, the surface sediments contained high EOX concentrations and even higher concentrations in the deeper sediments. Lateral transport of polluted sediments takes place from near the town to the outer sea area. Most of the organochlorine pollution in the Kotka area originates from the pulp mill in the town and, to a lesser extent, from the Kuusankoski mill. Pulp mill discharges and also the earlier production of chlorophenol on the Kymi River are responsible for most of the organochlorine pollution in sediments in the western Kotka area. According to EOX and AOX measurements, organochlorine pollution in other parts of the Gulf of Finland is negligible and, in the case of the non-polluted sediments, it is the background EOX that constitutes by far the major part of the organic halogen material in the Gulf of Finland.

The Kotka sediments may constitute a threat to marine organisms. Sediment monitoring in the Kotka area is recommended and can be carried out using the same EOX method employed in this study, together with analysis of chlorophenolics.

Acknowledgements

References

Abrahamsson K. & Klick S. 1991. Degradation of halogenated phenols in anoxic natural marine sediments. *Mar. Pollut. Bull.* 22 (5): 227-233.

Ahokas J.T., Holdway D.A., Brennan S.E., Goudey R.W. & Bibrowska H.B. 1994. MFO activity in carp (Cyprinus carpio) exposed to treated pulp and paper mill effluent in Lake Coleman, Victoria, Australia, in relation to AOX, EOX, and muscle PCDD/PCDF. *Environ. Tox. Chem.* 13: 41-50.

Andersin A.-B. & Sandler H. 1991. Macrobenthic fauna and oxygen deficiency in the Gulf of Finland. *Memoranda Soc. Fauna Flora Fennica* 67: 3-10.

Anonymous 1992. Chlorine and the environment: A dialogue of the deaf. *ENDS Report* 213:15-18. Environmental Data Services, UK.

Anonymous 1996. *Programmy mer po sokrastseniyu zagryazneniya vodnych obyektof i osustsestvleniyu vodoochrannych meropriyatniy v basseyne Baltiyskogo morya.* (Action plan for reducing pollution of water-courses and improving water protection within the Baltic Sea area). St. Petersburg 1996, 118 pp. (In Russian.)

Apajalahti J.H.A. & Salkinoja-Salonen M.S. 1987. Dechlorination and para- hydroxylation of polychlorinated phenols by Rhodococcus chlorophenolicus. *J. Bacteriol.* 169: 675-681.

Asplund G. & Grimvall A. 1991. Organohalogens in nature-more widespread than previously assumed. *Environ. Sci. Technol.* 25 (8):1346-1350.

Asplund G., Grimvall A. & Jonsson, S. 1994. Determination of the total and leachable amounts of organohalogens in soil. *Chemosphere* 28 (8):1467-1475.

Asplund G., Grimvall A. & Pettersson C. 1989. Naturally produced adsorbable organic halogens (AOX) in humic substances from soil and water. *Sci. Total Environ.* 81/82: 239-248.

Balk L., Förlin L., Söderström M. & Larsson Å. 1993. Indications of regional and large-scale biological effects caused by bleached pulp mill effluents. *Chemosphere* 27 (4): 631-650.

Baltic Marine Environment Protection Commission - Helsinki Commission - 1996: Third periodic assessment of the state of the marine environment of the Baltic Sea, 1989-1993; Executive summary. *Baltic Sea Environment Proceedings* 64 A, 25 pp.

Berry R.M., Luthe C.E., Voss R.H., Wrist P.E., Axegård P., Gellerstedt G., Lindblad P.O. & Pöphe I. 1991. The effect of recent changes in bleached kraft mill technology on organochlorine emission. An international perspective. *Pulp Paper Can.* 93 (6): T155-T165.

Bollag J.M. & Dec J. 1995. Incorporation of halogenated substances into humic material. In: Grimvall, A. & de Leer E. W. B. (eds.). *Naturally-produced organohalogens.* Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 161-169.

Boström K., Burman J., Ponter C. & Ingri I. 1981. Selective removal of trace elements from the Baltic by suspended matter. *Mar. Chem.* 10: 335-354.

Bruun J.-E. & Kankaanpää H. 1996. A method for visualization of the sea-floor topography to achieve higher precision in locating sampling sites. *ICES C.M. 1996/R:10*, ICES Annual Science Conference, 84th Statutory Meeting 27 September to 4 October, 1996, Reykjavik, Iceland. p. 233. (mimeogr.)

Craig G.R., Orr P.L., Robertson J.L. & Vrooman W.M. 1990. Toxicity and bioaccumulation of AOX and EOX. *Pulp Paper Can.* 91 (9): 39-45.

Crusius J. & Anderson R.F. 1995. Evaluating the mobility of ^{137}Cs, $^{239+240}$Pu and ^{210}Pb from their distributions in laminated lake sediments. *J. Paleolimn.* 13: 119-141.

Dahlman O., Mörck R., Ljungquist P., Reimann A., Johansson C., Borén H. & Grimvall A. 1993. Chlorinated structural elements in high molecular weight organic matter from unpolluted waters and bleached-kraft mill effluents. *Environ. Sci. Technol.* 27:1616-1620

Dahlman O., Reimann A., Ljungquist P., Mörck R., Johansson C., Borén H. & Grimvall A. 1994. Characterization of chlorinated aromatic structures in high molecular weight BKME-materials and in fulvic acids from industrially unpolluted waters. *Water Sci. Tech.* 29 (5-6): 81-91.

Dolfing J. & Salomons W. 1995. Kinetic control of the biogeochemical formation of halogenated humic acids. In: Grimvall A. & de Leer E. W. B (eds.). *Naturally-produced organohalogens.* Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 221-226.

Dörnemann D. & Senger H. 1982. Physical and chemical properties of chlorophyll RCI extracted from photosystem I of spinach leaves and from green algae. *Photochem. Photobiol.* 35: 821-826.

Dörnemann D. & Senger H. 1986. The structure of chlorophyll RC I, a chromophore of the reaction center of photosystem I. *Photochem. Photobiol.* 43 (5): 573-581.

Elmgren R. 1984. Trophic dynamics in the enclosed, brackish Baltic Sea. *Rapp. P.-v. Réun. Cons. int. Explor. Mer.* 183: 152-169.

Faulkner D.J. 1993. Marine natural products. *Natural Product Reports* 10: 497-539.

Flinkman J., Aro E., Vuorinen I., Kotilainen P. 1991. The annual changes in food selection of Baltic herring. *ICES C.M. 1991/J:14.* 11 pp.

Förlin L., Andersson T., Balk L. & Larsson Å. 1995. Biochemical and physiological effects in fish exposed to bleached kraft mill effluents. *Ecotoxicol. Environ. Saf.* 30: 164-170.

Gribble G.W. 1994. The natural production of chlorinated compounds. *Environ. Sci. Technol.* 28 (7): 310A -318A.

Grimvall A. & Asplund G. 1991. Natural halogenation of organic macromolecules. *Finnish Humus News* 3: 41-51.

Grimvall A. & de Leer E.W.B (eds.). 1995. *Naturally-produced organohalogens.* Kluwer Academic Publishers, Dordrecht, The Netherlands, 437 pp.

Grimvall A., de Leer E.W.B., Grøn C. & Carlsen L. (eds.). 1995. Halogenation of organic macromolecules in the environment. *Humus - Nordic Humus Newsletter* 2 (1), 43 pp.

Grøn C. 1990. Organic halogens: Determination in marine media of adsorbable, volatile, or extractable compound totals. *Techniques in marine environmental sciences.* No. 10. International Council for the Exploration of the Sea, 19 pp.

Grøn C. & Dybdahl H.P. 1996. Determination of total organic halogens (TOX); Bias from a non-halogenated organic compound. *Environ. Internat.* 22 (3): 325-329.

Gunnarsson J., Broman D., Jonsson P., Olsson M. & Rosenberg R.1995. Interactions between eutrophication and contaminants: towards a new research concept for the European aquatic environment. *Ambio* 24 (6): 383-384.

Haahti H. 1995. Silakan vieraat ainect. *Ympäristökatsaus 7.* Suomen ympäristökeskus, p.12. (In Finnish).

Hager L.P. 1982. Mother nature likes some halogenated compounds. *Basic Life Sci.* 19: 415-429.

Haley R.K., Hall T. & Bousquet T.M. 1995. Effects of biologically treated bleached-kraft mill effluent before and after mill conversion to increased chlorine dioxide substitution: results of an experimental streams study. *Environ. Toxicol. Chem.* 14 (2): 287-298.

Haynes D., Mosse P. & Levay G. 1995. The use of transplanted cultured mussels (*Mytilus edulis*) to monitor pollutants along the ninety mile beach, Victoria, Australia - I. Extractable organohalogens (EOX). *Mar. Pollut. Bull.* 30 (7): 463-469.

Higashi R.M., Cherr G.N., Shenker J.M., Macdonald J.M. & Crosby D.G. 1992. A polar high molecular mass constituent of bleached kraft mill effluent is toxic to marine organisms. *Environ. Sci. Technol.* 26: 2413-2420.

Hoekstra E. & de Leer E.W.B. 1994. AOX levels in the River Rhine: Fifty percent of natural origin?! *Water Sci. Tech.* 29 (3): 133-136.

