



CONTAMINANTS IN THE BALTIC SEA SEDIMENTS  
Results of the 1993 ICES/HELCOM Sediment Baseline Study

Matti Perttilä (Editor), Horst Albrecht, Rolf Carman, Arne Jensen,  
Per Jonsson, Harri Kankaanpää, Birger Larsen, Mirja Leivuori,  
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# **CONTAMINANTS IN THE BALTIC SEA SEDIMENTS**

## **Results of the 1993 ICES/HELCOM Sediment Baseline Study**

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This report constitutes the description and the main findings of the 1993 ICES/HELCOM Sediment Baseline Study.

This report has been written by the following group:

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### **ABSTRACT**

A baseline study on the concentrations of contaminants in the Baltic Sea surface sediments was carried out in 1993. The study was initiated by the International Council for the Exploration of the Sea as a response to the request by the Helsinki Commission. All subareas of the Baltic Sea were covered. In addition to surface sediment samples for contaminant analyses, sedimentation rates were determined and a mineralogical study as well as a sediment characterization of the sediment cores were carried out.

A recommendation is given on the use of sediment studies in relation to the monitoring of the state of the Baltic Sea.

Keywords: Baltic Sea, sediments, sedimentation, contaminants, mineralogy

## 1. INTRODUCTION

Matti Perttilä, Birger Larsen, Lauri Niemistö & Boris Winterhalter

Marine sediments provide a possibility to assess in a consistent manner the changes in the environment. Not only the present-day distribution of contaminants can be exposed, but also at the same time the depositional history of the sampling site, providing certain hydrochemical and biological conditions are met. The use of biota as a pollution indicator in the Baltic Sea suffers from the drawback that only very few, if any, species are represented in all the subareas in sufficiently large quantities.

The possibility of using sediments as a means of pollution monitoring was widely discussed in the early 1980's within the ICES/SCOR Working Group on the Pollution of the Baltic Sea. An ad hoc Working Group was formed which in close cooperation with the ICES Working Group of the Marine Sediments in Relation to Pollution intersessionally had the task to study the feasibility of such monitoring. An interlaboratory comparison exercise was carried out in order to assess the analytical skills of the different laboratories of the Baltic Sea Region. Only trace elements were included in the exercise. It was concluded that in most of the participating laboratories the analytical work was well established (Brüggmann & Niemistö 1986).

At the same time, the Scientific Technological Committee of the Helsinki Commission was considering the inclusion of monitoring of pollutants in sediments in the Baltic Monitoring Programme. It was agreed that first a review of the existing investigations of contaminants in the Baltic Sea sediments and the relevant methods should be carried out. This review was published as an ICES Cooperative Research Report 180 (Perttilä & Brüggmann 1992). A multitude of interesting investigations was identified. In spite of the results of the afore mentioned interlaboratory exercise, one of the conclusions was that both sampling, positioning and analysis methods of the existing data sets obtained from different laboratories seldom are comparable, mainly because different methods have been used. Consequently it was recommended that a baseline study should be carried out. It was not expected that the baseline study should result in major new information on the distribution of trace metals and other contaminants, but it was intended to produce a reliable set of data which may serve as reference for further studies, and to identify and evaluate the suitability of sediment stations for regional type of trend monitoring of contaminants in the major Baltic basins. With this as a starting point the requirements in regard to procedures and quality assurance of all elements of a reliable sediment monitoring system for all the Baltic Basins has been tested. In this contribution we briefly report the general conduct of the study, review the experiences gained with respect to selection of sampling sites and the necessary quality assurance procedures.

The prevailing opinion has been that in the Baltic Sea there are basins in which the sediments form a final sink for many elements and substances. This concept of course does not imply that all atoms and compounds reaching the bottom remain where they have settled, but, depending on local conditions, a part of the deposited material does. When benthic fauna is absent, the sediments in these basins are often laminated and seasonal changes layer by layer can be recognized. Many of the best examples of such sediments are found in the nearshore basins where shallow ridges and islands effectively shelter the local basin from any disturbances and erosion (e.g. Morris & al. 1988).

The Baltic Sea floor is extremely variable both in topography and in quality (see, e.g. Emelyanov 1988 and ref. therein). The deeper basins often show thick sedimentary packages of soft sediments, as observed by echo soundings. In these basins, stagnant dead bottom periods alternate with nonstagnant periods characterized by a recolonisation of benthic fauna and thus a return of bioturbation. This alternation may govern the vertical sedimentary record, in some cases rendering age determination difficult. Only the deep basins of the Baltic Sea seem to act as final sinks for particles to form continuous packages of layers. The effects of eutrophication have been discussed in detail by e.g. Jonsson & Carman (1994), and by Jonsson (1996).



It appears that sediment deposition varies in time and space in most of the open sea basins shallower than around 60 m, independent of the region of the Baltic Sea (Arkona and Mecklenburg basin in the South, the Gulf of Finland and the Gulf of Bothnia in the North). The observed effects of bioturbation and wave and current induced redeposition of the sediment surface may severely distort the assumed continuous deposition. Such sediments are probably not suitable for ordinary annual monitoring. However, it seems a reasonable assumption that repeated sampling and analysis at prefixed intervals will give information on possible changes in sediment quality.

Recently laminated sediments ranging from a few to some 30-35 laminae on the top of homogenous looking, older sediments have been found in the open Baltic Proper (Jonsson & al. 1990). An explanation for this change of facies has been assumed to be the long stagnation, lasting until 1993 and thereby the increased area of anoxic conditions with no bioturbation caused by benthic macrofauna. Former dynamic bottom areas populated with benthic animals have been transformed into tranquil sedimentation bottom areas where seasonally influenced laminae are formed. The 1993 and 1994 intrusions of saline water have in many areas reversed this development.

In the Gulf of Bothnia the dominant feature is the almost constant erosion of older sediments in depths less than 60-70 m due to crustal uplift which continuously exposes to erosion former areas of sediment deposition to the hydrodynamically active zone. The eroded material is transported towards the deeps. The sediments currently deposited consist of a mixture of very old and presently forming autochthonous material.

In the Gulf of Finland, the recent hydrographic development has been the opposite to the development in the Baltic Proper. The halocline so characteristic at the depth of some 50 m in the western Gulf and at 30 m in the East has been degrading slowly as a consequence of the decreasing salinity (Perttilä & al. 1995). The recent inflows of high-salinity sea water into the Baltic Sea have now ended this development at least temporarily. Several seasonal turnovers of the whole water body have obviously taken place resulting in oxidizing conditions at the sediments surfaces down to 80-85m depth. The benthic fauna has recolonized these areas (Andersin & Sandler 1991). The topmost laminae of the sediments have disappeared probably as a result of bioturbation. Contrast to the Baltic Proper basins, the sedimentation basins in the Gulf of Finland are numerous and a mosaic of small basins is characteristic especially in the Finnish side where the crystalline Pre Cambrian bedrock dominates with rugged forms. On the Estonian side the Cambrian and Ordovician basement has smoothed the ruggy forms and some larger sedimentation basins are found.

In addition to bioturbation and deep-water currents, also the presence of Fe/Mn-micronodules in surface sediments of the oxidised parts of many basins of the Baltic Sea obscures possible contamination by human input of heavy metals. Often, linear relations between Fe- and/or Mn-normalized ratios of heavy metal concentrations are used as contamination indicators. However, the drastic increase of those metals (e.g., Cu, Ni, Zn) in scarcely visible micronodules (less than about 2 mm) must be taken into account. Additionally, these relations are influenced by the diameter of the nodules (redox regime). The Fe/Mn nodules are known to show high trace metal concentrations.

The large areas of nondeposition do not accumulate contaminants. Therefore the maximum concentrations are expected to be small. The metals seem to pass by the nondeposition areas. Some metal concentrations, e.g. zinc, may even represent good background levels of the sediments in general, sometimes including the mineral anomalies. There are some high metal (cadmium) concentrations which indicate that at least temporarily some material may rest on this bottom type, but most probably they are flushed away as soon as suitable conditions occur (Leivuori & Niemistö 1995). Fe/Mn nodules are frequently found in the deep non-depositional areas, and they may act as traps of heavy metals in areas of nondeposition.

### *What is sediment monitoring?*

Sediment monitoring is constituted of a series of repeated measurements of concentrations of contaminants in surface sediments in order to detect changes. The motivation for the monitoring can be a periodic health check of the local benthic environment or it can be used to detect long-term changes in the contaminant discharge fluxes (e.g.  $\text{mg m}^{-2}\text{a}^{-1}$ .) through time “pollution historical records”. The first requirement is that the chemical determination has the detection limits and the stability through time to produce comparable and significant results.

The trend monitoring of contaminants in sediments can be based on at least two different methods; either a statistic evaluation of many samples or the development of the pollutant concentrations in few stations in areas of constant sediment accumulation. The first is based on a statistical comparison of a large number of determinations made on bottom samples from the same general area through the time. This is useful where the sediments are moving about frequently and where the areal variations at one time in concentrations in metal and other contaminants to a large extent is governed by variation in grainsize and associated mineralogical composition and organic contents. Measurements on the fine grained component in the mostly sandy sediments in the North Sea and especially in the German Bight is an example of this approach (reference).

The second approach – selected for the Baltic Baseline investigation – is based on one or few representative stations. It is assumed that the sediment type and the sedimentation rate ( $\text{mma}^{-1}$ ) is reasonably stable through time. For health check it is sufficient to know that the monitored sediments are comparable. In trend monitoring it is important to know the time interval represented by the individual samples.

The response to a given change in flux of a substance measured as change in concentrations of a surface sample (say 0-1 cm) of a sediment monitoring station is according to (Larsen & Jensen 1989) a function of:

- the accumulation rate of the sediment,
- intensity of mixing and thickness of involved layer (bioturbation),
- the thickness of sample slice and time between samplings and the chemical reproducibility. The two first factor can be assessed using Pb210 see below, the last is technical choices. An essential factor for the representability of the samples is that the spacial variability is low compared with the precision obtainable in refinding the sampling station.

The Sediment Baseline Study was planned and organized within the ICES Working Group on Baltic Marine Environment. In this contribution, we report the general conduct of the study, give a list of the selected sedimentation sites, together with a preliminary characterization of the sites and approximate sedimentation rates, and trace element distribution in the surface sediments.

In this report we give the description of the cruise and the main findings and conclusions (Chapter 2), together with more detailed contributions on the different parameters in the later chapters.

The pictures describing the spatial distribution of substances have been drawn with the aid of the DAS program (Sokolov & al. 1997), available at the www site of Stockholm University, Department of Systems Ecology.

## 2. THE 1993 HELCOM/ICES BALTIC SEA SEDIMENT BASELINE STUDY

### – conduct of the study and conclusions –

Matti Perttilä, Per Jonsson, Birger Larsen, Lauri Niemistö, Boris Winterhalter & Walter Axelsson

### 2.1 THE CRUISE

The expedition was carried out on board the R/V Aranda in June-July 1993, covering the whole Baltic Sea (Fig. 2.1). Differential GPS was used for the positioning, with an accuracy of  $\pm 20\text{m}$  or better.

The initial selection of the sampling areas in each of the major Baltic basins was based on previous marine geological and chemical experience.

The cruise itinerary and the approximate location of the stations are displayed in Fig. 2.1.

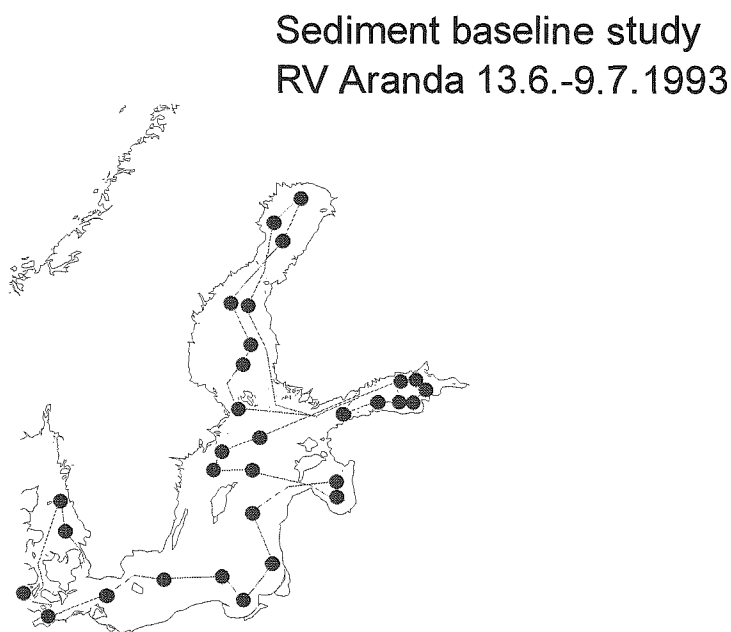


Fig. 2.1.

### 2.2 SELECTION OF THE SAMPLING POSITIONS

At each pre-selected site, a grid was run in order to facilitate the selection of the exact position for sampling. 100 KHz echo sounding equipment was used for the inspection of the bottom topography. Depth measurements by the echo sounding were combined with the ship's navigation data, and at each station, a three dimensional picture of the bottom was made. Promising areas were selected from the bathymetric data. However, the stratigraphy of the bottom sediment bed cannot be deduced only from the topography. The areas were also surveyed using low-frequency (12 or 15 KHz) echo sounders that in addition to the water depth also give information on the sediment stratigraphy. Thus the thickness of the soft-sediment layer can be measured and used for the selection of the most suitable site. To a certain extent, also other qualities of the sediment bed could be deduced from the low-frequency echogram; e.g. the occurrence of gas, which may have mixed up the sediment layer or will mix the sample when taken on board.

In areas of less than 200m of depth, the possibility of mechanical disturbance of the bottom, caused by e.g. bottom trawling for fishery purposes, was also checked before sampling. This was carried out by

means of side-scan sonar. For details, the sediment surface was inspected with a video camera system provided and run by Ingemar Cato, and in some cases by a sediment camera (Per Jonsson) giving a picture of the uppermost 20cm. The final selection of the sampling site was done by means of an evaluation of all these sources of information.

Exact positioning was ensured by the Differential Global Positioning System, DGPS. Bruun & Kankaanpää (1996) have shown the ship to be able to hold its position accurately within  $\pm 20\text{m}$  over a prolonged period of time.

### 2.3 SAMPLING AND SAMPLE PRETREATMENT

The sediment samples were taken with the double corer (the Gemini designed by Lauri Niemistö) internal diameter 80mm, providing two cores of length ca 30-50 cm. Sediment type, layering, bioturbation structures etc. was described on one core onboard and later by X-ray photos using a special rectangular corer (Axelsson, unpublished results). Several cores were taken on each station and immediately cut into 1cm thick slices and deep frozen. Samples for mineralogical studies were kept at  $+4^{\circ}\text{C}$ .

In most cases they were later freeze-dried and distributed for chemical and other analysis to the participating laboratories. Redox potential and  $^{137}\text{Cs}$  activity were measured on board the ship.

Strict quality control measures were applied throughout the sampling (see, e.g. Pertilä & Pedersen 1995, Pertilä & Albrecht 1996).