Hoffmann H.-J., Bühler-Neiens G. & Laschka D. 1988. AOX in sludges and sediments - method for determination and results. *Vom Wasser* 71: 25-134. (In German with English summary).

Hyötyläinen J., Knuutinen J. & Vilén E. 1995. Characterization of high molecular mass fractions of receiving waters and sediments of a pulp mill by CuO-oxidation and HPLC. *Chemosphere* 30 (5): 891-906.

Håkanson L., Jonsson P., Jonsson B. & Martinsen K. 1988. Distribution of chlorinated organic substances from pulp mills. *Water Sci. Tech.* 20 (2): 25-36.

Häkkinen A. & Åker K. 1991. Kotkan, Pyhtään ja Vehkalahden merenpohjan maalajikerrostumat. *Geological Survey of Finland, Tutkimusraportti 109 - Report of Investigation* 109, 30 pp. (In Finnish with English summary).

Ilus E., Sjöblom K.-L., Ikäheimonen T.K., Saxén R. & Klemola S. 1993. Monitoring of radionuclides in the Baltic Sea in 1989-1990. *Report STUK-A103. Supplement 10 to Annual report STUK A-89.* Finnish Centre for Radiation and Nuclear Safety, 35 pp.

Ilus E., Mattila J., Klemola S. and Ikäheimonen T.K., 1997. Evaluation of sedimentation rate at two sampling stations in the Gulf of Finland based on Pb-210, Cs-137 and Pu-239,240 profiles in sediments. *The second NKS/EKO-1 Seminar,* Finnish Centre for Radiation and Nuclear Safety, Helsinki, Finland, April 2-3, 1997. 7 pp. (To be published in the Report Series STUK-A).

ISO 9562. *Water quality. Determination of adsorbable organic halogens (AOX).* International Organization of Standardization, Geneve, 1989.

Johnson K.S., Coale K.H. & Jannasch H.W. 1992. Analytical chemistry in oceanography. *Anal. Chem.* 64 (22): 1065A-1075A.

Jokela J. K., Laine M., Ek M. & Salkinoja-Salonen M. 1993. Effect of biological treatment on halogenated organics in bleached kraft pulp mill effluents studied by molecular weight distribution analysis. *Environ. Sci. Technol.* 27 (3): 547-557.

Jokela J., Salkinoja-Salonen M.S., Elomaa E. 1992. Adsorbable organic halogens (AOX) in drinking water and the aquatic environment in Finland. *J. Water SRT -Aqua* 41 (1): 4-12.

Jonsson P. 1992. Large-scale Changes of Contaminants in Baltic Sea Sediments during the Twentieth Century. PhD Dissertation. *Acta Univ. Ups., Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science* 407, 52 pp.

Jonsson P., Rappe C., Kjeller L.-O., Kierkegaard A., Håkanson L. & Jonsson B. 1993. Pulp mill related polychlorinated organic compounds in Baltic Sea sediments. *Ambio* 22 (1): 37-43.

Jonsson S., Pavasars I., Johansson C., Borén H. & Grimvall A. 1995. Origin of organohalogens found in Baltic Sea sediments. In: Grimvall, A. & de Leer E. W. B. (eds.). *Naturally-Produced Organohalogens*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 339-352.

Juuti S., Vartiainen T., Joutsenoja P. & Ruuskanen J. 1996a. Volatile organochlorine compounds formed in the bleaching of pulp with ClO_2. *Chemosphere* 33 (3): 437-448.

Juuti S., Vartiainen T. & Ruuskanen J. 1996b. Formation of organochlorine compounds in kraft pulp bleaching processes. *Chemosphere* 33 (12): 2431-2440.

Kankaanpää H. 1996. Analysis of the ICES-HELCOM Sediment Baseline Study samples for EOX gives more evidence of natural organohalogen production in the Baltic Sea. *ICES CM 1996/R:1*. ICES Annual Science Conference, 84th statutory meeting 27 September to 4 October, 1996, Reykjavik, Iceland. p. 231. (mimeogr.)

Katoh T., Dörnemann D. & Senger H. 1985. Evidence for chlorophyll RC I in cyanobacteria. *Plant Cell Physiol.* 26 (8): 1583-1586.

Koistinen J., Paasivirta J., Nevalainen T. & Lahtiperä M. 1994a. Chlorophenantrenes, alkylchlorophenantrenes and alkylchloronaphtalenes in kraft pulp mill products and discharges. *Chemosphere* 28 (7): 1261-1277.

Koistinen J., Paasivirta J., Nevalainen T. & Lahtiperä M. 1994b. Chlorinated fluorenes and alkylfluorenes in bleached kraft pulp and pulp mill discharges. *Chemosphere* 28 (12): 2139-2150.

Koistinen J., Paasivirta J., Suonperä M. & Hyvärinen H. 1995. Contamination of pike and sediment from Kymijoki River by PCDEs, PCDDs, and PCDFs: Contents and patterns compared to pike and sediment from the Bothnian Bay and seals from Lake Saimaa. *Environ. Sci. Technol.* 29 (10): 2541-2547.

Kovacs T.G., Gibbons J.S., Tremblay L.A., O'Connor B.I., Martel P.H. & Voss R.H. 1995. The effects of a secondary-treated bleached kraft mill effluent on aquatic organisms as assessed by short-term and long-term laboratory tests. *Ecotoxicol. Environ. Saf.* 31: 7-22.

Kringstad K.P. & Lindström K. 1984. Spent liquors from pulp bleaching. *Environ. Sci. Technol.* 18 (8): 236A-248A.

Kukkonen J. 1992. Effects of lignin and chlorolignin in pulp mill effluents on the binding and bioavailability of hydrophobic organic pollutants. *Water Res.* 26 (11): 1523-1532.

Kyzyurov V., Mikheev Y., Niemistö L., Winterhalter B., Häsänen E. & Ilus E. 1994. A simple method for the determination of deposition rates of recent sediments based on cesium-137 activity following the Chernobyl accident. *Baltica* 8: 64-67.

Landner L. (ed.) 1989. *Chemicals in the Aquatic Environment*. Springer-Verlag. Berlin. 406 pp.

Larsson Å., Andersson T., Förlin L. & Härdig J. 1988. Physiological disturbances in fish exposed to bleached kraft mill effluents. *Water Sci. Tech.* 20 (2): 67-76.

Laturnus F., Wiencke C. & Klöser H. 1996. Antarctic macroalgae - sources of volatile halogenated organic compounds. *Mar. Environ. Res.* 41 (2): 169-181.

Leivuori M. & Niemistö L. 1995. Sedimentation of trace metals in the Gulf of Bothnia. *Chemosphere* 31 (8): 3839-3856.

Lindström M. & Lindström A. 1980. Changes in the swimming activity of Pontoporeia affinis (Crustacea, Amphipoda) after exposure to sublethal concentrations of phenol, 4-chlorophenol and styrene. *Ann. Zool. Fennici* 17: 221-231.

Lindström M. 1992. The migration behaviour of the amphipod Pontoporeia affinis Lindström. PhD Dissertation. Division of Physiology, University of Helsinki. *Walter and Andrée de Nottbeck Foundation scientific reports* No. 7. 18 pp.

Liu S.-H., Kuo C.-E. & Hsu T.-B. 1996. Reductive dechlorination of chlorophenols and pentachlorophenol in anoxic estuarine sediments. *Chemosphere* 32 (7): 1287-1300.

Lund Kvernheim A., Martinsen K., Carlberg G.E., Berg B. E., Fresvig M. & Greibokk T. 1993. Characterization of organohalogen matter in sediments from the receiving water of a bleach plant. *Chemosphere* 27 (5): 733-745.

Lyden A. & Landner L. 1979. Inverkan av skogsindustriella utsläpp på växtplanktons fotosyntes och tillväxt. *Svenska Papperstidn.* 16: 473-476. (In Swedish).

Maatela P. 1995. Determination of organically bound chlorine in industrial and environmental samples. PhD Dissertation, Department of Chemistry, *University of Jyväskylä Research report* No. 53, 83 pp.

Manninen P. 1990. Determination of total organic chlorine and bromine in environmental aquatic samples by activated carbon adsorption and neutron activation analysis. PhD Dissertation. University of Helsinki. *Annales Academiae Scientiarum Fenniae, Ser. A11. Chemica* 225, 123 pp.

Martinsen K., Kringstad A. & Carlberg G.E. 1988. Methods for determination of sum parameters and characterization of organochlorine compounds in spent bleach liquors from pulp mills and water, sediment and biological samples from receiving waters. *Water Sci. Tech.* 20 (2): 13-24.

Martinsen K., Lund Kvernheim A. & Carlberg G.E. 1992. Distribution of organohalogens in sediments outside pulp mills using sum parameters. In: Södergren A. (ed.). Environmental fate and effects of bleached pulp mill effluents. *Swedish Environmental Protection Agency Report* 4031, pp. 143-148.

Martinsen K., Lund Kvernhem A. & Carlberg G.E. 1994. Distribution of organohalogen in sediments outside pulp mills using sum parameters. *Sci. Total Environ.* 114: 47-57.

Mehrtens G. 1994. Haloperoxidase activities in Arctic macroalgae. *Polar Biol.* 14: 351-354.

Miettinen I.T., Martikainen P.J. & Vartiainen T. 1994. Humus transformation at the bank filtration water plant. *Water Sci. Tech.* 30 (10): 179-187.

Moore J.M. & Ramamoorthy S. 1984. *Organic chemicals in natural waters.* Springer-Verlag. New York. 289 pp.

Munkittrick K.R., Van Der Kraak G.J., McMaster M.E. & Portt C.B. 1992. Response of hepatic MFO activity and plasma sex steroids to secondary treatment of bleached kraft pulp mill effluent and mill shutdown. *Environ. Tox. Chem.* 11: 1427-1439.

Müller G., Nkusi G. & Schöler H. F. 1996. Natural organohalogens in sediments. *J. Prakt. Chem.* 338: 23-29.

Mäkelä T.P., Lindström-Seppä P. & Oikari A.O.J. 1992. Organochlorine residues and physiological condition of the freshwater mussel Anodonta anatina caged in River Pielinen, eastern Finland, receiving pulp mill effluent. *Aqua Fennica* 22 (1): 49-58.

Neidelman S.J. & Geigert J. (eds.) 1986. *Biohalogenation: Principles, basic roles and applications.* Ellis Horwood Limited, Frome, Somerset, Great Britain, 201 pp.

Neilson A.H., Allard A.-S., Hynning P.-E., Remberger M. & Viktor T. 1990. The environmental fate of chlorophenolic constituents of bleachery effluents. *Tappi J.* 73: 239-247.

Niemistö L. 1974. A gravity corer for studies of soft sediments. *Merentutkimuslaitoksen Julk./ Havsforskningsinst. Skr.* 238: 33-38.

Nkusi G. & Müller G. 1995. Naturally produced organohalogens: AOX-monitoring in plants and sediments. In: Grimvall A. & de Leer E. W. B (eds.). *Naturally-produced organohalogens.* Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 261-268.

Oanh N.T.K. & Bengtsson B.-E. 1995. Toxicity to Microtox, micro-algae and duckweed of effluents from the Bai Bang Paper Company (BAPACO), a Vietnamese bleached kraft pulp and paper mill. *Environ. Poll.* 90 (3): 391-399.

Østfeldt P., Gustavson K., Jansson B., Jonsson P., Miettinen V., Ringstad, O. & Wesén C. 1994. Halogenated organic compounds in the marine environment 1989-1990. *TemaNord* 1994:591, Nordic Council of Ministers, Copenhagen, 115 pp.

Owens J.W. 1991. The hazard assessment of pulp and paper effluents in the aquatic environment: A review. *Environ. Tox. Chem.* 10: 1511-1540.

Paasivirta J. 1991. *Chemical ecotoxicology.* Lewis Publ. Inc., Boca Raton, Florida, USA, 209 pp.

Paasivirta J., Knuutinen J., Knuuttila M., Maatela P., Pastinen O., Virkki L., Paukku R. & Herve S. 1988a. Lignin and organic chlorine compounds in lake water and the role of chlorobleaching effluents. *Chemosphere* 17 (1): 147-158.

Paasivirta J., Knuutinen J., Maatela P., Paukku R., Soikkeli J. & Särkkä J. 1988b. Organic chlorine compounds in lake sediments and the role of the chlorobleaching effluents. *Chemosphere* 17 (1): 137-146.

Paasivirta J., Palm H., Rantio T., Koistinen J., Maatela P. & Lammi R. 1997. Environmental fate of originated organochloro compounds from pulp mills. In: Turoski V. (ed.). *Chlorine and chlorine compounds in the paper industry.* Ann Arbor Press, Inc, Chelsea, Michigan, The USA, pp. 105-113.

Pacyna J.M., Broström-Lunden E., Cleeman M., Jansson B., Korhonen M., Oehme M., Paasivirta J., Erecius Poulsen M., Sinkkonen S. and Zuber A. 1994. Regional and global cycling of persistent organic pollutants (POPs). *NILU:* OR 58/94. The Norwegian Institute for Air Research. 176 pp.

Pacyna J.M., Broström-Lunden E., Paasivirta J., Runge E. and Wania F. 1996. Emissions and behaviour of selected persistent organic pollutants (POPs) in the Northern Environment. *NILU:* OR 17/96. The Norwegian Institute for Air Research. 59 pp.

Palm H. 1995. Fate of chlorophenols and their derivatives in sawmill soil and pulp mill recipient environments. PhD Dissertation, Department of Chemistry, *University of Jyväskylä Research report* No. 56, 52 pp.

Palm H. & Lammi R. 1995. Fate of pulp mill organochlorines in the Gulf of Bothnia sediments. *Environ. Sci. Technol.* 29 (7): 1722-1727.

Pellinen J. 1994. Sorption of high molecular weight chlorolignin on sediment. *Chemosphere* 28 (10): 1773-1789.

Pellinen J., Kukkonen J., Herb A., Mäkelä P. & Oikari A. 1993. Bioaccumulation of pulp mill effluent-related compounds in aquatic animals. *Sci. Total Environ.* (suppl.): 499-510.

Pellinen J. & Soimasuo R. 1993. Toxicity of sediments polluted by the pulp and paper industry to a midge (Chironomus riparius Meigen). *Sci. Total Environ.* (suppl.): 1247-1256.

Pellinen J., Ruokolainen M., Mäkelä P. & Taskinen J. 1994. Organic halogen compounds, EOX, in mussels from a clean lake and a pulp mill recipient. *Chemosphere* 29 (7): 1515-1526.

Pempkowiak J. 1991. Enrichment factors of heavy metals in the Southern Baltic surface sediments dated with ^{210}Pb and ^{137}Cs. *Environ. Int.*, 17 (5): 421-428.

Perttilä M. & Haahti H. 1986. Chlorinated hydrocarbons in the water and sediments of the sea areas around Finland. *Publications of the Water Research Institute,* National Board of Waters and Environment, Finland, No. 68: 197-200.

Perttilä M., Niemistö L. & Mäkelä K. 1995. Distribution, development and total amounts of nutrients in the Gulf of Finland. *Estuar. Coast. Shelf Sci.* 41: 345-360.

Pesonen M. & Andersson T. 1992. Toxic effects of bleached and unbleached paper mill effluents in primary cultures of rainbow trout hepatocytes. *Ecotoxicol. Environ. Saf.* 24: 63-71.

Pitkänen H. 1994. Eutrophication of the Finnish coastal waters: Origin, fate and effects of riverine nutrient fluxes. PhD Dissertation. *Publications of the Water and Environment Research Institute.* National Board of Waters and the Environment, Finland. No. 18., 45 pp.

Pitkänen H., Tamminen T., Kangas P., Huttula T., Kivi K., Kuosa H., Sarkkula J., Eloheimo K., Kauppila P & Skakalsky B. 1993. Later summer trophic conditions in the north-east Gulf of Finland and the River Neva Estuary, Baltic Sea. *Estuar. Coast. Shelf Sci.* 37: 453-474.

Poutanen E.-L. 1985. Humic and fulvic acids in marine sediments. PhD Dissertation. *Finnish Mar. Res.* 251, 45 pp.

Rantio T. 1992. Chlorocymenes, cymenes and other chlorohydrocarbons in pulp mill effluents, sludges and exposed biota. *Chemosphere* 25 (4): 505-516.

Rao S.S., Burnison B.K., Rokosh D.A. & Taylor C.M. 1994. Mutagenicity and toxicity assessment of pulp mill effluents. *Chemosphere* 28 (10): 1859-1870.

Reemtsma T. & Jekel M. 1996. Potential of ethyl acetate in the determination of extractable organic halogens (EOX) from contaminated soil, sediment, and sewage sludge. *Chemosphere* 32 (5): 815-826.

Remberger M., Allard A.-S. & Neilson A.H. 1986. Biotransformations of chloroguaiacols, chlorocatechlos, and chloroveratroles in sediments. *Appl. Environ. Microbiol.* 51 (3): 552-558.

Remberger M., Hynning P.-Å. & Neilson A.H. 1990. Gas chromatographic analysis and gas chromatographic-mass spectrometric identification of components in the cyclohexane-extractable fraction from contaminated sediment samples. *J. Chromatogr.* 508: 159-178.

Robbins J.A., Krezoski J.R. & Mozley S.C. 1977. Radioactivity in sediments of the Great Lakes: Post-depositional redistribution by deposit-feeding organisms. *Earth Planet. Sci. Lett.* 36: 325-333.

Roots O. 1996. *Toxic chlororganic compounds in the ecosystem of the Baltic Sea.* Eesti Vabariigi Keskkonnaministeerium Info- ja Tehnokeskus, Tallinna Raamatutrükikoda, Tallinn, 144 pp.

Salo A., Tuomainen K. & Voipio A. 1986. Inventories of some long-lived radionuclides in the Baltic Sea. *Sci. Total Environ.* 54: 247-260.

Sandström O. & Thoresson G. 1988. Mortality in perch populations in a Baltic pulp mill effluent area. *Mar. Poll. Bull.* 19 (11): 564-567.

Saunamäki R. 1997. Kohti suljettuja vesikiertoja metsäteollisuudessa. *Kemia-Kemi* 24 (4): 271-276. (In Finnish with English summary).