### 2.4 CHEMICAL ANALYSES AND QUALITY CONTROL

The objective was to provide a baseline study, which should provide a reliable set of data which may serve as reference for future studies. Consequently considerable effort was put into producing a comprehensive quality assurance plan including objectives and data quality, site selection criteria, sampling procedures for each major measurement including subsampling, storage procedures and a plan for laboratory quality control checks. Each step of the procedures was duly documented in order to provide a possibility for tracing the results both in time and quality. It was decided that analysis should be carried out by few expert laboratories with formal accreditation and/or quality assurance systems checked by external intercomparisons. It was also decided to determine total metal contents (total digestion), because partial leaching fractions is not well defined. The following parameters were determined: Inorganic constituents: Al, Li, As, Cd, Cr, Cu, Hg Ni, Pb, Ti, V, Zn, Fe, Mn and in some cores also Ag and Co. Organic compounds: PCBs, PAHs, PBDEs, DDTs, EOCi, EPOCi, EOBr, EPOBr and EOX. Supporting parameters: C, N, P, TC, TOC (S, LOI), watercontent. Dating: Cs-137 and Pb-210. Grain size and mineralogical composition was determined on selected samples.

The two laboratories involved in the metal analyses, the Bundesamt für Seeschifffahrt und Hydrographie (BSH) and the Finnish Institute of Marine Research (FIMR), had produced very compatible results. Both laboratories had participated in the EU/QUASIMEME quality assurance programme. The nutrient data come from three sources; the Stockholm University (Department of Geology and Geophysics), BSH, and the FIMR. PCBs and PAHs were analysed by the Stockholm University (Department of Zoology). EOCi, EPOCi, EOBr and EPOBr were analyzed by SINTEF, Oslo. AOX and EOX were analysed by FIMR. The screening data from one sediment sample from the Baltic proper have been obtained from various laboratories, mainly the Swedish Environmental Protection Agency (at present ITM, Stockholm university). EOX was analysed by FIMR.

X-ray photographs of the cores were taken on board immediately after the sampling by Valter Axelsson with equipment provided by him, as well as the redox measurements (by FIMR personnel).

The mineralogical and grain size analyses have been carried out at the Polish Geological Institute (Branch of Marine Geology).

Quality assurance is the total system of activities required to guarantee the appropriate quality of the product and is therefore an integrated part of all sampling programs and analytical methods. The

sample to be analyzed has to be taken adequately, otherwise all efforts in the laboratory for good quality control are futile, since the obtained analytical result, however accurate, does not represent the concentration at the sampling site. This principle was stringently observed during the entire exercise.

## 2.5 AGE DETERMINATION

The  $^{210}\text{Pb}$  analyses, and sediment age determination based on these, were carried out by the Danish Water Quality Institute. It appears that in several cases, especially in the northern parts of the Baltic Sea, the stations covered during the Baseline Study yielded excellent dating by means of  $^{210}\text{Pb}$ . However, in the central areas, notably the eastern and western Gotland Deep areas, a very disturbed  $^{210}\text{Pb}$  distribution was obtained.

The interpretation of  $^{210}\text{Pb}$  profiles provide a mass accumulation rate ( $\text{gm}^{-2}\text{a}^{-1}$ ) and for the uppermost 2 cm a linear accumulation rate ( $\text{mm/yr.}$ ) and an indication of the mixing depth and intensity. Using the CRS (Constant Rate of Supply of unsupported  $^{210}\text{Pb}$ ) model a estimate of the age with depth in the sediment core is provided (Chapter 7). In cores, with intensive mixing to depths covering 10 years or more of deposition, the age of the sediment in the individual slices was not well defined, even when the mass accumulation rate was reasonably well known from the modelling of the  $^{210}\text{Pb}$  profile.

During the cruise, samples were taken also for  $^{137}\text{Cs}$  measurements, parallel to the samples intended for chemical analysis and  $^{210}\text{Pb}$  determinations. The  $^{137}\text{Cs}$  activity can be followed down in the sediment core. At most of the stations of the Sediment Baseline Study, the topmost sediment layers showed high activity, with a peak at the depth of 3-10 cm. In sediment layers below the peak, the  $^{137}\text{Cs}$  activity decreased rapidly (Kyzyurov & al. 1994). It can be assumed (Perttilä & Niemistö 1993) that the sediment layer with the activity peak corresponds to the immediate Chernobyl fallout in 1986, giving thus a rough estimate of the net sedimentation rate.

In many of the cores sampled from the Baltic proper and Gulf of Finland clearly visible lamination was found in the upper parts of the cores.  $^{210}\text{Pb}$  dating showed to be inaccurate in this type of sediment. However, comparison between  $^{137}\text{Cs}$  profiles and varve counting obtained from photographs and x-ray images generally showed good concordance, thus confirming earlier findings that the lamination generally is annual (Morris & al. 1988, Jonsson & al. 1990, Jonsson 1992). Since these laminated sediments provided high vertical time resolution in the cores, they are advisable for future monitoring purposes.

## 2.6 CHARACTERIZATION OF THE SEDIMENTATION BASINS

The sampling localities for the baseline study were deliberately chosen in an attempt to represent the main sedimentary basins of the Baltic Sea. Furthermore, only large uniform basins were chosen to maximize the possibility to acquire representative samples for environmental studies and possible annual monitoring. Thus the sites were chosen on the basis of former knowledge of the extent and quality of the basins. This site screening had the tendency to favour large deep water basins, thus effectively emphasizing fine-grained sediments. This naturally also had an effect on the mineralogical composition.

Anoxic conditions generally prevail within the recent basin sediments due to the oxydation of organic matter. In basins where temporary anoxia prevails in the bottom near waters even the sediment surface is reducing. Most of the silicate minerals being deposited in the basins are resistant, however, e.g. ferrous and manganous oxyhydroxides are dissolved. In the reducing environment several authigenic minerals are formed, including pyrite and manganous carbonate (kutnahorite).

X-ray radiography of sediment cores is a fast, non-destructive scanning and recording technique, which facilitates the calculation of sediment accumulation and simplifies the determination of sedimentary properties. The radiographs provide permanent records of the internal structure of sampled sediment cores and thus represent valuable documents for future studies of growing sedimentary sequences. They may therefore be used for monitoring environmental changes.

The character and activity level of physical, chemical, and biological processes regulate the deposition and redistribution of sediment and thereby also the composition and structural organization of the sedimentary sequence. The vertical sequence of sedimentary structures reflects variation in processes and rates of sedimentation with time. Often the sequence consist of a combination of cyclic and event types of stratification. Continuous, growing sedimentary sequences of cyclic type are normally found in low-energy environments. Time gaps in the sedimentary sequence due to erosion characterize high-energy environments, where storm deposits are formed.

The erosion and resuspension of sediment along shallow and steep parts of a basin may be rather considerable in connection with heavy storms. This reworking of the sediment, which results in accumulation of greater amounts of sediment in the deeper part of a basin, is favoured by the land uplift and is therefore of special importance in the Gulf of Bothnia.

### *Granulometry*

As anticipated the bulk of the sediment samples were in the clayey and silty size range. The proximity to wave and current influenced high energy areas, as e.g. sandy coastal stretches and shoals and banks of limited water depth have a definite effect on the grain size distribution of the recent sediments. Furthermore the basins are limited in size. This is especially true for the southern Baltic Sea where silty and even sandy sediments abound.

The sampling locations in the central and northern Baltic Sea are separated from land based sources by rather deep stretches of water that act as traps for terrigenous components of larger grain size. Thus, the low energy regime of the deep basins, i.e. weak currents and lack of wave erosion and augmented by density stratification in the water column are the main reasons for the prevalence of clay and to some extent silt sized fractions in the studied sediment samples.

The high concentration of very fine-grained sediment in the deep basins of the northern Baltic Sea can be attributed to the provenance of vast areas of late and post glacial sediments exposed to erosional forces due to crustal uplift. This resuspended material constitutes an important source of material taking part in present day sediment accumulation.

### *Mineralogy*

The mineralogical composition of the sediment portrays the geology of the source region. Thus sediments derived from riverine input will ultimately contain terrigenous minerals, including quartz, feldspars and even kaolinite and calcite/dolomite. However, most of the samples from the Baltic Sea, consisting mainly of redeposited, glacially derived sediments, contain in addition to varying amounts of quartz and feldspar also abundant clay minerals like illite and chlorites. The variations in mineral composition reflect not only the composition of the source material but also the mechanism of sediment transport. The fine-grained "flaky" clay minerals were during the Baltic fresh water phases easily transported in suspension and often deposited very far from the source. Thus, especially in the north central Baltic Sea the erosion, transport and deposition of formerly deposited seabed sediments exposed to erosional forces due to crustal uplift contribute substantially to the accumulation of material in the deep basins.

Although carbonates (calcite) from shells can often be a major mineral constituent in shallow marine sediments, shell fragments occur only sporadically in the soft clayey deep basin sediments. Opal derived from diatoms is also found in the sediments although quartz makes up the bulk of the silica. Although the production of biogenic carbonate and silica can be considerable the open sea conditions in the Baltic Sea are not really conducive to the preservation of these minerals.

The formation and preservation of other authigenic minerals is also highly dependent on the environmental conditions both in the water column and in the pore waters of the sediments. The suite of minerals forming as a result of diagenesis reflect variations in the physicochemical (environmental) conditions prevailing in the bottom-near water and the sediment itself. Minerals like pyrite (incl. hydrotroilite), kutnahorite (incl. rhodocrosite), vivianite, etc. are specific of anoxic conditions while

goethite and crypto crystalline manganous manganite are typically formed in an oxic environment. It should be pointed out that the latter minerals will disintegrate in the anoxic conditions prevailing within the sediment with a high content of organic matter.

The mineralogical composition of the sediments was studied at the Institute of Marine Geology in Sopot, Poland. The main constituents and especially the silicate minerals could be reliably identified. However, the use of standard sample treatment for X-ray diffraction measurements involving the exposure of the samples to atmospheric oxidation is probably the main reason for the occurrence of such minerals as gypsum and anhydrite. Also the co-occurrence of pyrite and goethite may be due to oxidation during sample preparation.

### *Station descriptions*

The content of unsupported  $^{210}\text{Pb}$  (that is  $^{210}\text{Pb}$  not produced in the sediment) decreases regularly downwards in undisturbed and steadily deposited sediment due to radioactive decay. Departure from this predictable profile permits an assessment of the mixing and/or intermittent erosion as well as the rate of deposition. This provides an estimate of the sensitivity of the sediment station (Larsen & Jensen 1989). As a supplement the  $^{137}\text{Cs}$  profile and X-ray pictures of the sedimentary structures, has been used for an estimate of the expected response of on a change of the flux of a persistent contaminant. Of the 25 stations investigated 4 was so disturbed, that no dating or estimate of accumulation rates was possible. Core stations with high accumulation rates ( $4.5\text{-}15\text{ mma}^{-1}$ ) and/or low mixing by bioturbation, which is excellent for dating and trend monitoring purposes were identified in the Gdansk Basin (169), near the Lithuanian coast (170), in the Gulf of Riga (172, 175), two stations in the Gulf of Finland (187, 185) and 3 in the Bothnian Sea and Gulf (190, 192, 195). the sediment stations. Most of the other stations have accumulation rates at  $1.5\text{-}2.5\text{ mma}^{-1}$  or  $250\text{-}500\text{ gm}^{-2}\text{a}^{-1}$  and with mixing of the upper 2-4 cm. Assuming a sampling of the uppermost 1 cm every 5 years, and steady state in relation to net accumulation rate and mixing rate, and a 10% relative standard deviation for chemical analysis, the sensitivity analysis indicates that we expect to be able to detect changes in flux of a contaminant in the order of 10-15% (in the 5 years) in the excellent stations. 60-200% change is needed to cause a significant change in concentrations in the other stations. In the deep western and eastern Gotland deep- a 7-10 cm layer of fluffy very water rich material was seen on top. The fluffy stuff contains relatively high concentrations of  $^{210}\text{Pb}$  and high but variable  $^{137}\text{Cs}$  contents. Both the  $^{210}\text{Pb}$  and the distribution of metals suggests that some section is missing below the the fluffy layer. The disturbed  $^{210}\text{Pb}$  profiles do not permit a dating. Niemistö has seen the fluffy stuff at F-81 in 1992-before the inflow (pers. comm.) The fluffy layer could be the result of a disturbance (slides) before the inflow of new bottom water in 1993, in a period where the stability of the water column according to Fonselius was very low. Per Jonsson and Valter Axelsson have based on the lamination and the distribution of organic pollutants suggested that in station F81 (171) in the E Gotland deep the linear sedimentation rate of the fluffy top layer is very high ca 15 mm 1990-1992 but the mass accumulation is only  $310\text{ gm}^{-2}\text{a}^{-1}$ . and also that the laminated sediments at the West Gotland station 1978 could be used for monitoring- this has to be verified.

The following characteristics have been used for the description of the cores:

1. General description of the sedimentary basin in relation to the area of the Baltic Sea.
2. The sediment package as seen with the echo sounder.
3. Description of the sediment core and the x-ray analysis.
4.  $^{210}\text{Pb}$  dating and relation to  $^{137}\text{Cs}$  depth.

In addition a remark of the characteristics and the representability of the sampled station with respect to future monitoring. The detailed characterization of the visited stations and cores was carried out by Birger Larsen.

*Remarks based on the X-ray studies of the cores*

Gaps in X-ray intensity due to erosion characterizes especially the core 155 from the southeastern part of Kattegatt and probably to some extent also several of the cores from the southern Baltic as well as core 183 (GF4) from the Gulf of Finland. The content of Fe-Mn-rich flat concretions and spherical nodules in the sedimentary sequence is high in the cores from the Bothnian Bay. The geochemistry and the occurrence of these ferromanganese concretions is described by Ingri (1985).

The concretion sequences may be caused by a succession of events or by gradual periodic changes (minor cycles or periodites). In shallow water repeated reworking and redeposition of sediments obliterate primary sedimentary structures. In deep water the sediments can be completely mixed by bioturbation if the rate of sediment accumulation is low. Annually laminated modern deposits reflecting seasonal variations in sedimentation rate as well as in composition of settled particles are therefore most likely to be found in low-energy environments, where the rate of sediment accumulation is high or where the bottom water permanently or periodically is anoxic. This has been and is still the case in parts of the Baltic Sea, especially in several coastal bays, where the annual nature of modern, laminated bottom deposits has been documented by X-raying of sediment cores, collected from selected locations during different seasons and different years.

Modern, laminated deposits have also been found in several of the larger deep basins of the Baltic sea as further discussed by e.g. Jonsson & al. (1990). The topmost sedimentary sequence in cores 176 (Fårö Deep), 179 (Landsort Deep), and 180 (LL 19), with a number of thin couplets on top of a dense network of tube burrows, seems to characterize large bottom areas in the northwestern part of the Baltic Proper. In general the density contrast between the upper, laminated and the lower, bioturbated part is considerable.