Song Y. & Müller G. 1993. Freshwater sediments: Sinks and sources of bromine. *Naturwissenschaften* 80 (12): 558-560.

de Sousa F., Strömberg L.M. & Kringstad K.P. 1988. The fate of spent bleach liquor material in receiving waters: characterization of chloroorganics in sediments. *Water Sci. Tech.* 20 (2):153-160.

Stevenson F.J. 1982. *Humus chemistry.* John Wiley & Sons, Inc., New York, 443 pp.

Sundelin B. 1988. Effects of sulphate pulp mill effluents on soft bottom organisms - a microcosm study. *Water Sci. Tech.* 20 (2): 175-177.

Södergren A., Adolfsson-Erici M., Bengtsson, B.-E., Lagergren S., Rahm, L. & Wulff F. 1993. In: Södergren A. (ed.). Bleached pulp mill effluents - composition, fate and effects in the Baltic Sea. *Swedish Environmental Protection Agency Report* 4047., Berlings, Arlöv, pp. 7-120.

Tana J., Rosemarin A., Lehtinen K.-J., Härdig J., Grahn O. & Landner L. 1994. Assessing impacts on Baltic coastal ecosystems with mesocosm and fish biomarker tests: a comparison of new and old wood pulp bleaching techniques. *Sci. Total Environ.*145: 213-234.

Tavendale M.H., Wilkins A.L., Langdon A.G., Mackie K.L., Stuthridge T.M. & McFarlane P.N. 1995. Analytical methodology for the determination of freely available bleached kraft mill effluent-derived organic constituents in recipient sediments. *Environ. Sci. Technol.* 29 (5): 1407-1414.

Vallius H., Kankaanpää H. & Winterhalter B. 1996. Sedimentation basin characteristics in the Gulf of Finland, Baltic Sea. *ICES C.M. 1996/R:7*, ICES Annual Science Conference, 84th Statutory Meeting 27 September to 4 October, 1996, Reykjavik, Iceland. p. 231-232. (mimeogr.)

Vallius H., Kankaanpää H., Niemistö L. & Sandman O. 1997. Sedimentation and within basin variations in the Gulf of Finland as determined by ^{137}Cs tracer. *The Second NKS/EKO-1 Seminar*, Finnish Centre for Radiation and Nuclear Safety, Helsinki, Finland, April 2-3, 1997. 4 pp. (To be published in the Report Series STUK-A).

Vartiainen T., Kiviranta H., Tuomisto J., Kohonen T. & Salonen V.-P. 1997. *Sköldvikin läheisen merialueen PCDD-, PCDF- ja PCB-määrät pohjasedimentissä.* Kansanterveyslaitos ja Turun Yliopisto. 28 pp. (mimeogr., in Finnish with English summary).

Vartiainen T., Liimatainen A. & Kauranen P. 1987. The use of TSK size exclusion columns in determination of the quality and quantity of humus in raw waters and drinking waters. *Sci. Total Environ.* 62: 75-84.

Virkki L. 1993. Structural characterization of chlorolignins by spectroscopic and liquid chromatographic methods and a comparison with humic substances. PhD Dissertation, Department of Chemistry, *University of Jyväskylä Research report* No. 43, 62 pp.

Voipio A. (ed.) 1981. *The Baltic Sea.* Elsevier Scientific Publishing Company, Amsterdam, 418 pp.

Wesén C. 1988. Chemical characterization of chlorinated lignin derivatives in organisms, sediment and air. *Water Sci. Tech.* 20 (2): 185-188.

Wesén C., Carlberg G.E. & Martinsen K. 1990. On the identity of chlorinated organic substances in aquatic organisms and sediments. *Ambio* 19 (1): 36-37.

Wulff F. & Rahm L. 1993. Accumulation of chlorinated organic matter in the Baltic Sea from 50 years of use - A threat to the environment? *Mar. Pollut. Bull.* 26 (5): 272-275.

Wulff F., Rahm L., Jonsson P., Brydsten L. Ahl T. & Granmo Å. 1993. A mass-balance model of chlorinated organic matter for the Baltic Sea - a challenge for ecotoxicology. *Ambio* 22 (1): 27-31.

Wuosmaa A.M. & Hager L.P. 1990. Methyl chloride: A carbocation route for biosynthesis of halometabolites. *Science* 249: 160-162.

Yosie T.F. 1996. The changing landscape of the chlorine debate. *Environ. Sci. Technol.* 30 (11): 498A - 501A.

Appendix 1. List of sampling stations and their main characteristics. STAT = station. SYN = station (in paper VI). SECTOR = sampling area. LAT = latitude (degrees). LON = longitude (degrees). POS = positioning system (or accuracy in m) and co-ordinate system (WGS-84 unless otherwise indicated). D = depth (m). PLATF = platform (MB = motorboat). BOTTOM = sediment core characteristics. PUB = original publication (96 = Kankaanpää 1996, new = unpublished results). MIX = mixing intensity (INT = Intense). S = average dry-matter accumulation rate (g cm^{-2} a^{-1}). v' = average linear accumulation rate (cm a^{-1}). AOX = surface AOX concentration (μg Cl g^{-1} dw). SUM EOX = integrated EOX content in the 1986 - 1994 layer (μg Cl). EOX = surface EOX concentration (μg Cl g^{-1} dw). EOXC = surface C-normalised EOX concentration (μg Cl g^{-1} C). TOC% = total surface carbon (%). N.D. = not determined.

STAT	SYN	SECTOR	LAT	LON	POS	D	DATE	PLATF	BOTTOM	PUB	MIX	S	v'	AOX	SUM EOX	EOX	EOXC	TOC%
KO1		KO IN	60.468	26.975	100 m, KKJ	13	9/93	MB	anoxic mud	III				490		40	600	6.9
KO2		KO IN	60.48	26.965	100 m, KKJ	8	9/93	MB	anoxic mud	III				520		36	490	7.6
KO3		KO IN	60.492	26.936	100 m, KKJ	2	9/93	MB	anoxic clay	III				120		1.4	120	1.2
KO4		KO IN	60.48	26.984	100 m, KKJ	7	9/93	MB	anoxic mud	III				620		15	220	6.8
KO5		KO IN	60.441	26.945	100 m, KKJ	15	9/93	MB	anoxic mud	III				430		21	380	5.4
KO6		KO IN	60.449	26.925	100 m, KKJ	10	9/93	MB	anoxic mud	III				570		32	500	6.5
KO7		KO IN	60.461	26.916	100 m, KKJ	9	9/93	MB	anoxic mud	III				560		37	570	6.5
KO8		KO IN	60.467	26.909	100 m, KKJ	6	9/93	MB	anoxic mud	III				620		60	680	8.8
KO9		KO IN	60.447	26.981	100 m, KKJ	14	9/93	MB	anoxic mud	III				430		24	500	5.4
K1		KO IN	60.4685	26.9728	GPS	12	6/94	MB	anoxic cl. silty mud	V						34.6	430	8.1
K2	I3	KO IN	60.4802	26.9648	GPS	10	6/94	MB	N.D.	V					2820	42.5	410	10.4
K3		KO IN	60.4263	26.94	DGPS	20	6/94	ARANDA	oxic clayey silt	V	INT	0.3	1.42			45.7	560	8.2
K4		KO IN	60.4802	27.0077	GPS	10	6/94	MB	oxic clayey mud	V						27.9	540	5.2
K5		KO IN	60.44	26.9442	GPS	15	6/94	MB	oxic clayey mud	V						31.4	480	6.5
K6		KO IN	60.4643	26.8668	GPS	5	6/94	MB	clayey mud	V						38.2	460	8.3
K7		KO IN	60.4683	26.8878	GPS	6	6/94	MB	anoxic clayey mud	V						51	490	10.4
K8		KO IN	60.4683	26.9087	GPS	5	6/94	MB	anoxic cl. silt / mud	V						49.7	500	9.9
K9	I2	KO IN	60.4502	26.974	DGPS	15	6/94	ARANDA	clayey mud	V	INT	0.3	1.55		4150	64.5	920	7
K10		KO IN	60.4538	26.8235	GPS	9	6/94	MB	clayey sand	V						6.1	160	4
K11		KO IN	60.4303	26.8043	GPS	20	6/94	MB	oxic clayey mud	V						26.4	370	7.1
K12	I6	KO OUT	60.3897	26.7338	DGPS	33	6/94	ARANDA	oxic clayey mud	V	INT	0.18	1.18		1020	13.5	200	6.9
K13	I5	KO OUT	60.4063	26.8125	DGPS	32	6/94	ARANDA	anoxic clayey mud	V	INT	0.12	0.93		850	23.1	340	6.9
K14	I4	KO OUT	60.4052	26.8915	DGPS	27	6/94	ARANDA	oxic sandy mud	V	LOW	0.08	0.31		310	15.6	330	4.7
K15	I9	KO OUT	60.401	26.9548	DGPS	20	6/94	ARANDA	N.D.	V		0.19	1.05		1430	116	460	
K16	I10	KO OUT	60.3802	26.97	DGPS	24	6/94	ARANDA	N.D.	V	INT	0.14	1.3		1100	26.7	270	9.8
K17	I7	KO OUT	60.3737	26.7338	DGPS	39	6/94	ARANDA	ox. clayey mud/sand	V	LOW	0.06	0.31		240	35.5		
K18	I8	KO OUT	60.3508	26.727	DGPS	35	6/94	ARANDA	anoxic clayey mud	V	INT	0.16	1.3		1230	89	700	12.7
K19	I11	KO OUT	60.3298	26.8922	DGPS	40	6/94	ARANDA	N.D.	V		0.1	0.8		700	17	180	9.2
K20	I12	KO OUT	60.3287	27.0232	DGPS	40	6/94	ARANDA	N.D.	V	LOW	0.06	0.43		330	16.7	170	9.7
K21	I13	KO OUT	60.3355	27.1143	DGPS	45	6/94	ARANDA	N.D.	V		0.11	0.68		270	34.9	250	14
K22	I14 (XV1a)	HAAPAS	60.2502	27.248	DGPS	63	5/94	ARANDA	N.D.	V	LOW	0.06	0.56		210	20.8	240	8.5
K23	I15 (XV1b)	HAAPAS	60.2388	27.259	DGPS	62	6/94	ARANDA	N.D.	V		0.15	1.2		400	17.5	160	10.7
K24	I16	AHVENK	60.405	26.4917	GPS	15	6/94	MB	N.D.	V			1.94		5600	28.2	500	5.7
K26		AHVENK	60.3825	26.5138	GPS	12	6/94	MB	N.D.	V						37.6	640	5.8
K27	I1	KO OUT	60.3317	26.5908	DGPS	29	6/94	ARANDA	N.D.	V		0.08	0.56		600	18	250	7.3

Appendix 1. List of sampling stations and their main characteristics. STAT = station. SYN = station (in paper VI). SECTOR = sampling area. LAT = latitude (degrees). LON = longitude (degrees). POS = positioning system (or accuracy in m) and co-ordinate system (WGS-84 unless otherwise indicated). D = depth (m). PLATF = platform (MB = motorboat). BOTTOM = sediment core characteristics. PUB = original publication (96 = Kankaanpää 1996, new = unpublished results). MIX = mixing intensity (INT = Intense). S = average dry-matter accumulation rate (g cm^{-2} a^{-1}). v' = average linear accumulation rate (cm a^{-1}). AOX = surface AOX concentration (µg Cl g^{-1} dw). SUM EOX = integrated EOX content in the 1986 - 1994 layer (µg Cl). EOX = surface EOX concentration (µg Cl g^{-1} dw). EOXC = surface C-normalised EOX concentration (µg Cl g^{-1} C). TOC% = total surface carbon (%). N.D. = not determined.

| STAT	SYN	SECTOR	LAT	LON	POS	D	DATE	PLATF	BOTTOM	PUB	MIX	S	v'	AOX	SUM EOX	EOX	EOXC	TOC%
KY1		KYMI	60.899	26.619	KKJ	1.5	9/94	PIER	oxic mud	V				300		22.5	350	6.5
KY2		KYMI	60.851	26.621	KKJ	1.5	9/94	PIER	oxic clayey mud	V				280		24.8	950	2.6
KY3		KYMI	60.787	26.774	KKJ	1.5	9/94	PIER	oxic clayey mud	V				570		110.5	1290	8.6
KY4		KYMI	60.69	26.828	KKJ	1.5	9/94	MB	ox. cl. mud, sand	V				50		3.2	640	0.5
KY5		KYMI	60.582	26.719	KKJ	1.5	9/94	PIER	ox. cl. mud, sand	V				70		1.4	160	0.2
KY6		KYMI	60.5752	26.57	KKJ.	2	9/94	MB	oxic clayey mud	V				110		0.5	25	1.9
KY7		KYMI	60.5	26.455	KKJ	1.5	9/94	MB	oxic clayey mud	V				160		3.5	65	5.5
S1		SAIMAA	61.236	28.759	GPS	13	7/94	MUIKKU	oxic mud	V				805		126	1340	9.4
S2		SAIMAA	61.198	28.525	GPS	22	7/94	MUIKKU	oxic mud	V				118		102	860	11.8
S3		SAIMAA	61.138	28.375	GPS	10	7/94	MUIKKU	oxic mud	V				119		151	1310	11.5
S4		SAIMAA	61.113	28.319	GPS	9	7/94	MUIKKU	oxic mud	V				580		64	557	11.4
S5		SAIMAA	61.338	28.091	GPS	43	7/94	MUIKKU	oxic mud	V				220		2	23	9.1
V1	I7	VYBORG	60.6705	28.6378	DGPS	14	6/94	ARANDA	clayey mud	V						7.9	130	6.1
V2	I6	VYBORG	60.6485	28.6147	DGPS	10	6/94	ARANDA	oxic clayey mud	V						3.6	70	5.2
V3		VYBORG	60.5427	28.6263	GPS	23	6/94	MB	oxic clayey mud	V						4.9	60	9.3
V4		VYBORG	60.555	28.6485	GPS	6	6/94	MB	clayey mud	V						2.9	35	7.9
V5	I10	VYBORG	60.5502	28.5233	DGPS	22	6/94	ARANDA	oxic clayey mud	V	LOW	0.09	0.8		200	7.6	90	8.6
V6	I9	VYBORG	60.5685	28.5255	DGPS	16	6/94	ARANDA	oxic clayey mud	V						7.9	130	6
V7	I8	VYBORG	60.5924	28.5048	DGPS	14	6/94	ARANDA	oxic clayey mud	V			0.93			3.4	60	5.6
V8	I5	VYBORG	60.5667	28.3712	DGPS	25	6/94	ARANDA	oxic clayey mud	V		0.11	0.43			6.5	90	7.4
V9	I4 (F38)	VYBORG	60.4968	28.4377	DGPS	27	6/94	ARANDA	oxic clayey mud	V	LOW	0.13	0.8			6.7	100	7
V10	I3	VYBORG	60.5118	28.3403	DGPS	31	6/94	ARANDA	oxic clayey mud	V		0.14	1.05			10	100	9.9
V11	I2	VYBORG	60.4522	28.3138	DGPS	40	6/94	ARANDA	anoxic clayey mud	V	INT	0.1	0.93			9.2	100	9.5
V12	I1	VYBORG	60.4688	28.237	DGPS	30	6/94	ARANDA	oxic clayey mud	V		0.08	0.68			9.6	100	8.8
N1		NEVA	59.925	30.233	100 m, KKJ	11	8/93	RADUGA	oxic clayey mud	III						1.7	84	1.9
N2		NEVA	59.9	29.937	100 m, KKJ	4	8/93	RADUGA	sandy	III						0.2	83	0.2
N4		NEVA	59.938	29.683	100 m, KKJ	3	8/93	RADUGA	sandy	III						0.05	25	0.3
N6		NEVA	59.967	29.78	100 m, KKJ	8	8/93	RADUGA	oxic sandy mud	III						1	140	0.7
N7		NEVA	59.987	29.842	100 m, KKJ	5	8/93	RADUGA	oxic clay	III						0.5	23	2.1
N8		NEVA	59.975	29.883	100 m, KKJ	6	8/93	RADUGA	oxic clay	III						1.4	64	2.2
N9		NEVA	59.992	29.995	100 m, KKJ	5	8/93	RADUGA	oxic sand	III						0.7	92	0.8
N11		NEVA	59.953	29.97	100 m, KKJ	4	8/93	RADUGA	sandy	III						0.1	15	0.8
N13		NEVA	59.978	30.088	100 m, KKJ	4	8/93	RADUGA	sandy	III						<0.1	20	0.2
N16		NEVA	59.932	30.13	100 m, KKJ	4	8/93	RADUGA	sand, gravel	III						<0.1	25	0.2

Appendix 1. List of sampling stations and their main characteristics. STAT = station. SYN = station (in paper VI). SECTOR = sampling area. LAT = latitude (degrees). LON = longitude (degrees). POS = positioning system (or accuracy in m) and co-ordinate system (WGS-84 unless otherwise indicated). D = depth (m). PLATF = platform (MB = motorboat). BOTTOM = sediment core characteristics. PUB = original publication (96 = Kankaanpää 1996, new = unpublished results). MIX = mixing intensity (INT = Intense). S = average dry-matter accumulation rate (g cm^{-2} a^{-1}). v′ = average linear accumulation rate (cm a^{-1}). AOX = surface AOX concentration (µg Cl g^{-1} dw). SUM EOX = integrated EOX content in the 1986 - 1994 layer (µg Cl). EOX = surface EOX concentration (µg Cl g^{-1} dw). EOXC = surface C-normalised EOX concentration (µg Cl g^{-1} C). TOC% = total surface carbon (%). N.D. = not determined.