The hardness index is used to compare the density of the upper part of the X-rayed sediment cores. The rather high values of the hardness index in cores K1 from the Kattegatt and GF4 from the Gulf of Finland indicate a rather high dynamic activity in the bottom water at these sampling stations. Due to the flocculated nature of the uppermost part the core from the East Gotland Deep, core 171, had the lowest hardness index of these cores. However, the gas-rich core LL 19 (180) from the northernmost part of the Baltic Proper had a lower accumulated amount of solids in the upper 20 cm than core 171. The void ratio is very high in the upper, underconsolidated parts of these two cores. Deposits with such high void ratios may be eroded by very weak currents.



Table 2.1. Station position list (originally on Finnish coordinate system KKJ, transferred later in the international coordinate system WGS94).

Station	Latitude	longitude	depth
155 KATT1	56 26,57	11 38,02	28
156 KATT2	57 17,57	11 28,59	75
157 KIELBIGHT	54 44,30	10 10,54	23
158 KIELBIGHT2	54 43,23	10 13,05	24
159 MECKLENBURG	54 19,03	11 32,57	27
160 LÜBECKBAY	54 04,59	11 10,00	22
161 LÜBECKBAY2	54 07,00	11 10,00	23
162 ARKONA-1	54 58,32	13 42,33	50
163 ARKONA-2	55 01,27	13 47,43	47
164 ARKONA-3	54 58,50	13 47,21	42
165 ARKONA-4	55 01,45	13 42,47	42
166 ARKONA(BY2)	54 59,97	13 45,01	45
167 BORNHOLM	55 15,29	15 57,56	90
168 BCSIII-10	55 32,53	18 23,48	89
169 GDANSKBAY	54 55,00	19 14,44	107
170 LITHUANCOAST	55 34,59	20 29,47	68
171 GOTLAND(F81)	57 18,28	20 03,33	240
172 RIGABAY-1	57 31,14	23 13,14	45
173 RIGABAY-2	57 30,20	23 14,07	44
174 RIGABAY-4	57 28,58	23 13,18	62
175 RIGABAY-3	57 40,50	23 36,06	54
176 FARODEEP	58 05,44	19 50,57	183
177 FARODEEP-2	58 06,01	19 47,07	155
178 WGOTDEEP	58 10,59	18 09,11	145
179 LANDSORTBAS	58 37,50	18 31,59	215
180 LL19	58 50,57	20 13,05	200
181 GF-1	59 42,29	24 41,512	84
182 GF-2	59 50,30	25 51,59	84
183 GF-4	59 32,57	27 46,09	35
184 GF-5	59 45,51	28 14,21	24
185 GF-6	60 20,29	28 00,29	44
186 GF-3	59 47,21	27 07,39	67
187 XV-1	60 14,16	27 15,29	61
188 LL-7	59 50,57	24 49,58	77
189 Åland Sea	60 01,18	19 32,48	214
190 EB-1	60 59,21	19 43,59	130
191 EB-2	61 18,51	20 07,36	130
192 Harnosand	62 39,02	18 59,56	200
193 BO-3	64 18,50	22 19,14	110
194 F-9	64 41,26	22 02,57	137
195 F-2X	64 58,28	23 23,20	100
196 US-5B	62 35,13	19 58,28	210

## 2.7 SUMMARY AND CONCLUSIONS

The contaminant concentrations in the sediments are often controlled also by other factors than direct inputs. The sediments are chemically and sometimes also biologically very active. Post-depositional changes result in the formation of authigenic mineral phases which, together with changes in the redox regime, lead in changes in the metal chemistry and mobility within the sediments. Hydrochemistry of the bottom-near water layer also affects the contaminant chemistry on the sediment surface. Changes in

long-term wind pattern may also result in drastic changes in the sedimentation rate, rendering difficult the evaluation of the chemical results. The signal from changes in inputs may thus be completely obscured by other factors.

Eutrophication of the Baltic Sea inevitably increases the sedimentation of organic matter, thus increasing the sedimentation of contaminants, bound to the sedimenting carbon either chemically or by adsorption. Sedimentation itself is also affected by weather conditions. During high storm frequency, mixing of the water masses seems to enhance the aggregation of the particulate matter and increase sedimentation. Also the more high-energy conditions close to the erosion and transportation bottoms during years characterised by high storm frequency increase resuspension and erosion processes and are manifested in depositional areas by substantially increased deposition. In cases of long-period water movements, the saline water inflows being an example, the sediment surface can be swept over large areas and the detached soft fluffy material is resedimented elsewhere. This is what probably happened in the Eastern Gotland Basin 1-2 years before the 1993 Baseline Study and is the reason for the anomalous structure of the Gotland Deep sample, described above. These events coincided in time well with high storm frequency registered at Gotska Sandön lighthouse during 1991 and 1992 (data from SMHI). In consequence of the various factors affecting both transport and sedimentation of particulate material, as well as sediment chemistry, development of the eutrophication status and the documentation on general oceanographic events should be available when interpreting sediment results.

In spite of the several obscuring factors the surveillance of contaminant concentrations in sediments gives valuable, indeed essential information. For years the chemical monitoring of water and biota has been continued without consideration of the full cycling of materials in the marine environment. Especially in the Baltic Sea, with its limited water exchange, the role of the sediments should not be overlooked. Several investigations (e.g. Wulff & al. 1993 concerning chlorinated compounds; Borg & Jonsson 1996 concerning metals) have shown that the sediments constitute the major store/sink of contaminants in the Baltic Sea. Depending on the hydrochemical factors in the water and the conditions within the sediments, the sediments may act either as sinks or sources of materials. Due to the large bulk of contaminants in the sediments even small changes in the sediment store may cause substantial changes in water and biota. Thus the understanding of factors controlling the sediment/water fluxes of contaminants/nutrients is crucial for a realistic interpretation of the monitoring results.

While the purpose of monitoring is to give a description of the current situation, and this picture is in part given in the sediment surface, the understanding of the changes in the concentrations and the controlling factors deeper down in the sediment core must be included in the monitoring programme for a correct interpretation of the sediment surface results. Thus, in addition to the chemical analysis of the core, also an evaluation of the sedimentation activity should be included in the programme. Several methods exist for this purpose, including the  $^{210}\text{Pb}$  method, X-ray and lamination study, and the use of the  $^{137}\text{Cs}$  profiles.

The trace element concentrations (Chapter 4) in the surface samples feature high concentrations of Cd, Cu, Zn, Ag, Ni, and Co in the central deep basins, and the very high concentration of As in the Bothnian Bay. For Pb, Cd and Hg apparently anthropogenically influenced distribution patterns were found in the deep basins, with high concentrations in the Western Baltic and Gdansk Bay, in the eastern part of the Gulf of Finland and in the Bothnian Bay, but not for lead. The baseline study include also localities which previously were difficult to access by western research: The Gulf of Riga, offshore Lithuania and the Gulf of Finland. These areas are contaminated to some degree, however, generally the trace element concentrations are not particularly high relative to other areas of the Baltic. The overall levels of the trace element concentrations in the Baltic Sea sediments seem to be attributed to the degree of pollution of the area, but the history of the pollution as reflected in the vertical profiles is complicated by the controlling processes, most important of which is probably the variability of the oxygen conditions, and hence the redox potential, in the sediment core. The variability of the redox potential may be due to the variability of the redox potential in the overlaying water mass as a consequence of the hydrographic events like stagnation or inflow periods, or due to the diagenetic processes leading to oxygen deficiency.

Analysis of organic compounds (Chapter 6) shows for PCBs and PAHs an even spatial distribution pattern with somewhat higher concentrations in the south, indicating significant input from the atmosphere. PBDE seems to be spread out all over the Baltic while EOCi (extractable organic chlorine's) show a similar spatial and downcore distribution pattern in the Gulf of Bothnia and the Baltic proper as in the mid 1980s, with high concentrations outside pulp mills. PAHs show a somewhat different down core trend with peak values in the 1970s, thereafter decreasing. In some cores, the PCBs concentration in sediments seems to indicate constant or even increasing PCB concentrations upwards, in contrast to the development noted in biota. This is possibly partly explained by the increased deposition of organic matter due to eutrophication and consequently increased burial of PCB into the sediments, reducing their residence time in biota.

There are also indications that eutrophication processes has changed the fate of halogenated compounds in the ecosystem in a large-scale perspective. This may also be valid on a local level. This problem may serve as an example of the importance of a holistic approach, considering all the different environmental problems in the Baltic when remedial measures are to be defined.

Substantial parts of the contaminants were buried in the mostly tranquil environment of the laminated sediments of the Baltic proper. As a result of an improved oxygen situation in the deep water, for example due to a major inflow of oxygen-rich water through The Danish Sounds, many contaminants may have been mobilized back into the water mass.

Concerning the monitoring of sediments, it seems that EOCi and EOX alone are not suitable parameters for sediments from many of the stations studied. Long-term changes in pulp mill pollution can be traced only when data from chlorophenolics and possibly dioxins are combined with sum parameter data.

The content of unsupported  $^{210}\text{Pb}$  (that is  $^{210}\text{Pb}$  not produced in the sediment) decreases regularly downwards in undisturbed and steadily deposited sediment due to radioactive decay (Chapter 7). Departure from this predictable profile permits an assessment of the mixing and/or intermittent erosion as well as the rate of deposition. This provides an estimate of the sensitivity of the sediment station (Larsen & Jensen 1989). Of the 25 stations investigated 4 were so disturbed, that no dating or estimate of accumulation rates was possible by means of the  $^{210}\text{Pb}$  method. Core stations with high accumulation rates ( $4.5\text{-}15\text{ mma}^{-1}$ ) and/or low mixing by bioturbation, which is excellent for dating and trend monitoring purposes were identified in the Gdansk Basin (169), near the Lithuanian coast (170), in the Gulf of Riga (172, 175), two stations in the Gulf of Finland (187, 185) and 3 in the Bothnian Sea and Gulf (190, 192, 195). Most of the other stations have accumulation rates of  $1.5\text{-}2.5\text{ mma}^{-1}$  or  $250\text{-}500\text{ gm}^{-2}\text{a}^{-1}$  and with mixing of the upper 2-4 cm. Assuming a sampling of the uppermost 1 cm every 5 years, and steady state in relation to net accumulation rate and mixing rate, and a 10% relative standard deviation for chemical analysis, the sensitivity analysis indicates that we expect to be able to detect changes in flux of a contaminant in the order of 10-15% (in the 5 years) in the most favourable conditions. 60-200% change is needed to cause a significant change in concentrations in the other stations. As discussed above, prolonged storm conditions and strong water movements may alter this.

In cases where a highly bioturbated layer in the deeper parts of the core is overlaid by a subsequent lamination in the upper parts of the core, the  $^{210}\text{Pb}$  method has been considered unsuitable for dating. In these areas, the  $^{137}\text{Cs}$  profiles, X-ray images and regular photographs of the sedimentary structures, have been used to date the cores and estimate the net sedimentation rates. In general these laminated sediment show very high down-core time resolution. Thus, laminated sediments, in this investigation best represented by stations W. Gotl. Deep (178), LL-19 (180), GF-2 (182) and XV-1, proved to be excellent tools for sediment monitoring of contaminants in the Baltic proper and the Gulf of Finland.

The highest total concentration of carbon and nitrogen are found in the central deep part of the Baltic proper. The inorganic concentration of carbon is normally far below 1% in the entire Baltic Sea except for some localities with anoxic conditions where autigenic precipitation of mixed manganese carbonates occurs, e.g. eastern Gotland deep. Manganese seems to be of essential importance for such precipitation.

Differences in primary production, water depths, salinity and biogeochemical conditions in the bottom and pore water of the Baltic Sea results in completely different diagenetic and burial patterns of supplied organic and inorganic substances of carbon, nitrogen and phosphorus. Most of the carbon and nitrogen found in the sediments are in organic form. For carbon the main explanation is that both organic and inorganic carbonates under most circumstances are thermodynamically unstable.

Though a comparatively high concentration of inorganic nitrogen is reported from the Baltic Sea than from other marine areas the percentage amount at examined deposition bottoms exceeds seldom 10% of the total amount of nitrogen. However, the inorganic amount of nitrogen could not be neglected in, for instance, burial calculations and in the interpretation regarding alterations of Redfield ratios within and between different localities in the Baltic Sea.

For phosphorus, on the other hand, most of the total amounts in the sediment are inorganically bound. The main reason for that is that phosphorus during most natural conditions only exist as orthophosphate, a molecule with high reactivity to solid particles through either adsorption or precipitation. The highest total concentrations are found in the eastern part of Gulf of Finland. High concentrations are also found in the well-oxidized sediments of the Bothnian Bay and Bothnia Sea.

The constant vertical organic C/N ratio in the sediments of the Baltic Sea suggests that the release of nitrogen occur during a very early diagenetic stage. The average C/N ratio in the southern part of the Baltic Sea is close to ten. The corresponding ratio values in the Bothnian Bay and Sea are 12.1 and 13.1, respectively. The explanation for higher organic C/N ratios in the northern part of the Baltic Sea is most likely due to a high terrestrial organic material supply through the streams in that area of the Baltic Sea.

### *Recommendations*

It is emphasized that the chemical results, as well as the mineralogical and the age determination data contain a large amount of information. Further inspection of this data will probably open new interpretations. However, based on the present survey of the dating, chemistry and the mineralogy of the cores, the following observations can be made on the use of sediments in the follow-up of contaminants in the Baltic Sea marine environment:

A reliable set of sediment parameters has been established, covering the major open sea sedimentation basins of the Baltic Sea. The major exception is the Eastern Gotland Deep area.

Sediments give valuable information on the development of the contaminant status at least in certain areas, and thus can be included in the pollution monitoring programme of HELCOM. Monitoring, in this sense, is to be understood rather as a programme of repeated baseline studies. The main use, however, of the sediments is to indicate areal variations rather than variations in time.

Especially bioturbated sediments respond slowly to input changes. Frequency of sampling for possible monitoring/baseline studies should thus be not higher than once in five years

Some of the regions sampled during the Sediment Baseline Study should be investigated again to find better sampling sites; this is particularly the case for Kattegat, the Bornholm Basin, the Arkona Basin and the northern central Baltic Proper.

A selected set of Sediment Baseline stations appear to be suitable (Fig. 2.2) for use as future reference stations:

Station name	Baseline Study number	Suitable sampling frequency	
		5 years	10 years
Lübeck Bight	157	X	X
Bornholm Basin	167		X
Gdansk Bay	169	X	X
Lithuanian Coast	170	X	X
Gulf of Riga	175	X	X
LL19	180	X	X
GF-2	182	X	X
GF-3	186		X
GF-6	185	X	X
XV-1	187	X	X
EB-1	190	X	X
Härnösand	192		X
BO-3	193		X
F2X	195	X	X

(Note: there being several suitable stations in the Gulf of Finland, one, GF-4, has been dropped.)

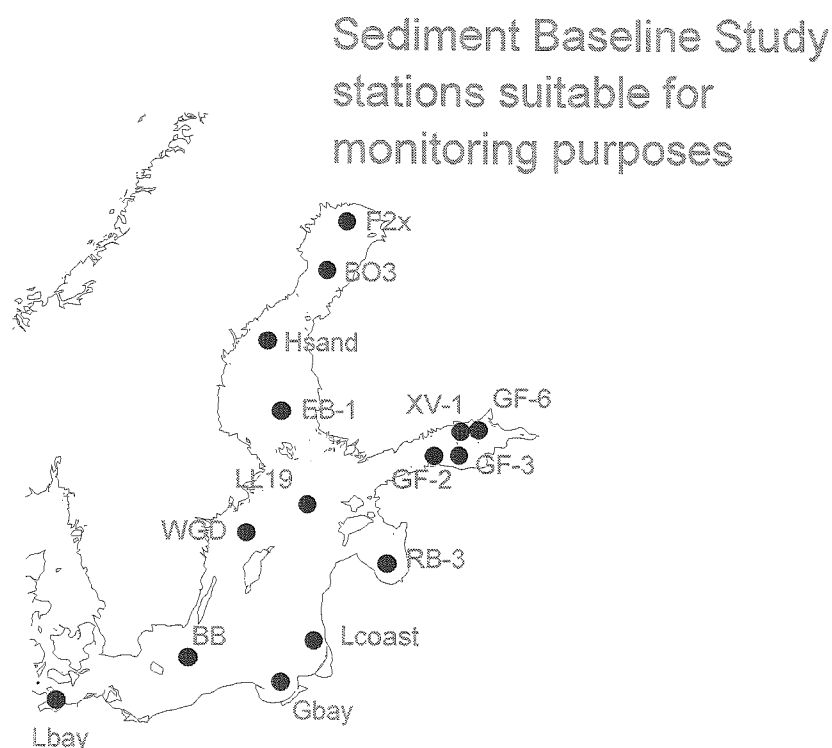


Fig. 2.2. Location of stations suitable for long-term monitoring.

The monitoring should be carried out as a joint Baseline Study, assigning only recognized expert laboratories (laboratories with formal accreditation and/or quality assurance systems checked by external interlaboratory tests) to carry out the analysis of the samples. Only equipment to be specified in this report should be used for sampling.

Utmost care should be exercised in the precise positioning of the ship for sediment sampling, and in the accuracy of the position holding. The positioning and ship-holding techniques should allow a navigational accuracy of  $\pm 20\text{m}$  or better.

The sediment cores should be documented by description, X-rays and photographs.

Redox conditions should be measured on board as soon as possible after sampling.

Samples for post-cruise analyses should be deep-frozen immediately after sampling (except those intended for possible mineralogical and grain-size analysis). Analysis of authigenic minerals formed in anoxic conditions should be performed in a manner preventing alteration through oxidation.

The total sample should be used (no size fractionation).

For the trace elements, total digestion should be used.

The primary trace elements to be analysed are Al (or Li), As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn.

The primary organochlorine compounds are PCBs (the congeners used in the HELCOM BMP), PAHs, PBDEs, and the DDTs. Moreover, also the sum parameters EOC<sub>l</sub>, EPOC<sub>l</sub>, EOBr, EPOBr, EOX and AOX should be analysed.

The supporting parameters are P, N, TC, TOC and the near-bottom water salinity.

### 3. MINERALOGICAL COMPOSITION AND GRANULOMETRY

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#### 3.1 INTRODUCTION

To a significant degree, the chemical composition of deposits depends on grain size and mineralogical composition. Contaminants, in that heavy metals, concentrate in the fines. Grain size distribution is one of the normalizing parameters, used in the comparison of the chemical composition of deposits with different grain sizes. Mineralogical composition was analysed in order to determine the regional differences between Baltic sedimentation basins, and to determine changes in the vertical profile of sediments, which occur in early diagenesis, or due to a change in the properties of the sedimentary environment.

Granulometric and mineral composition of slices taken from 36 cores was analysed. Grain size distribution was determined for samples from the following layers: 0-1, 4-5, 9-10, 19-20, 24-25 cm, and mineralogical composition for the 0-1 and 19-20 cm layers. In total, 129 grain size analyses and 55 mineralogical composition determinations were performed.

#### 3.2 ANALYTICAL METHODS

Details of the experimental methods are given elsewhere (Uzciniowicz & al. 1996).

**The grain size** analyses were made in the 1 to 500  $\mu\text{m}$  range, and the percentage of grains belonging to the following classes was determined <1, 1-2, 2-4, 4-8, 8-16, 16-32, 32-63, 63-125, 125-250 and 250-500  $\mu\text{m}$ .

Results of grain size distribution analyses performed on the laser particle sizer show systematic differences in comparison with distributions obtained by sedimentation methods. Depending on particle size spectrum of the sample, on particle shape, and on mineralogical composition, results of particle size measurements with the laser sizer show a 10-20% lower content of clayey fractions, and a higher silty fraction content, than results obtained by sedimentation methods. The largest differences occur in case of analyses of very fine deposits, with a high content of clayey minerals with flaky fabric, but relative differences between samples with different grain sizes are maintained.

**Analyses of mineralogical composition** of the sediments were made using the X-ray powder diffraction method, and additionally – the thermal differential analysis method. The diffractometer measurements were made on raw samples in the  $3^\circ$ - $60^\circ$   $2\theta$  range of angles on pressed specimens, and in case of clayey fraction (<0.002 mm) samples in the  $3^\circ$ - $20^\circ$   $2\theta$  range on orientated and heated specimens.

Quantitative evaluation of the mineral composition of the Baltic Sea sediments is very difficult. The biggest problems are encountered in the selection of reference samples, preparation of which from components with possibly similar structural and grain size characteristics is not always possible. In the investigation of the Baltic Sea sediments, calibration curves prepared on the basis of the chemical standard of Granite GM, containing mixed feldspar (plagioclase + potash feldspar), were used.

#### 3.3 RESULTS

##### 3.3.1 Granulometry

Granulometry of the deposits covering the seafloor in Baltic Sea sedimentation basins varies relatively little. Silty (0.032-0.062 mm) and clayey (<0.004 mm) fractions predominate. Additions of sandy fractions (2.0-0.063 mm) are very small, and outside the Kattegat, Kiel and Lübeck Bights only occasionally exceed 1%. In the sandy fraction particles of 0.063-0.125 mm diameter predominate.

According to Shepard's (1963) classification the Baltic Sea basin sediments consist mainly of clayey silts and silty clays, more rarely silts. Only in the southern part of Kattegat (station 155) additions of sandy fractions occur in amounts of 31.83 to 33.99%, which classifies the deposit as sandy silt. In sediment samples from the western and southern Baltic (Kattegat, Kiel, Mecklenburg and Lübeck Bights, and Arkona, Bornholm and Gdańsk Basins), and also from the Riga and Finland Gulfs, and the northern part of the Gulf of Bothnia, clayey silts predominate. In samples from sedimentation basins in the central part of the Baltic Sea (Eastern Gotland Deep, Western Gotland Deep, Fårö Deep, Landsort Deep), besides clayey silts also silty clays occur. Deposits with highest content of the clayey fraction occur in samples from the Åland Sea (station 189) and from the southern part of the Bothnian Sea (stations 190, 191). In these areas most often silty clays are present.

Grain size variability in vertical profiles differs. In the western and southern parts of the Baltic, and in the Gulf of Riga and Gulf of Finland, generally there is no clear trend in vertical grain size variability. In the rest of the Baltic, content of the clayey fraction (<0.004 mm) decreases more or less distinctly upwards with a simultaneous increase of silty (0.004-0.063 mm) fraction. This regularity is especially distinct in the Eastern Gotland, Western Gotland, Faaro and Landsort Deeps and in the Gulf of Bothnia (Stations 171, 178, 176, 179, 193). Clayey fraction content increases upwards only locally.

### 3.3.2 Mineralogical composition of the sediments

The Baltic Sea muds (silts, clayey silts and silty clays) consist mainly of: quartz, feldspar, illite and chlorites. These minerals were found in all tested sediment samples. Locally, and less often occur: kaolinite, mixed-packet minerals; (illite-montmorillonite, illite-chlorite) and calcite, manganoan calcite, dolomite, magnesian and calcian kutnohorite, rhodochrosite, witherite, pyrite, siderite, goethite, gypsum, bassanite, anhydrite and amphiboles.

**Quartz**  $\text{SiO}_2$  (5-490) occurs in all tested samples in amounts from 3% in the Eastern Gotland Deep (station 171, 0-1 cm) to 55% in Kattegat (station 155, 0-1 cm), the average content is about a dozen per cent. Quartz content in the deposits depends on grain size, and distinctly decreases with growing percentage of silty and clayey fractions.

**Feldspar** occurs in amounts ranging from 5% in the Landsort Deep (station 180, 0-1 cm) to 27% in Kattegat (station 155, 0-1 cm). It was absent in one sample only from seabed surface in the Eastern Gotland Deep (station 171, 0-1 cm). Feldspar content shows a weak positive correlation with the content of quartz. However, this content is most often lower than that of quartz by several per cent. Feldspar is represented mainly by plagioclases and potash feldspars.

**Illite** predominates among clayey minerals present in Baltic Sea deposits. Only in seven samples (171, 0-1 cm and 19-20 cm; 174, 19-20 cm; 189, 0-1 cm; 193, 19-20 cm; 195, 0-1 cm and 19-20 cm) it occurs in smaller amounts than other clayey minerals.

**Chlorites**, similarly to illite, were found in all tested samples. Content of chlorites is generally lower than of illite. Only locally in the Gulf of Riga (sample 174, 19-20 cm) and in the Gulf of Bothnia (samples 193, 19-20 cm; 195, 0-1 cm and 19-20 cm) chlorites dominate among the clayey minerals, and in the Eastern Gotland Deep (sample 171, 19-20 cm) they occur in second place after kaolinite.

**Kaolinite** was found only in some regions of the Baltic Sea: in deposits of the southern part of the Gulf of Finland (stations: 181, 0-1 cm and 19-20 cm; 183, 0-1 cm; 186, 0-1 cm), in the Gulf of Riga (stations: 172, 0-1 cm and 19-20 cm; 173, 0-1 cm; 174, 0-1 cm), in the Eastern and Western Gotland Deeps (stations: 171, 0-1 cm and 19-20 cm; 178, 19-20 cm), in north-eastern part of the Gdańsk Basin (Station 170, 0-1 cm and 19-20 cm), and in Kattegat and Kiel Bight (stations: 156, 19-20 cm; 157, 0-1 cm and 19-20 cm; 158, 19-20 cm). In total, kaolinite was found in 17 samples. Generally, of all clayey minerals, kaolinite content is third largest after illite and chlorites. Only in the Eastern Gotland Deep it is on the first place among clayey minerals, and in the north-eastern part of the Gdańsk Basin it is only second to illite.

**Illite-montmorillonite** occurs mainly in the Åland Sea and Bothnia Sea, where locally it is the most often occurring clayey mineral (sample 189, 0-1 cm) or second to illite (samples 189, 19-20 cm; 190, 0-



1 cm and 19-20 cm). The mixed-packet mineral of this type occurs also in the southern part of the Gulf of Bothnia (193, 19-20 cm), in the western part of the Gulf of Finland (181, 0-1 cm), and also in the Gdańsk Basin (169, 0-1 cm), Bornholm Basin (167, 19-20 cm), Arkona Basin (166, 19-20 cm), and in Kattegat (156, 19-20 cm). In these areas illite-montmorillonite is third among clayey minerals – after illite and chlorites.

**Illite-chlorite** occurs locally in the eastern part of the Gulf of Finland (185, 19-20 cm; 186, 19-20 cm) and in the Gulf of Riga (174, 19-20 cm). This mineral was found only in three samples, in which it occurs in second or third place among the clayey minerals, and always below bottom surface.

**Calcite**  $\text{CaCO}_3$  (5-586); was identified in deposits in most of the Baltic Sea sedimentation basins. Most often it occurs only on the surface of the bottom (layer 0-1 cm) in lower than 1% amounts. Larger calcite contents (3-4%) were found only in Kattegat (stations 155 and 156). This mineral was not found in deposits of the Bornholm Basin (167), Gdańsk Basin (169, 170), Western Gotland Deep (178), Åland Sea (189) and in the southern part of the Gulf of Finland (183).

**Calcite, manganoan**  $(\text{Ca},\text{Mn})\text{CO}_3$  (2-714); as calcite, it occurs in deposits of most of the Baltic Sea sedimentation basins, and in similarly small amounts. This mineral was not found in the Bornholm and Gdańsk Basins, in Åland Sea and in the southern part of the Gulf of Finland. In the Eastern Gotland Deep (Station 171) calcite and manganoan calcite were found only at the 19-20 cm horizon below bottom surface.

**Dolomite**  $\text{CaMg}(\text{CO}_3)_2$  (11-78); was found in the deposits in the Kiel and Lübeck Bights, in Arkona, Bornholm and Gdańsk Basins, in Landsort, Eastern Gotland and Western Gotland Deeps, and in the Gulf of Riga. In contradistinction to calcite and manganoan calcite, dolomite occurs only locally in Kattegat, Gulf of Finland and Bothnia Sea (stations 156, 185, 191).

**Kutnohorite magnesian**  $(\text{Ca}_{.97}\text{Mn}_{.5}\text{Mg}_{.5})(\text{CO}_3)_2$  (20-225) and **kutnohorite calcian**  $\text{Ca}_{.74}(\text{MnMg})_{.26}(\text{CO}_3)_2$  (19-234); occurs in deposits in nearly all Baltic Sea sedimentation basins. These minerals were not found in the sediment samples of the Kiel and Lübeck Bights, of Western Gotland and Landsort Deeps, neither in the northern parts of the Bothnian Sea and Gulf of Bothnia. Kutnohorite occurrence shows no clear regional differentiation.

**Rhodochrosite**,  $\text{MnCO}_3$  (7-268) was found only in the Kiel Bight (station 157) in a sample from the 19-20 cm depth below sediment surface.

**Witherite**,  $\text{BaCO}_3$  (5-378) occurs exclusively in the northern part of the Gulf of Bothnia (station 195), both on bottom surface (0-1 cm) and in the 19-20 cm below the sediment surface layer.

**Siderite**,  $\text{FeCO}_3$  (8-133) was found in sediments of most of the Baltic Sea net sedimentation basins. This mineral was absent only in Western Gotland, Eastern Gotland and Landsort Deeps. Occurrence of siderite in the vertical profile varies. In the Bornholm and Gdańsk Basins it is present only in the sediment surface layer (stations 167, 169, 170, layer 0-1 cm). In all the other areas siderite occurs both in the 0-1 cm and 19-20 cm layers.

**Goethite**  $\text{FeO}(\text{OH})$ , (29-7131) most often occurs in Baltic Sea deposits together with siderite and pyrite. Only in southern Kattegat (station 155, 0-1 cm), in samples from the Western Gotland and Eastern Gotland Deeps (171, 19-20 cm; 178, 0-1 cm), and locally in the Gulf of Riga (station 174, 0-1 cm), goethite is the only observed autigenic mineral of iron.