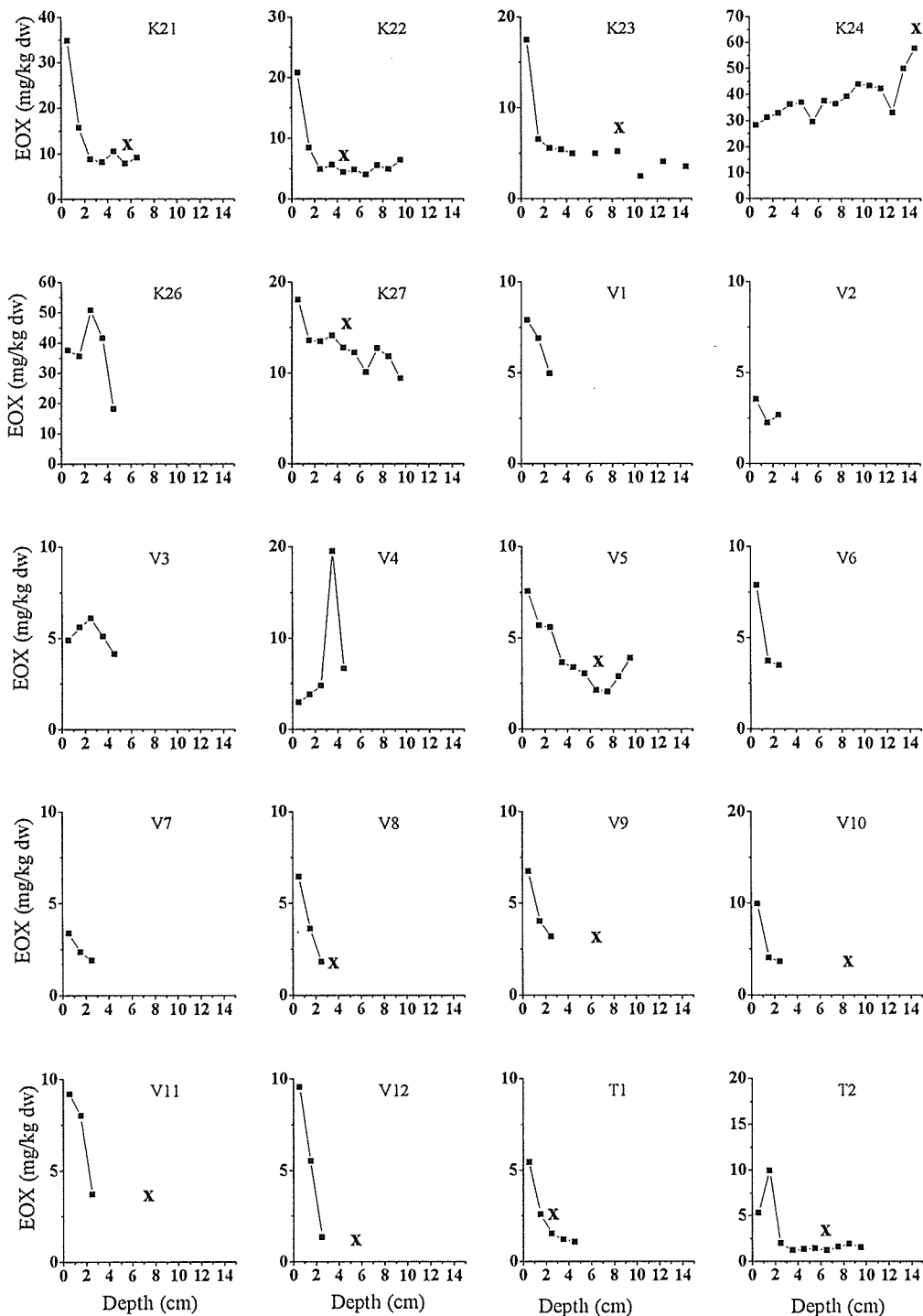| STAT	SYN	SECTOR	LAT	LON	POS	D	DATE	PLATF	BOTTOM	PUB	MIX	S	v′	AOX	SUM EOX	EOX	EOXC	TOC%
KP1	III1	KOPOR	59.9167	28.8333	100	22	8/94	PERSEY	oxic clayey mud	V	LOW		0.42			8	130	6.1
KP2	III2	KOPOR	59.9167	28.75	100	27	8/94	PERSEY	black mud	V	LOW		0.42			13.1	190	7
KP3	III3	KOPOR	59.875	28.5833	100	28	8/94	PERSEY	black mud	V	LOW		0.42			7.6		
L1	III5	LUZHSKA	59.9183	28.1717	100	34	8/94	PERSEY	oxic mud	V	LOW		0.3			5.9	80	7.2
L2	III6	LUZHSKA	59.8967	28.185	100·	30	8/94	PERSEY	oxic mud	V			0.67		150	6.2	90	7
L3	III7	LUZHSKA	59.875	28.1667	100	23	8/94	PERSEY	oxic clayey mud	V			0.91			6	80	7.3
L4	III8	LUZHSKA	59.8	28.1767	100	22	8/94	PERSEY	oxic clayey mud	V	INT		0.91			5.9	80	7.1
GF5	III10	LUZHSKA	59.7585	28.2368	DGPS	24	6/93	ARANDA	N.D.	96		0.1	0.49		130	4.1		
LL12		OPEN	59.487	22.908	DGPS	82	2/93	ARANDA	N.D.	=				180		0.6	15	4.4
F55		OPEN	59.649	25.183	GPS	95	2/93	ARANDA	N.D.	=				150		4.5	100	4.6
F62		OPEN	59.323	23.269	DGPS	94	2/93	ARANDA	N.D.	=				90		0.5	20	3.6
F56		OPEN	59.608	24.354	DGPS	82	2/93	ARANDA	N.D.	=						0.6	20	3.3
GF1	V1	OPEN	59.7048	24.6853	DGPS	84	6/93	ARANDA	N.D.	96		0.11	0.49		170	3.8	60	4.4
LL7		OPEN	59.851	24.832	DGPS	78	2/93	ARANDA	N.D.	=				100		2.2	60	4.4
39A		OPEN	60.07	24.986	DGPS	42	2/93	ARANDA	N.D.	=				80		1	40	2.9
GF2	V2	OPEN	59.8333	25.8598	DGPS	84	6/93	ARANDA	N.D.	96		0.05	0.28			10.1		
LL3A	~V17	OPEN	60.067	26.349	DGPS	67	2/93	ARANDA	N.D.	=	INT			130		4	70	5.4
GF3	V3	OPEN	59.7868	27.1232	DGPS	67	6/93	ARANDA	N.D.	96	INT	0.09	0.49		170	7		
XV-1		HAAPAS	60.252	27.252	DGPS	60	2/93	ARANDA	N.D.	=				80		6	80	7.6
XV-3		OPEN	60.384	27.3	DGPS	40	2/93	ARANDA	N.D.	=				100		4.5	60	8
F42		OPEN	60.133	27.467	DGPS	63	2/93	ARANDA	N.D.	=				90		2	60	3.3
GF4	V4	NARVA	59.5428	27.7682	DGPS	35	6/93	ARANDA	N.D.	96	INT	0.27	0.64		240	4.8		
NAR-4		NARVA	59.55	27.803	DGPS	32	2/93	ARANDA	N.D.	=				50		0.5	25	2.2
SPIR-2		OPEN	60.315	27.988	DGPS	49	2/93	ARANDA	N.D.	=				60		3.4	60	6.1
GF6	V5	OPEN	60.3382	28.0048	DGPS	44	6/93	ARANDA	N.D.	96	INT	0.21	1.33			4.1		
F41		OPEN	60.117	28.071	DGPS	61	4/93	ARANDA	oxic mud	III						4	60	3.9
F38	~V9	VYBORG	60.499	28.432	DGPS	28	2/93	ARANDA	N.D.	III				50		2.2	60	4.3
F40		OPEN	60.063	28.727	DGPS	36	4/93	ARANDA	oxic mud	III						1.8	45	1.7
F40E		NEVA	60.108	29.5	DGPS	22	4/93	ARANDA	oxic mud	III						2.2	115	2.2
J1		IHASALU	59.5857	24.9174	DGPS	82	6/94	ARANDA	clayey mud	V						4.4	120	3.6
J2	IV5	IHASALU	59.5802	24.9612	DGPS	94	6/94	ARANDA	clayey mud	V		0.12	0.43			4	120	3.3
J3		IHASALU	59.5706	25.0079	DGPS	83	6/94	ARANDA	oxic silt and clay	V						2.1	80	2.6
J4	IV1	IHASALU	59.5595	25.0493	DGPS	71	6/94	ARANDA	oxic clayey mud	V		0.09	0.06		110	1.9	80	2.4
J5		IHASALU	59.541	25.047	DGPS	58	6/94	ARANDA	oxic clayey mud	V					110	1.9	80	2.4

Appendix 1. List of sampling stations and their main characteristics. STAT = station. SYN = station (in paper VI). SECTOR = sampling area. LAT = latitude (degrees). LON = longitude (degrees). POS = positioning system (or accuracy in m) and co-ordinate system (WGS-84 unless otherwise indicated). D = depth (m). PLATF = platform (MB = motorboat). BOTTOM = sediment core characteristics. PUB = original publication (96 = Kankaanpää 1996, new = unpublished results). MIX = mixing intensity (INT = Intense). S = average dry-matter accumulation rate (g cm^{-2} a^{-1}). v' = average linear accumulation rate (cm a^{-1}). AOX = surface AOX concentration (µg Cl g^{-1} dw). SUM EOX = integrated EOX content in the 1986 - 1994 layer (µg Cl). EOX = surface EOX concentration (µg Cl g^{-1} dw). EOXC = surface C-normalised EOX concentration (µg Cl g^{-1} C). TOC% = total surface carbon (%). N.D. = not determined.