**Pyrite**  $\text{FeS}_2$ , (6-710) occurs in most of the Baltic Sea sedimentation basins. Pyrite was absent only in samples from the Western Gotland and Eastern Gotland Deeps (178, 0-1 cm and 171, 19-20 cm), and locally in the Gulf of Riga (173, 0-1 cm) and Gulf of Finland (station 183). As a rule pyrite and siderite appear together in the same samples, much less often pyrite occurs together with goethite. Samples containing pyrite, siderite and goethite were found mainly in the Gulf of Bothnia and in the Bothnian Sea.

**Gypsum**  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (6-46), occurs in deposits of the Kiel and Lübeck Bights (stations 157, 160), in Arkona, Bornholm and Landsort Basins (stations 163, 164, 165, 166, 167 and 180), and in Western

Gotland, Eastern Gotland, Landsort and Faro Deeps (stations 171, 178, 179, 176), and also locally in the Gulfs of Riga (174), Finland (185) and Bothnia (193).

**Bassanite**,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  (33-310), occurs in deposits of the Kiel Bight (stations 157, 158) and in the Arkona Basin (162), but it is less often found in this area than gypsum. Bassanite was also found in one sample from the southern part of the Gulf of Bothnia (190, 19-20 cm).

**Anhydrite**,  $\text{CaSO}_4$  (6-226) was found only in the northern part of the Gulf of Bothnia (Station 195, samples 0-1 and 19-20 cm).

**Amphiboles** were identified in the clayey fraction of samples from the Gulf of Bothnia (193, 19-20 cm; 195, 0-1 and 19-20 cm).

### 3.4 Conclusions

The recent muds of the Baltic Sea are composed mainly of terrigenous minerals, and – to a lesser degree – of autigenic minerals.

The composition of terrigenous minerals depends on the composition of source material present on the destroyed coasts and in the catchment areas, from which they are transported by rivers to the sea. The following are commonly occurring terrigenous minerals: quartz, feldspar, illite and chlorites. Other terrigenous minerals: kaolinite, illite-montmorillonite, illite-chlorite and amphiboles, calcite and dolomite appear locally, often in trace amounts only. In the Baltic Sea there is only a slight regional differentiation of terrigenous minerals. Specially distinct are kaolinite and illite-montmorillonite, which were found together only in Kattegat (156) and in the south-west part of the Gulf of Finland (181).

Occurrence of kaolinite is limited to the southern part of the Gulf of Finland, the Gulf of Riga, Western Gotland and Eastern Gotland Deeps and the north-eastern part of the Gdańsk Basin. Presence of kaolinite in this area is probably connected with the kaolinite-bearing sedimentary rocks of Estonia, Latvia and Lithuania. A second, smaller area with kaolinite is in the Kattegat and in the Kiel Bight.

Illite-montmorillonite occurs in the northern (Åland Sea, Bothnia Sea, Gulf of Bothnia) and southern part of the Baltic Sea (Arkona and Bornholm Basins and the south-western part of the Gdańsk Basin).

The following autigenic minerals were found in the analyzed samples: calcite manganoan, kutnohorite (magnesian and calcian), rhodochrosite, witherite, siderite, goethite, pyrite, gypsum, bassanite and anhydrite. Variability of occurrence of each of the autigenic minerals, both regional and in vertical profile, is much larger than in the case of terrigenous minerals. This results from the present and past differentiation of hydrological conditions in the various parts of the sea, and from the complexity of early diagenesis. The variability of hydrological conditions, and especially of the redox potential and of oxygen content, are well reflected by the various forms of occurrence of iron – both in the sedimentation basins and between them.

Among the autigenic minerals, the most distinct is the behaviour of gypsum, which is limited to two areas: 1) Landsort Basin, Western Gotland, Eastern Gotland, Landsort and Faro Deeps, and Gulf of Riga; 2) The Kiel and Lübeck Bights, and the Arkona and Bornholm Basins. In the second area gypsum locally appears with bassanite.

A special area is the northern part of the Gulf of Bothnia, where besides the typical terrigenous and autigenic minerals present in Baltic Sea muds, also amphibole, anhydrite and witherite were found in clayey fraction, which have not been observed in other parts of the Baltic Sea.

The basic aim of this elaboration was, first of all to give the data of grain size distribution and mineralogical composition as a parameters for interpretation of chemical composition of sediments. Secondly, there is given short description of the results of the analyses. Many questions concerning reasons of regional and vertical distributions of minerals, specially about autigenic minerals are still open.

## 4. DISTRIBUTION OF TRACE METALS IN THE BALTIC SEA SEDIMENTS

Horst Albrecht, Matti Perttilä & Mirja Leivuori

### 4.1 ANALYTICAL METHODS

Two laboratories were involved in the trace element analyses; Bundesamt für Seeschifffahrt und Hydrographie (BSH, Hamburg), and the Finnish Institute of Marine Research (FIMR, Helsinki). FIMR analysed the cores 172-174, and 180-196 (see Table 1.1 for the station names). BSH analysed the cores 156-171, 176, 178 and 179. FIMR analysed the samples for aluminium, arsenic, cadmium, chromium, copper, iron, mercury, lithium, nickel, manganese, phosphorus, lead, titanium, vanadium and zinc. BSH analysed the samples for the above mentioned elements, and in addition for silver, cobalt, total organic carbon (TOC), nitrogen and carbonate carbon.

**Digestion:** In both laboratories the samples were dissolved by a modification of the method of Loring & Rantala (1992). In this method, HCl, HNO<sub>3</sub> and HF are used in a closed teflon vessel. While at FIMR, microwave oven was used for heating, bomb digestion was used at BSH. Boric acid was added after cooling, followed by reheating. For mercury analyses the samples were extracted with nitric acid in an autoclave (Nordfors 1975) in both laboratories. The resulting extract was used at BSH for the determination of Ag. Zn was measured at BSH after total digestion and nitric extraction.

**Detection:** At FIMR, a Perkin Elmer 5100 ZL AAS instrument with graphite furnace HGA-400 was used for the determinations of Pb, Cd and As. Mercury was determined by a hybrid technique with a PE 5100 AAS combined with a FIAS-400 and an amalgamation system. An ICP-AES instrument (TJA-25) was used in the measurement of other elements. At BSH, flame AAS (PE 5100) for all metals with the exception of Cd, As, Ag and Hg. Cadmium, arsenic and silver were detected using a Zeeman AAS with platform and matrix modifier (Ag and As only). Mercury was determined using the PE FIMS (Flow Injection Mercury System).

**Quality assurance:** At FIMR, the commercial certified sediment reference materials SRM 2704 (NIST), MESS-1 and BEST-1 (NRCC) were used to control the analytical reliability. Nearly 100 % recoveries (84-110 %) of the studied elements were obtained from the reference materials. At BSH, at least two intakes of the (not certified) in-house reference material ABSS1 in each batch. For external laboratory performance control, both laboratories were at the same time participating in the EU/QUASIMEME program, obtaining good results.

### 4.2 GENERAL OBSERVATIONS ON THE OVERALL HORIZONTAL DISTRIBUTION OF THE TRACE ELEMENTS

The distribution of trace elements in the surficial sediments of the Baltic Sea are displayed in Figs. 4.1.1-4.1.8 (as averages of the 0-1 and 1-2cm layers). The original data, as well as all the spatial distribution pictures of the studied elements in surface sediments are available at request from the Finnish Institute of Marine Research. In the following, only a few distribution pictures are shown as examples.

*Fig. 4.1. Areal distribution of trace element concentrations in the surficial sediments of the Baltic Sea (as averages of the 0-1 and 1-2 cm layers). Salinity corrected concentrations have been used throughout the presentations. Minimum and maximum values are indicated.*

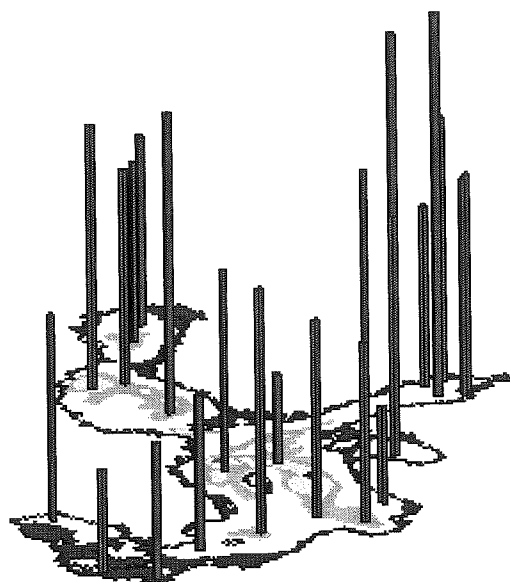


Fig. 4.1.1 Al surface distribution (3.5-10.3 %).

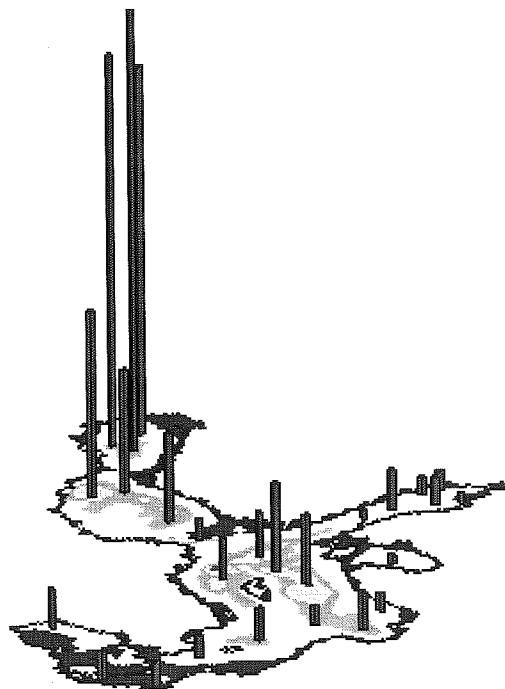
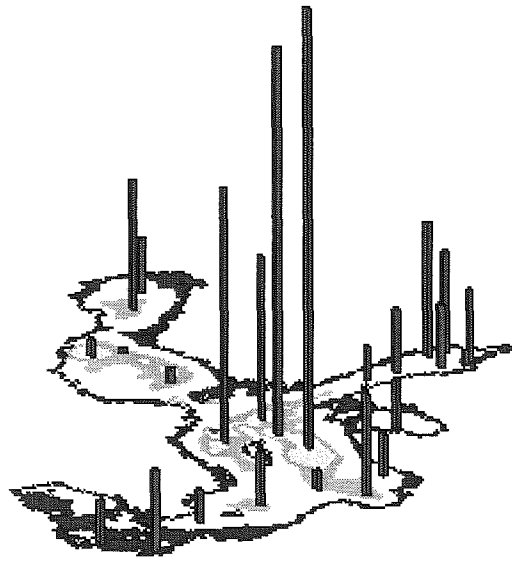


Fig. 4.1.2 As surface distribution (3.89-221 µg/g).



4.1.3 Cd surface distribution (0.085-10.93  $\mu\text{g/g}$ ).

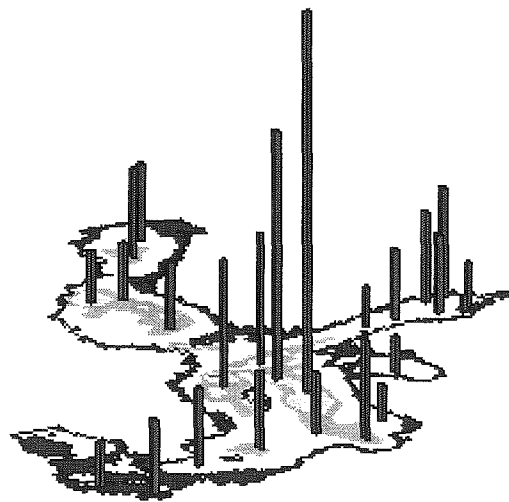


Fig. 4.1.4. Cu surface distribution (20.5-211  $\mu\text{g/g}$ ).

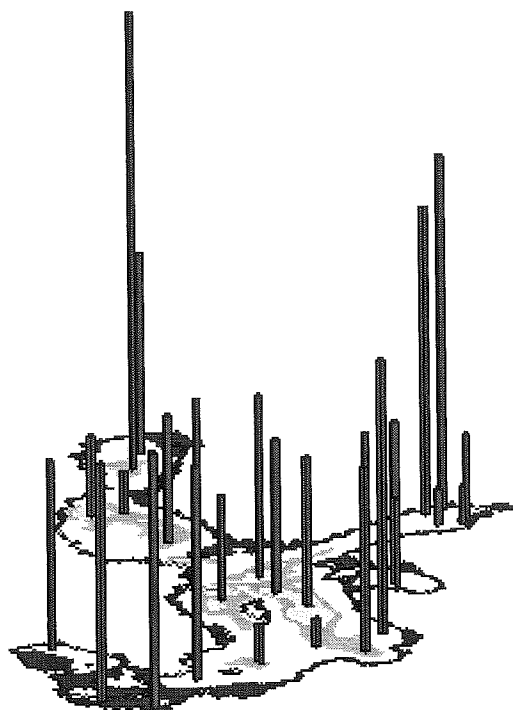


Fig. 4.1.5. Hg surface distribution (0.013-0.406  $\mu\text{g/g}$ ).

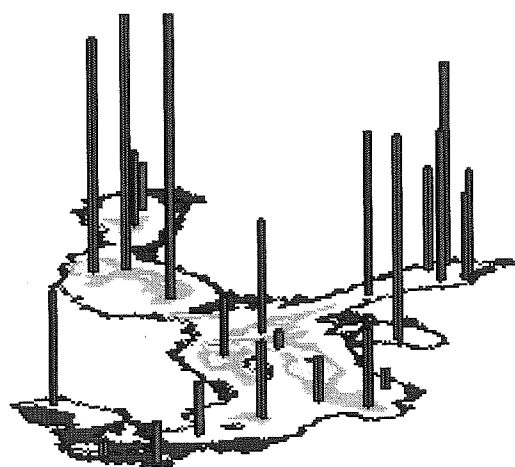


Fig. 4.1.6. Li surface distribution (33.3-140  $\mu\text{g/g}$ ).

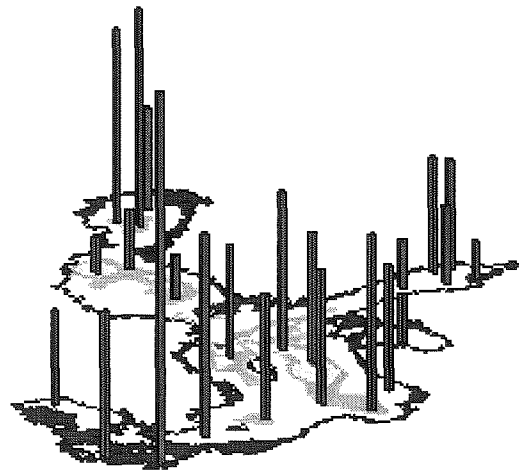


Fig. 4.1.7. Pb surface distribution (20.7-200  $\mu\text{g/g}$ ).