| STAT	SYN	SECTOR	LAT	LON	POS	D	DATE	PLATF	BOTTOM	PUB	MIX	S	v'	AOX	SUM EOX	EOX	EOXC	TOC%
J6	IV3	IHASALU	59.5265	25.0798	DGPS	43	6/94	ARANDA	oxic clayey mud	√	LOW	0.22	0.31		120	1.6	80	2
J7		IHASALU	59.5121	25.1149	DGPS	33	6/94	ARANDA	silty clay	√						2.7	120	2.2
J8	IV4	IHASALU	59.5055	25.1313	DGPS	26	6/94	ARANDA	sandy silt	√	LOW	0.17	0.31		100	1.2	40	2.3
T1	IV8	TALLINN	59.6253	24.7018	DGPS	10	6/94	ARANDA	clayey mud	√	LOW	0.08	0.31		140	5.5	200	2.7
T2	IV9	TALLINN	59.5818	24.6782	DGPS	94	6/94	ARANDA	clayey mud	√		0.27	0.8		390	5.3	140	3.8
T3	IV12	TALLINN	59.5618	24.7167	DGPS	66	6/94	ARANDA	clayey mud	√		0.07	0.31		110	17.1	310	5.5
T4		TALLINN	59.507	24.7654	DGPS	41	6/94	ARANDA	oxic silty clay	√					180	2.4	110	2.2
T5		TALLINN	59.483	24.7585	DGPS	37	6/94	ARANDA	silty mud and clay	√						2.4	110	2.2
T6g		TALLINN	59.4667	24.7636	DGPS	27	6/94	ARANDA	clayey mud	√						5.6	160	3.6
T7	IV10	TALLINN	59.4633	24.7873	DGPS	24	6/94	ARANDA	clayey silt	√						6.4	220	2.9
KEMI 17/1		BOTHNIA	65.643	24.499	GPS (KKJ)	15	9/90	ARANDA	N.D.	−				590				
KEMI 17/2		BOTHNIA	65.643	24.499	GPS (KKJ)	15	9/90	ARANDA	N.D.	−				520				
RAMP	-	ANTARCT	-72.516	-16.533	GPS	21	2/96	ARANDA	sandy clay, animals	new						0.6		

Appendix 2. Vertical EOX (μg Cl g^{-1} dw) distributions in cores from Kotka area (K1-K27), Vyborg Bay (V1-V12), Tallinn Bay (T1-T7), Ihasalu Bay (J1-J8), Luzhskaya Bight (L1-L4), Koporskaya Bight (KP1-KP3) and other open sea stations GF1-GF6 (Kankaanpää 1996). x = 1986 layer.

2
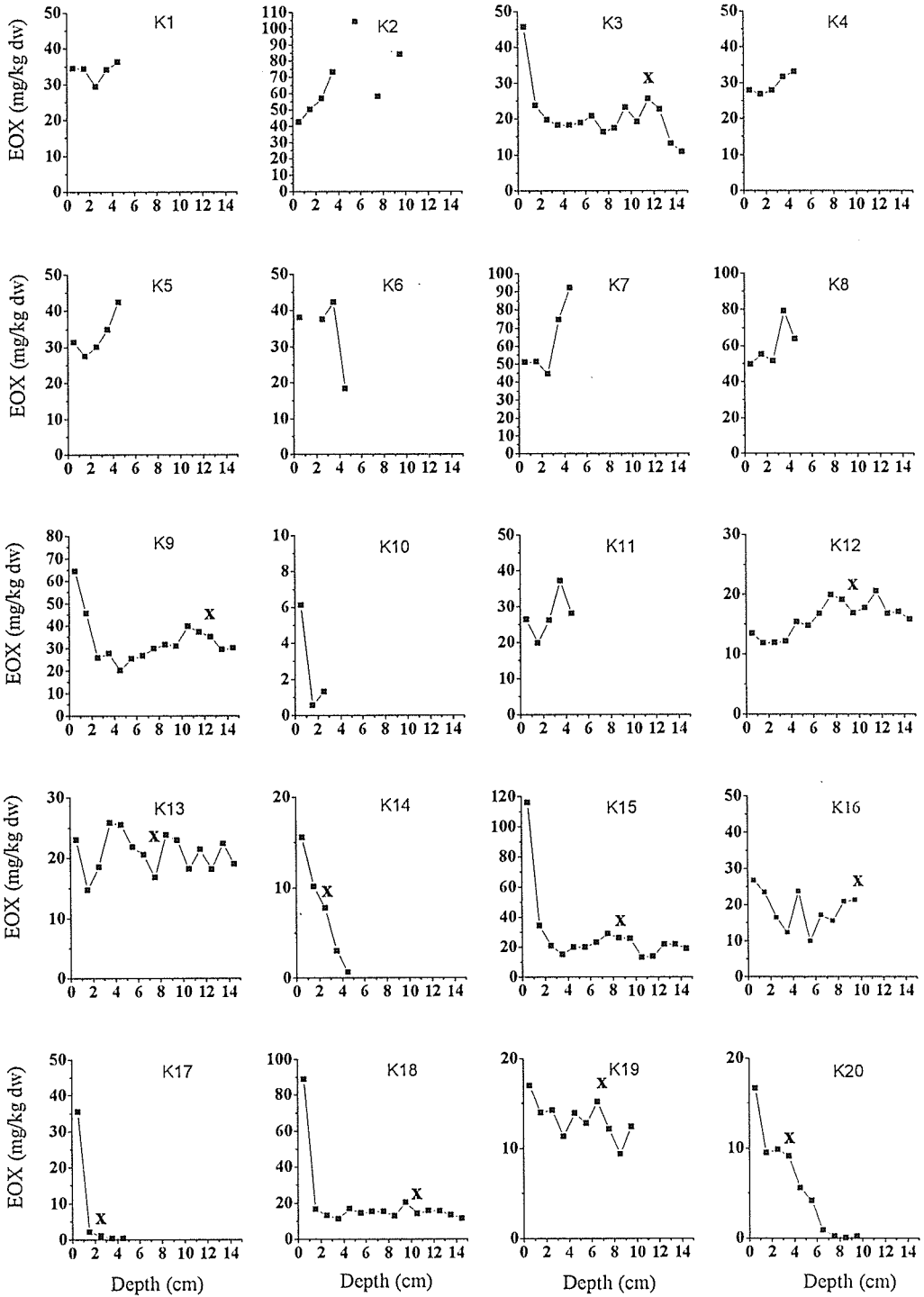
Appendix 2. Vertical EOX (µg Cl g^{-1} dw) distributions in cores from Kotka area (K1-K27), Vyborg Bay (V1-V12), Tallinn Bay (T1-T7), Ihasalu Bay (J1-J8), Luzhskaya Bight (L1-L4), Koporskaya Bight (KP1-KP3) and other open sea stations GF1-GF6 (Kankaanpää 1996). x = 1986 layer.

Appendix 2. Vertical EOX (µg Cl g^{-1} dw) distributions in cores from Kotka area (K1-K27), Vyborg Bay (V1-V12), Tallinn Bay (T1-T7), Ihasalu Bay (J1-J8), Luzhskaya Bight (L1-L4), Koporskaya Bight (KP1-KP3) and other open sea stations GF1-GF6 (Kankaanpää 1996). x = 1986 layer.

4
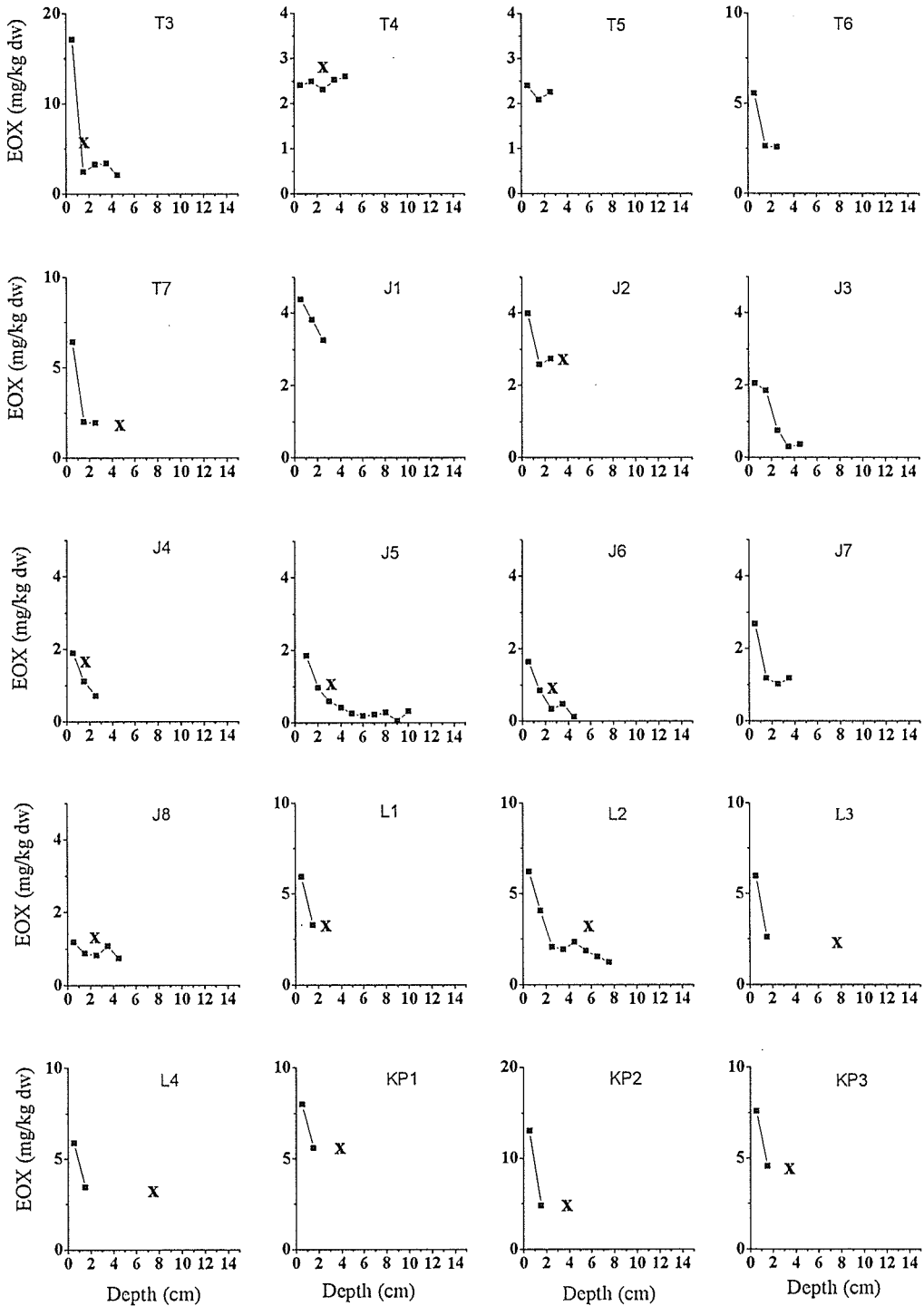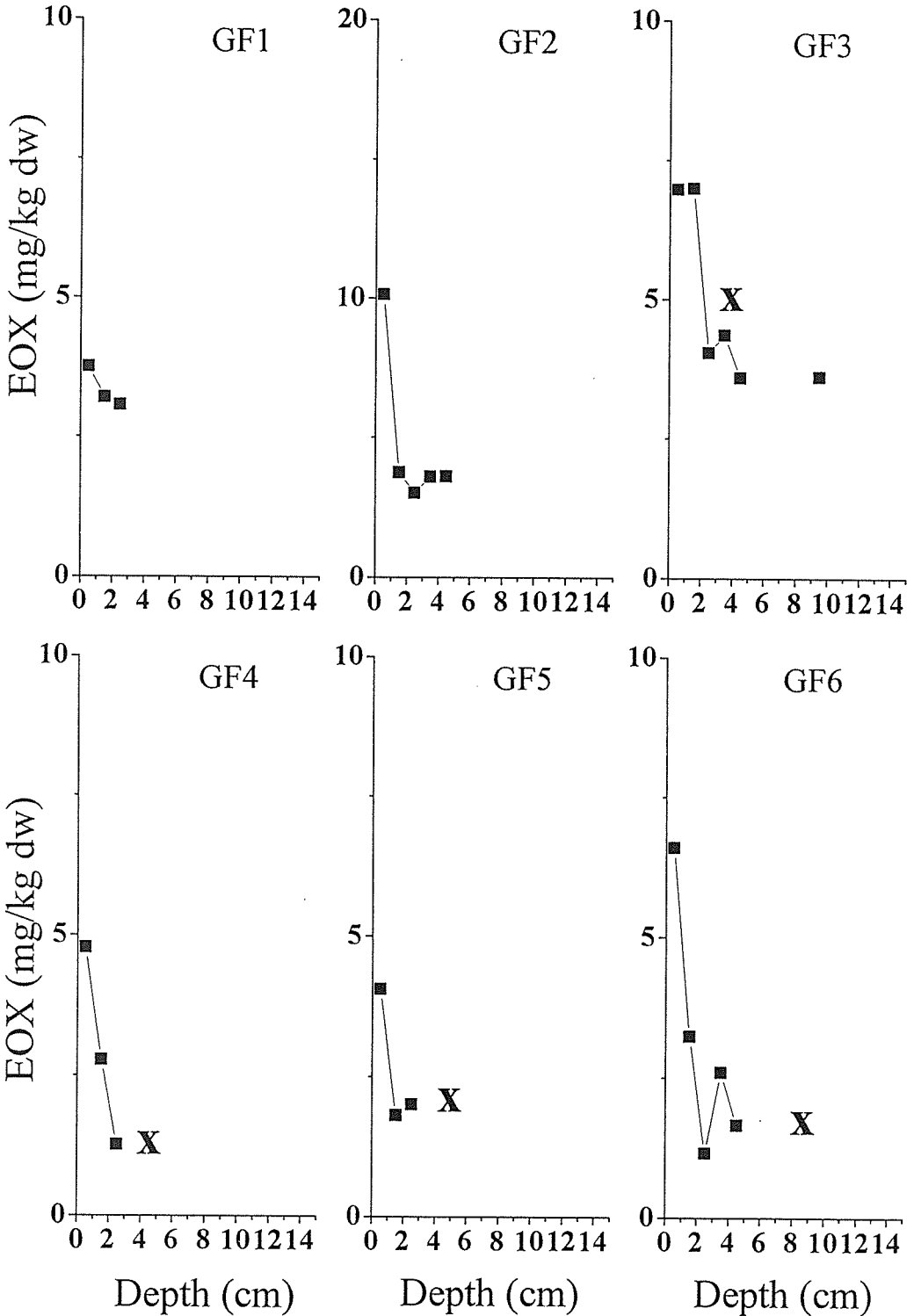
INSTRUCTION FOR AUTHORS

Typing

Use double-spacing and leave generous left-hand margin. All pages must be numbered, and all heading/subheadings must be numbered consistently. Latin species names should appear in *italics* everywhere except in the References. The manuscripts should be written in proper English, language edited, and either English or American spelling should be used consistently throughout the manuscript.

Title, Names

Provide the title in full, author's name, affiliciation, and present address if different from affiliation. If the title is longer than 30 characters provide a short title for use as a running heading.

Abstract

Include an abstract with maximum 150 words.

Acknowledgements

Gather all acknowledgements under one heading before the References.

Footnotes

Avoid using footnotes if possible.

Tables

Number all tables and include a short descriptive title. Vertical lines between columns are not to be used. All tables should be referred to as Table both in the text and in the titles.

Figures

(a) All illustration should be numbered, and submitted on separate sheets. Write your name and the figure number on the back of each figure. Figure captions are to be typed on a separate sheet, not included in the text.

(b) All illustrations should be referred to as Fig. both in the text and in the captions.

(c) Plan your figures for maximum a portrait (upright) A4 page.

(d) All figures should be suitable for reproduction without being redrawn. Check that all lettering will still be legible after the figure is reduced to fit the column or page.

Formulas

Number each equation in parenthesis right adjusted. Distinguish clearly between the letter O and zero (0), between the letter I and one (1), as well as between Greek and Lating letters. Use a full stop for decimals. Vectors are printed in **bold face**.

Units

The SI system is to be used. Abbreviate units only when preceded by a numeral. Indicate the units by negative superscripts (ms^{-1}), not by a division sign (m/s).

References

In the text, reference to other publication should be made using name(s), and year, e.g. Tamminen and Starr (1990) or (Tamminen and Starr 1990). If there are more than two authors use-e.g. Cosby *et al.* (1986). Use suffixes a, b, etc. to distinguish works by the same author in the same year. Only published work, or publications in press, should be included in the References.

Arrange all references in alphabetical and chronological order at the end of the manuscript. Note that the initials follow the name, all names are mentioned. Names of journals and titles of books should be in *italics*. Abbreviate journal names if a common abbreviation is known to you. For the references which are not in English, an English translation should be provided after the title if an official translation exists for the publication. The following examples show the general format to be used.

Books:
Tikkanen T. 1986. *Kasviplanktonopas* (Phytoplankton guide), Gaudeamus, Helsinki, 210 pp (In Finnish).

Journal articles:
Cosby B.J., Hornberger G.M., Frikt D.F. & Galloway J.N. 1986. Modeling the effects of acid deposition: control of long term sulfate dynamics by soil sulfate adsorption. *Water Resour. Res.* 22: 1238–1291.

Book chapters:
Tamminen P. & Starr M. 1990. A survey of forest soil properties related to soil acidification in Southern Finland. In: Kauppi P., Anttila P. & Kenttämies K. (eds.), *Acidification in Finland,* Springer, Berlin, pp. 237–251.

Proofs

The author will receive a set of page proofs which should be returned with corrections to the publisher without delay. A charge may be made for any substantial alterations to the manuscript at this stage.

Charges

No page charges are applied. However, illustration in color must be paid for. Price inquiries should be addressed to the editorial office.

Offprints

We supply 50 offprints free of charge. Additional offprints may be ordered when returning the proofs.