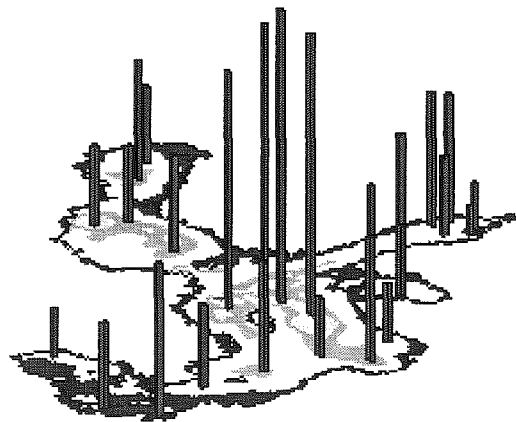


Fig. 4.1.8. Zn surface distribution (59.7-1021  $\mu\text{g/g}$ ).

For mercury, cadmium, lead, copper, zinc and arsenic the areal distribution of the surface concentrations in the present data set show considerable variations. The most striking is the case of arsenic (Fig. 4.1.2). The absolute maximum values are in the Bothnian Bay, and probably can safely be attributed to the heavy discharges of the Rönnskärsverket in Skellefteå, Sweden. The discharges have ended, but the effects can be seen clearly in the sediments. The arsenic concentrations in the surface sediments

diminish southwards, rising again slightly in the eastern Gotland Deep, indicating a different mechanism of accumulation.

For mercury, the high values in the Bothnian Bay are not quite as obvious, even though large scale construction of artificial lakes and draining of swamp areas may have increased the flushing of the catchment area. The high mercury concentrations in the Gulf of Finland are probably due to the use of mercury compounds as antifouling agents in the Finnish paper and pulp industry, an operation now replaced by other chemicals. The overall pattern seems to indicate that mercury is not effectively transported far from the original receiving areas; the elevated concentrations in all the coastal areas diminish towards the central Baltic Proper basin.

For lead, apparently anthropogenically governed distribution patterns were found, with maxima in the stations close to the coast all over the Baltic Sea. Similarly, high Pb values were also found in the Bothnian Bay and in the eastern end of the Gulf of Finland. The distribution pattern in these areas has been considered in more detail by Leivuori & Niemistö (1994), and Leivuori (1998). The highest values in the Bothnian Bay were found in the surficial sediments at the station 193 (BO-3 in the Bothnian Bay), possibly due to the Rönnskärverket discharges, and possibly also enhanced by the effects of the increased flushing of the land surface due to the construction of artificial lakes in the Lapland area. The Pb concentration at the station 189 (XV-1) in the Gulf of Finland close to the Finnish coast reflects land-based contamination, as in the near-coast stations in the Gdansk Bay and the Lübeck Bight. The lead concentrations in the Lübeck Bay are the highest found during the Baseline Study, and is in accordance with the results reported earlier by Brüggmann & Lange (1989). The moderate Pb concentrations in the central basin (Eastern Gotland Deep area) may indicate the absence of large-scale transport of lead by sedimenting/resuspending particles.

For cadmium, anthropogenic influences from land run-off or other anthropogenic activities seem to be reflected by higher concentrations in cores from the Lübeck Bight and from the Gdansk Deep. However, in the Baltic Proper area the highest values were found in the central basin area, a behaviour apparently opposite to that of lead, as noted already by Brüggmann & Lange (1989) (station 189 in the Åland Sea). According to them, mean values up to  $12 \mu\text{g g}^{-1}$  are extraordinary (with the exception of strongly contaminated spots in the Lübeck Bight) for the Baltic Sea. High values in the Bothnian Bay, as well as the strikingly different minimum values were noted for both the Gulf of Bothnia and the Gulf of Finland, are confirmed by the present study as well. However, Leivuori (1998) indicates also high cadmium values in the eastern end of the Gulf of Finland. Thus cadmium exhibits a dualistic behaviour, it seems to be effectively transported to and trapped in areas with increasing probability of the occurrence of anoxic conditions in bottom waters, and at the same time it appears to be a good indicator of local anthropogenic pollution.

Zinc appears to be effectively transported towards the central basin, with maximum values found at the stations 171 (Eastern Gotland Deep), 176 (Farö Deep), 178 (Western Gotland Deep) and 180 (LL19) in the northern Baltic Proper. Local maxima are also obvious in the Lübeck Bight, Gdansk Bay and the eastern Gulf of Finland.

The copper distribution pattern resembles that of zinc; with maxima in the central basins and locally high values in coastal stations. The high value at the station F9, Bothnian Bay, may again be attributed to the old discharges of the Rönnskärverket.

For Chromium, a relatively even distribution of the total concentrations throughout the area, together with an absence of higher concentrations at the sediment/water interface, seems to be typical, as already noted earlier. High concentrations appear in the central basins. High chromium values were found in the area of extremely active sedimentation in the eastern Gulf of Finland.

Aluminium, often used for normalization of nearshore sediments, shows only moderate variations.



### 4.3 VERTICAL PROFILES

In general, the strong thermohaline stratification together with the restricted water exchange in the Baltic Sea results in more or less prolonged periods of oxygen depletion in the central deep basins below about 150 m. Anoxic conditions are observed with probably increasing frequency even in the shallow parts of the Belt Sea below the 20 m depth line in late summer/early autumn, lasting typically for weeks up to months for the near-bottom layer. This causes a huge pool of dissolved Mn(II) compounds, partly dissolved from the sediment surface layer, in anoxic water bodies. Concentrations of trace metals such as Cu and Cd and to a lesser degree also Zn and Pb decrease in water, whereas under such anoxic conditions metals like Fe, Cr, As, Mn and Co are mobilized from the sediments. Oxygenation of such water bodies following salt water influxes into the Baltic Sea causes the oxidation of a great part of the dissolved Mn(II) and Fe(II) compounds and settling of the resulting hydroxides on the bottom. The resulting complexes bind an appreciable trace metal fraction (Moenke-Blankenburg & al. 1989).

The pattern of the vertical distribution of the elements varies markedly depending on the local conditions. The oxic-anoxic variations are crucial. In spite of the seemingly simple dissolution-precipitation mechanism of eg. manganese, the factor controlling the vertical profile would seem to be the variation in the oxic-anoxic conditions, resulting either from the redox variations of the overlaying watermass during stagnation periods and water inflow periods. In addition, dilution by the salt effect and the rate of sedimentation and the content of organic material complicate the interpretation of the history of the metal accumulation, as reflected in the concentration profile.

In areas of constant mixing, the permanently good oxygen conditions guarantee a stable sedimentation of manganese, which is demonstrated by the manganese profiles at the stations 156 (Kattegat) (Fig. 4.2) and 160 (Lübeck Bay). At the station 157 (Kiel Bight), the decrease is very sharp already at the depth of 1-2 cm.

In the Gulf of Finland, the manganese profile shows a maximum value (5-10 mg/g) in the sediment surface layer, decreasing to a minimum at 6-7 cm, having a second maximum at 8-14cm, and decreasing again in the deeper layers. This can possibly be related to the oxidation-reduction variability in the deep water layer of the region (see, eg. Pertilä & al.1995). In the Gulf of Finland, location 182 (station GF-2), manganese is quite high in the top few centimeters of the sediment (Fig. 4.3), in accordance with the observation that the bottom water and the top sediment layer were oxic at the time of sampling. There is, however, a strong subsurface manganese maximum at 14-15 cm in the strongly anoxic part of the sediment. This may perhaps be related to the invasion of anoxic waters which occurred in the area in the early 1980's.

In the Gulf of Bothnia, and especially in the Bothnian Bay, both the permanently high oxygen concentration in the bottom water and the relatively low load of organic matter to the sediment lead to a well developed subsurface Mn oxidation/reduction horizon at the oxic-suboxic boundary (Fig. 4.4).

In the central Baltic Sea, the Bornholm Deep, the eastern Gotland Deep and the Farö Deep and the LL19 (stations 167, 171, 176 and 180), and in areas affected by the conditions there, as in the Gdansk Bay, Lithuanian Coast area (stations 169 and 170), a more complicated pattern appears for the manganese accumulation. Especially the eastern Gotland Deep is exceptional (Fig. 4.5), indicating various oxic-anoxic transitions.

## Manganese profile at 156

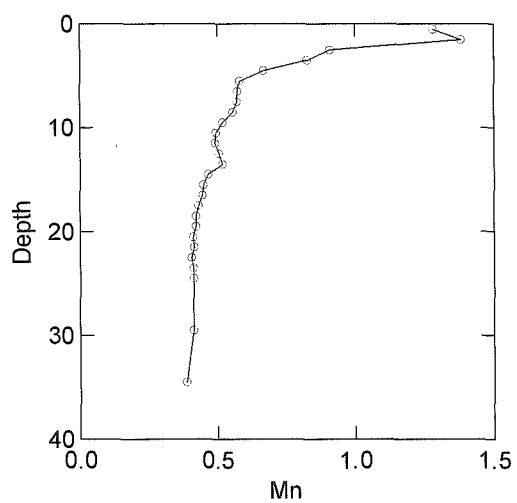


Fig. 4.2. Mn concentration vs. depth at the station 156 (Kattegat-2).

## Manganese profile at 182

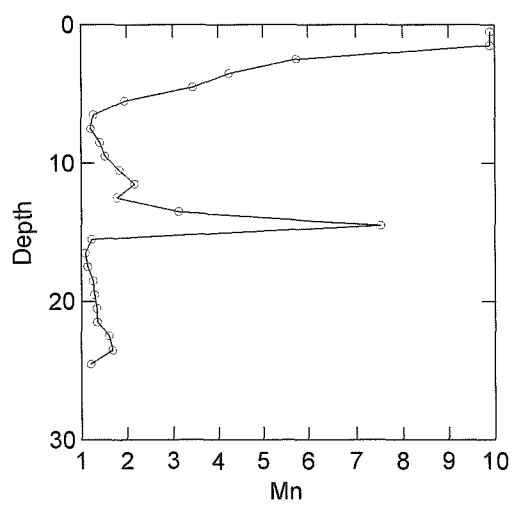


Fig. 4.3. Mn concentration vs. depth at the station 182 (GF-2).

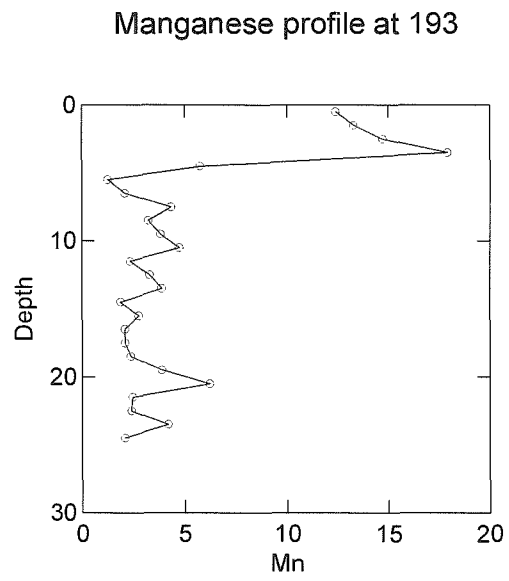


Fig. 4.4. Mn concentrations vs. depth at the station 193 (BO-3).

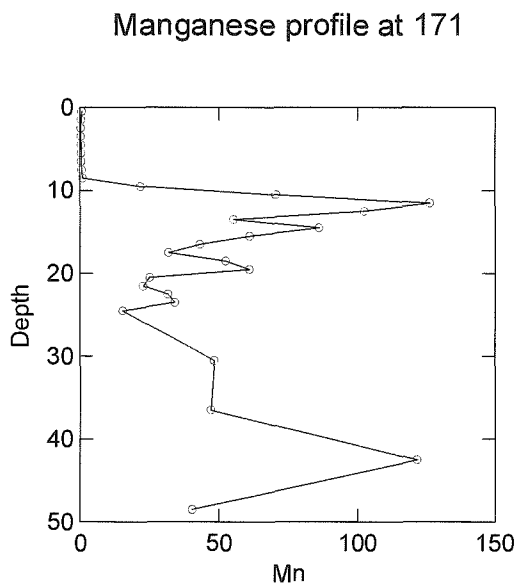


Fig. 4.5. Mn concentration vs. depth at the station 171 (Eastern Gotland Deep).

Both the Gotland Deep and the LL19 (Northern Baltic Proper) areas have very high manganese concentrations deeper down in the sediments, the highest in all the present data set. It appears that these basins collect manganese from a large area under suboxic conditions, the accumulation however having stopped almost totally under the practically constant anoxic stagnation. The abrupt maximum deeper (6-10cm, depending on the station) may indicate the effects of the 1976-77 major inflow. It should be noted that the inflow of the early 1993 is not yet seen in the surface sediment manganese concentrations. The complicated nature of the manganese profile can be attributed to the oxic-anoxic variations. As the conditions change from oxic to anoxic, part of manganese is dissolved, and depending on the sediment structure, some of the dissolved manganese moves to the water mass above, some may diffuse deeper into the sediment and precipitate as carbonate.

On the other hand, the sediment core at the station 171 (the Gotland Deep), can be affected drastically by the phenomenon discussed above; the uppermost 7-8 cm of the core was of a fluffy character, not resembling earlier observations in this area. There is thus a possibility of an underwater "landslide", possibly caused by the major inflow which occurred in the beginning of the year, some 6-7 months earlier. This water movement may have pushed into movement the fluffy material on the sediment surface over a large area, which had then settled down on the central basin. Similar structure, though only 1-1.5 cm thick, was found at the station 176 (Farö Deep). Consequently it is not possible to draw firm conclusions of the Gotland Deep area on the basis of the present data set.

The vertical distribution of cadmium follows very closely that of manganese, however in most cores the cadmium peak is slightly above the manganese peak. The distributions at the station 184 (GF-5 in the Gulf of Finland) serves as an example.

With a few exceptions, for cadmium, mercury and lead, the general tendency at the Baseline Study stations is towards diminishing values, below the intermediate concentration peaks deeper down in the sediment cores. Unless we attribute this to changes in the pollution load, a mechanism should be postulated to mobilize metals in the deep sediment layers, causing part of the metals to move upwards accumulating at a certain level. The observed lead profile at the station 160 (Lübeck Bay) exhibits a strong increase in the lead concentrations from the low background up to the depth of 6-7 cm, after which the concentration has remained more or less stable. The  $^{210}\text{Pb}$  data for this station indicates a linear accumulation rate of 2.3 mm/y, dating the 6-7 cm level to early 1970's. Thus the observed lead profile can probably best be related to the effects of dumping which was ended in the late 1960's.

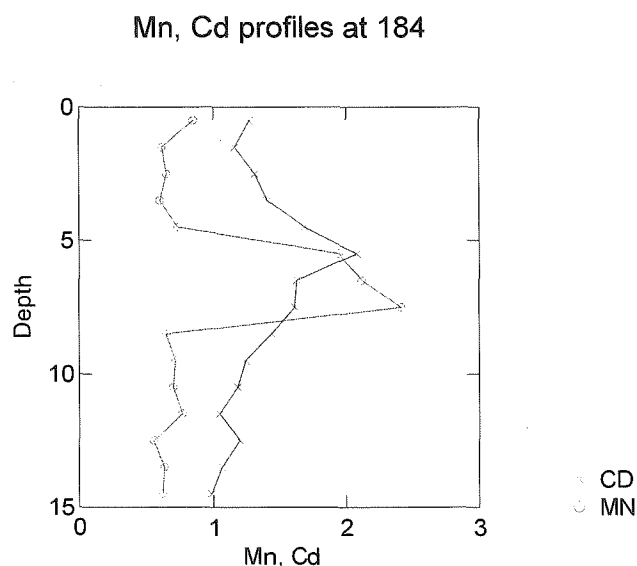


Fig. 4.6. Mn and Cd concentrations vs. depth at the stations 184 (GF-5 at the eastern Gulf of Finland).

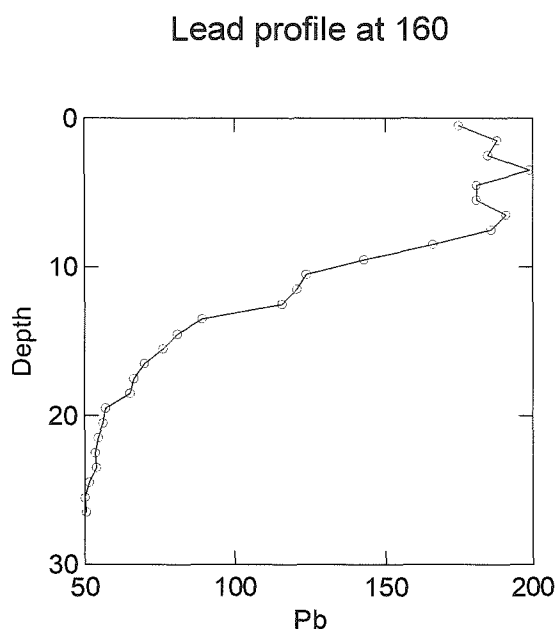


Fig. 4.7. Pb concentration vs. depth at the stations 160 (Lübeck Bay).

However, the assumption of discharges as the main cause for the observed profiles of the typically "polluting" elements like cadmium, mercury, lead and zinc is somewhat contradicted by the seemingly similar pattern of these profiles. Standardized profiles, obtained from the original concentrations by subtracting the mean value and dividing by the standard deviation, gives remarkably similar depth profiles at most stations.

It is difficult to imagine that such a result would be a consequence of changes in the discharges, because that would imply identical discharge variations for all the metals. The evident conclusion is thus that the profiles at least in the studies stations is, to a large extent, controlled by other mechanisms than the discharge history.

#### 4.4 DATA NORMALIZATION

The sediment grain size distribution is known to have an effect on the adsorption characteristics of the sediments. The Sediment Baseline Study samples were consequently analysed for the grain size distribution (Uscinowicz & al., chapter 3), even though the different grain size classes were not analysed separately. Plotting the metal concentrations against the relative share of the fine grain sediments ( $<20\mu\text{m}$ ), it can be seen that, concerning the whole data set, there is a certain amount of dependence of the metal concentrations (eg. Al in Fig. 4.9) on the relative amount of the fine grain sediments, as the metal concentrations seem to increase with increasing share of the fine grain sediments. It may be concluded that in future work the grain size distribution should be taken in account in comparative work, even though the absolute range of aluminium, excluding the central basins, is relatively small because the sediments of the Baseline Study cores are mainly of fine grain sizes. The larger range of variation in the central basins is probably mainly caused by "dilution" through sea salt, manganese carbonates and organic matter.

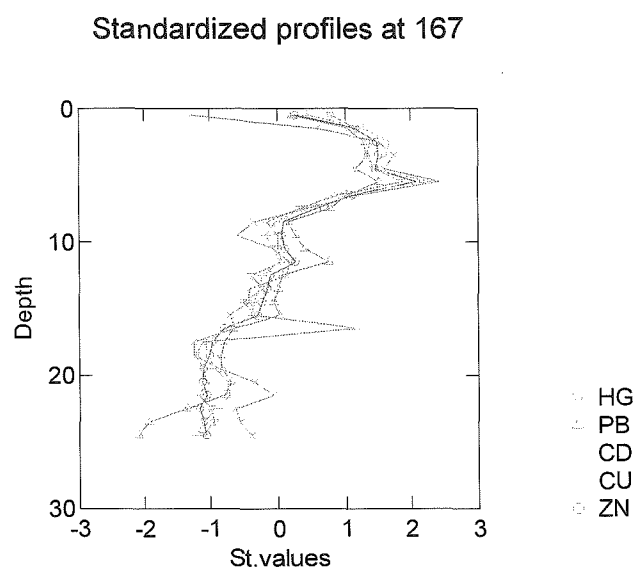


Fig. 4.8. Standardized concentrations of Hg, Cd, Pb, Zn and Cu at 167.

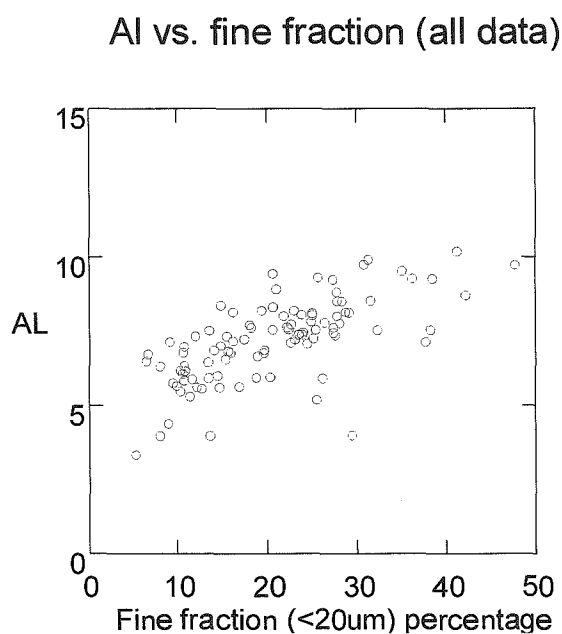


Fig. 4.9. Concentration of Al against fines (overall data).

Aluminium is frequently used to normalize trace metal concentration for natural variability, it being an indicator of the amount of aluminosilicates present in the sample. The use of aluminium has been questioned by Loring, if sediments originate from glacial erosion of igneous rocks. This is because, in such cases, sandy sediments still contain some feldspars, which have – with the possible exception of lead – low trace metal concentrations. Loring proposed to use lithium as normalizer because this element is mainly associated with clay minerals and micas.

Actually the Al/Li ratios in sediments of the Kiel Bight (and in sediments of the German Bight of the North Sea) vary strongly with grain size, the coarser sediments having higher Al/Li ratios. Trace metal concentrations, in these samples, correlate much better with lithium than with aluminium.

There is, however, a good linear relationship between Li and Al in those Baseline cores analyzed by BSH. Only the more sandy sediments of the Kiel Bight have higher Al concentrations in relation to Li. The low concentrations of lithium and aluminium in a few cases (such as core 171) are probably caused by "dilution" with sea salt (freeze dried samples), carbonates, and organic matter.

The use of lithium as normalizer may completely fail if one is dealing with strong variations of provenance, e.g. if the source rocks have very different proportions of felsics and mafics. Trace metal concentrations correlate also well with total organic carbon (TOC) and iron. TOC was used by some authors (e.g. Cato) as normalizer. This approach has been questioned because the content of TOC is no conservative property. TOC can not be used as normalizer for old subsurface sediments.

Correlations between TOC and trace metals are frequently "induced" correlations, simply because organic matter is similar distributed over grain size as the main (mineral) trace metal carriers.

In the Kiel Bight, there is a very close correlation between the content of TOC and the concentration of lithium in surficial sediments was found. This correlation ceases to exist if one deals with more fine grained organic rich sediments of the Baltic. In such cases it can be tested, if trace metal concentrations are really associated with organic matter concentration.

Iron has also be proposed to be used as normalizer. Iron, however, is strongly involved in diagenetic reactions. Iron diagenesis may lead to trace element enrichments, both in oxic surficial sediments (e.g. Zn, As, V, P) as well as in sulfidic subsurface sediments (e.g. As and V in a few cases).

If one understands normalizing as "an attempt to account for natural granulometric and mineralogical variability" one should avoid to compare trace metal data to non conservative properties. Any enrichment above "background values" [to be defined] should be considered as enrichment, also if enrichment is a result of diagenetic reactions or of high load of organic matter.

The situation differs if one attempts to detect anomalous values in a given area.

The close covariation of Li, Fe and TOC with proportion of fines (<20 $\mu$ m) allows to detect anomalous values of trace elements within the investigated area, using any of these properties as reference (not as "normalizer").

#### 4.5 EXCESS INVENTORIES

Pollution itself is difficult to define. One way is to look at the distribution pattern to find out possible hot spot areas. However, this might be misleading because of the natural metal concentrations that some typical minerals may contain. Therefore a few methods have been developed for the normalisation of the metal concentrations. The enrichment of a trace element in a medium as compared to background values is one way. The other way is to calculate so-called excess metal values by means of the metal-aluminium ratio, again compared to background values. In sediments, the background values can be expressed as the ratios in the deep core. Aluminium is often used as a normalising metal in sediment work, because both clay minerals and feldspars (detrital minerals) contain aluminium, and these aluminium containing minerals, especially the clay minerals, can also contain other metals in their crystal structure. However, the surface distribution of aluminium is roughly even in the whole Baltic Sea, and at least for lead the changes are weak. The other element used for normalising metal concentrations is lithium, because it appears that clay minerals, which are the most efficient metal absorbers, also contain lithium, whereas feldspars usually do not contain lithium. For this reason one could expect an enhanced correlation between lithium and trace elements.

## Excess inventories

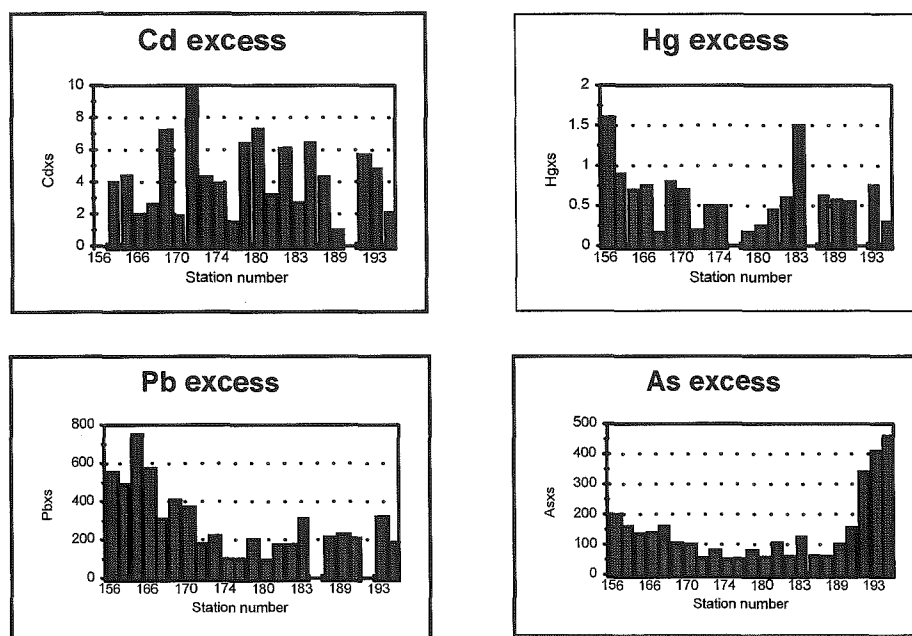


Fig. 4.10. Excess inventories for Cd, Hg, Pb and As.

The distribution pattern of cadmium indicates efficient transport. In terms of relative enrichment, cadmium seems to be the most enriched trace metals in the Baltic sediments, indicating strongly anthropogenic pollution. On the other hand, the varying oxygen conditions in the Baltic Sea may well affect the apparent enrichment of metals. Therefore high values do not necessarily indicate pollution (while it is to be expected); eg. in the Gulf of Finland from time to time anoxic situations are encountered, which accelerate the cadmium sedimentation. In the well-ventilated Gulf of Bothnia, however, the high cadmium concentrations probably indicate land-based pollution. There seems to be a tendency for cadmium to transport towards the deep basins.

Mercury is also efficiently enriched in the sediments, as expressed by the mercury-aluminium ratios. Also the mere distribution pattern of mercury shows it to be relatively efficiently trapped in the recipient basins. High mercury values are especially in the Gulf of Finland and the Bothnian Bay. The mercury-aluminium ratio is also highest in the Gulf of Bothnia. However, according to the profile analyses, the highest mercury concentrations are found in the subsurface layers, possibly indicating that the pollution load has diminished considerably since the 1970s.

The calculated relative enrichment for lead seems to be highest in the southern Baltic Sea. Considering the possible cause of lead accumulation being anthropogenic pollution, this seems plausible.

In the case of arsenic, the relative enrichment in the Bothnian Bay sediments is obvious.

Of course there are a number of corresponding figures and calculations for other metals as well, but their presentation would take space more time than can be reasonable. From the point of view of pollution, Cd, Pb, Hg and As are the most interesting.

### 4.6 METAL ACCUMULATION RATE

The horizontal distribution of the trace element does not necessarily indicate the rate of the metal accumulation. When the mean surface concentrations are multiplied with the mass accumulation rate of dry matter, one obtains a more reliable picture of the metal accumulation. This means, on the other hand, that the interstitial water fluxes and the fluxes caused by themixing processes are being ignored. Interstitial water fluxes and the dissolution/precipitation reactions have a strong influence on the down-



core profiles of components like Mn, Fe, As, P and Cd. Nevertheless, the accumulation in the Bothnian Bay stations appears to be less effective than in especially the Bothnian Sea and the Åland Sea, even though the actual concentrations in sediments are by far the highest in the Bothnian Bay. This shows the importance of the changes in the rate of mass accumulation over the changes in metal concentrations, due to the large differences in the sedimentation rates between the sea areas of the Baltic Sea.

#### 4.7 CONCLUSIONS

The problem of distinguishing between anthropogenic and diagenetic influences on the observed vertical trace-metal profiles and their horizontal distribution patterns cannot yet be completely solved.

Large amounts of potentially toxic metals (cadmium, mercury, lead) are stored in the sediments in remobilizable binding forms. This is particularly relevant for those elements which seem to occur in sulphide fractions (e.g., cadmium) which can be quickly released/bound due to oxidation-reduction variations following strong salt water (oxygen) inflows to the bottom water of the Gotland Basin, and the subsequent stagnation periods.

The overall levels of the trace element concentrations in the Baltic Sea sediments seem to be attributed to the degree of pollution of the area, but the history of the pollution as reflected in the vertical profiles is complicated by the controlling processes, most important of which is the variability of the oxygen conditions, and hence the redox potential, in the sediment core. The variability of the redox potential may be due to the variability of the redox potential in the overlaying water mass as a consequence of the hydrographic events like stagnation or inflow periods, or due to the diagenetic processes leading to oxygen deficiency.

The influence of other factors, including grain size distribution, mineralogical composition of the sediment layers, seems to be of minor importance, at least in the set of samples of the Sediment Baseline Study.

There seem to be certain degree of discrepancy between the results of the different methods of age determination of the sediment cores (see Chapter 7 below). This further weakens the analysis of the contaminant profiles in the cores.

## 5. CARBON AND NUTRIENTS

Rolf Carman

### 5.1. INTRODUCTION

The burial and processes of nutrients in the Baltic Sea sediments are highly dependent on oxygen conditions. Renewal of the deep water to the Baltic Proper is a result of an inflow of high salinity water during exceptional weather and large-scale atmospheric distributions and therefore occurs less frequently. The Gulf of Finland has weaker salinity stratification (Pertilä & al. 1995) whereas the Gulf of Riga normally exhibits lack of such stratification. The salinity stratification in the Baltic proper and Gulf of Finland result sometimes in more or less complete oxygen depletion, which in some areas of the Baltic Proper is quasi-permanent (Jonsson & al. 1990). During the periods between large saline water inflows, the halocline in e.g. the Gulf of Finland weakens and sinks down close to the bottom, thus easing the vertical circulation of the water masses and improving the oxygen conditions, whereas a strong inflow, ventilating the deep areas of the Baltic Proper, may lead to weakening conditions in the Gulf of Finland (Pertilä & al. 1995). In anoxic environments microorganisms will preferably use sulfate instead of oxygen in the oxidation of supplied dead organic matter. Subsequent production of hydrogen sulfide eliminate all benthic macrofauna which, in turn, entail formation of laminated sediments. Such lamination has been observed to cover large areas in the Baltic proper (Jonsson & al. 1990) as well as restricted areas in the Gulf of Finland (Morris & al. 1988). Changes in oxygen/redox condition in the water and within the sediment will highly alter the biogeochemical processes. Hence, the fate of supplied carbon and nutrients to the sediment surface will change in different degree as a result of altered diagenetic processes.

### 5.2 MATERIALS AND METHODS

During the sediment baseline study all together forty-two soft bottom sediment cores were sampled during one mount in summer 1993. However, since several of the sampled sediment cores were collected very close to each other only thirty-two sampling sites are examined in this study (Fig. 1.1).

The sediment sub-samples were taken for total C, N and P analyses and for different subfractions of these elements. Total carbon (TOT-C) and nitrogen (TOT-N) was measured on a Leco element analyser with a precision of 0.5%. Organic carbon (ORG-C) was determined on pretreated sediment samples with 1 M HCl in the same element analyser (Hedges & Stern 1984). Inorganic carbon (IN-C) was obtained from difference between the total and organic carbon values. Fixed nitrogen (FIX-N) and exchangeable nitrogen (EX-N) was measured only on selective sites down to a maximum depth of 5 cm below sea floor according to the method described by Silva & Bremner (1966) and Mackin & Aller (1984), respectively. Organic nitrogen (ORG-N) was obtained from differences between the total and the sum of FIX-N and EX-N. All wet extracts of N were measured according to Parsons & al. (1984). Total phosphorus (TOT-P) and inorganic phosphorus (IN-P) was measured according to Froelich & al. (1988). Mobile phosphorus (MOB-P) was measured according to Carman & Jonsson (1991) without pretreatment with other chemicals. Apatite phosphorus (AP-P) was obtained from the difference between IN-P and MOB-P whereas the amount of organic phosphorus (ORG-P) in the sediment was obtained by the difference between TOT-P and IN-P. All wet extracts of P were measured using standard spectrophotometric technique (e.g. Murphy & Riley 1962). Transition and trace metals in the sediments have been analysed by using ICP-AES technique.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Carbon

The spatial distribution of total carbon in the Baltic Sea is shown in Fig. 5.1.

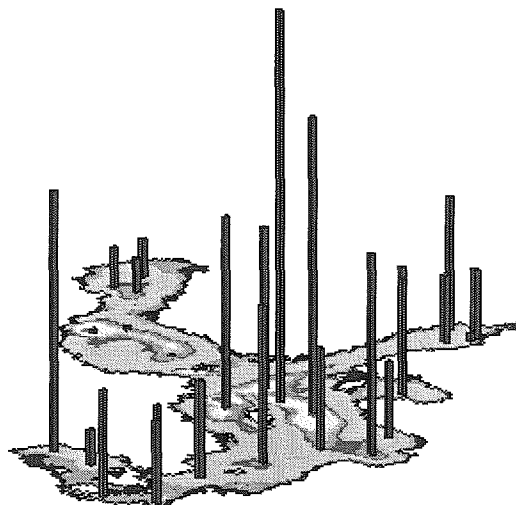


Fig. 5.1. Distribution of total carbon in the Baltic Sea sediments (0-1 cm layer) (concentrations 3.22-17.0% of dry matter).

Most of the carbons in the sediments of the entire Baltic Sea are in organic form. This is mainly due to that inorganic carbonates (e.g. calcium carbonates) are undersaturated in the water mass (e.g. Carman & Rahm 1996) which result in a dissolution of sedimented biogenic as well as abiogenic carbonates. Normally constitute the inorganic part for less than 0.5 mmol/g (< 1% d.w). In the adjacent Kattegatt (e.g. sites 155 and 156) and Skagerrak the concentration of inorganic carbonates often exceeds 1% d.w. and represents often a significant proportion of the total carbon content (>30%). Autigenic precipitation of mixed carbonates in the sediments with euxinic conditions of the Baltic proper (eastern Gotland Basin) is also a process that has been frequently suggested to occur (Manheim 1961, Suess 1979, Jakobsen & Postma 1989, Carman & Rahm 1996). Such autigenic precipitation could also be discovered in this study at site 171 (Gotland deep). The precipitation seems to start below 9 cm depths below sea floor (Fig. 5.2). The molar ratio Mn/IN-C of the precipitate is 0.64 (Fig. 5.3) with a very high coefficient of determination ( $R^2=0.97$ ). Thus, manganese is an important major cation for the mixed autigenic precipitate in this environment. The ratio found in this study is very close to that reported by Jakobsen & Postma (1989) who suggest that the precipitate is a Ca-rhodochrosite in which calcium constitute almost the remaining part of the precipitate. Hence, the prolonged euxinic conditions of the eastern Gotland basin with continuous reduction of manganese oxides together with microbial breakdowns of the organic matter using sulfate, with resulting increases in alkalinity, maintains a perfect environment for autigenic precipitation of mixed manganese carbonates. Relatively high manganese concentrations are also found in the sediments at site 167 and 180. However, even though Jakobsen & Postma (1989) found small amounts of Ca-rhodochrosite in the Bornholm basin (site 167) there is no such excellent correlation between manganese and inorganic carbons as that found at site 171.

### 5.3.2 Nitrogen

As for the carbon most of the nitrogen in the sediments of the Baltic Sea is organically bound even though Müller (1977) shows that the concentration of inorganic nitrogen (fixed and exchangeable; FIX-N and EX-N, respectively) in some areas of the Baltic Sea are quite high compared to many other marine areas. Hence, the spatial distribution pattern of total as well as organic nitrogen follows very closely the distribution pattern of carbon. Inorganic nitrogen is adsorbed on mineralogical particles (preferably on clay minerals) and organic matter as exchangeable ammonium (EX-N) and as fixed ammonium (FIX-N). While EX-N is adsorbed through an ion exchange reaction on the surface of certain organic or mineral surfaces, FIX-N is incorporated in the sediments through adsorption within the clay structure and not easily replaced by other cations. In soft bottom sediments constitute the sum of these two inorganic phases seldom more than 10% of the total nitrogen content of which FIX-N comprises the dominant proportion. However, even though they often represent a minor fraction their concentrations could not be disregarded when, for instance, investigations of alterations in organic C/N ratios within and between different sediment environments of the Baltic Sea are performed.

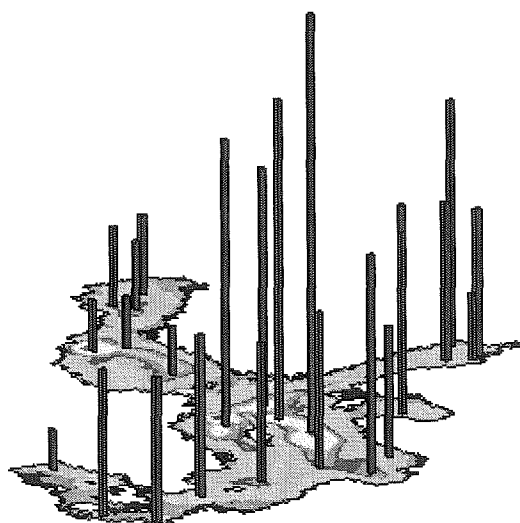


Fig. 5.2. Distribution of total nitrogen in the Baltic Sea sediments (0-1 cm layer) (concentrations 0.15-1.62% of dry matter).

### 5.3.3 Phosphorus

In difference to carbon and nitrogen a substantial portion of the phosphorus in the sediment is inorganically bound. Therefore, the spatial distribution pattern (0-1 cm sediment depth) of total phosphorus does not entirely follow that of the carbon and nitrogen (compare Fig. 5.1 and Fig. 5.4). The most obvious difference is that the total concentrations of phosphorus are about the same in the central Baltic proper and the Bothnian Sea whereas the concentration of both carbon and nitrogen are much lower in the Bothnian Sea than in the central part of the Baltic proper. Further, the high coefficient of determination between both the total and the organic content of carbon and nitrogen at each site of the Baltic Sea does not exist for carbon/nitrogen against phosphorus. The main reason for such a distribution pattern is that the degradation of the organic matter with respect to carbon/nitrogen versus phosphorus occurs in different ways, e.g. the utilization of phosphorus during decomposition of organic matter is independent of the concentration of carbon and seems in difference to carbon unaffected of variations in sedimentation rates (Froelich & al. 1982, Ingall & van Cappellen 1990). Inorganic phosphorus constitutes seldom for less than 50% of the total amount and the percentage of inorganic phosphorus at certain deposition bottoms could sometimes comprise up to 90% of the total

amount. The corresponding values for carbon and nitrogen are ~5% and ~10%, respectively. The nature of the sedimentary matrix (grain size, chemistry etc.) combined with redox condition depend how and to which amount the burial of P occurs. Due to low concentrations and often x-ray amorph phases preclude to a large extent direct identification of pure mineral phases. Therefore, a common and often the only way to interpret possible and dominating incorporation mechanisms and to quantify the buried amount of different more or less exclusive phosphorus fractions in the sediments are the use of different sequential leaching procedures (e.g. Williams & al. 1967, Balzer 1986, Carman & Jonsson 1991, Ruttenberg 1992).

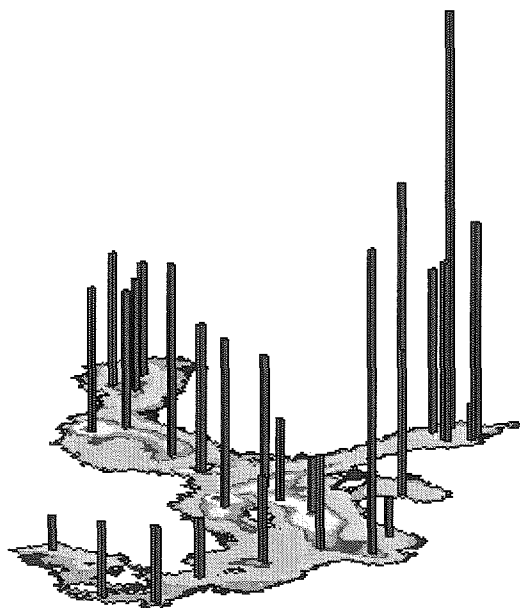


Fig. 5.3. Distribution of total phosphorus in the Baltic Sea sediments (0-1cm layer) (concentrations 0.15-1.62% of dry matter).

The burial pattern of carbon, nitrogen and phosphorus in the Baltic Sea sediments, based on the 1993 Baseline results, is described in detail by Carman (1998).

#### 5.4. SUMMARY AND CONCLUSIONS

The highest total concentration of carbon and nitrogen are found in the central deep part of the Baltic proper. The concentration at similar bottoms in the Bothnian Bay and Bothnian Sea is about 1.5 to two times lower. The inorganic concentration of carbon is normally far below 1% in the entire Baltic Sea except for some localities with anoxic conditions where autigenic precipitation of mixed manganese carbonates occurs, e.g. eastern Gotland deep. Manganese seems to be of essential importance for such precipitation. The average molar ratio of the precipitate is 0.64 (Mn/C) with a very high coefficient of determination ( $R^2=0.97$ ). As for carbon, a dominant proportion of the nitrogen found in the sediments is organically bound. The inorganic amount exceeds seldom 10% of the total amount of nitrogen.

Differences in primary production, water depths, salinity and biogeochemical conditions in the bottom and pore water of the Baltic Sea results in completely different diagenetic and burial patterns of supplied organic and inorganic substances of carbon, nitrogen and phosphorus. Commonly, most of the carbon and nitrogen found in the sediments are in organic form. For carbon the main explanation is that both organic and inorganic carbonates under most circumstances are thermodynamically unstable. However, in the euxinic parts of the Baltic proper (e.g. eastern Gotland Basin), with succeeding prolonged anoxic conditions in the pore waters, it is quite common to observe autigenic precipitation of mixed manganese carbonates. Manganese is very important for such precipitation. Though a

comparatively high concentration of inorganic nitrogen is reported from the Baltic Sea than from other marine areas the percentage amount at examined deposition bottoms exceeds seldom 10% of the total amount of nitrogen. However, the inorganic amount of nitrogen could not be neglected in, for instance, burial calculations and in the interpretation regarding alterations of Redfield ratios within and between different localities in the Baltic Sea.

For phosphorus, on the other hand, most of the total amounts in the sediment are inorganically bound. The main reason for that is that phosphorus during most natural conditions only exist as orthophosphate, a molecule with high reactivity to solid particles through either adsorption or precipitation. The highest total concentrations are found in the eastern part of Gulf of Finland. High concentrations are also found in the well-oxidized sediments of the Bothnian Bay and Bothnia Sea. In these latter areas phosphorus is highly linked to the vertical concentration trends of manganese even though the average molar ration (Mn/P) varies between the different sites of that region. Iron adsorbs large amounts of phosphorus during oxidized conditions whereas precipitation of different kinds of phosphorus minerals are common during reduced conditions. Manganese plays an important role for the burial of phosphorus in the Bothnian Bay and in some other restricted anoxic areas of the Baltic proper. In these areas of the Baltic Sea it is common to find a high coefficient of determination between phosphorus and manganese. Ferric manganese nodule formations in the Bothnian Bay together with autigenic manganese-calcium phosphate and apatite precipitation in the Baltic proper explains most likely the high coefficient of determination between manganese and phosphorus found at these sites.

The constant vertical organic C/N ratio in the sediments of the Baltic Sea suggests most likely that the preferential release of nitrogen occur during halmyrolysis or during a very early diagenetic stage. The average C/N ratio in the southern part of the Baltic Sea is close to ten. The corresponding ratio values in the Bothnian Bay and Sea are 12.1 and 13.1, respectively. The explanation for higher organic C/N ratios in the northern part of the Baltic Sea is most likely due to a high terrestrial organic material supply through the streams in that area of the Baltic Sea.

## 6. ORGANIC CONTAMINANTS

Per Jonsson & Harri Kankaanpää

### 6.1 INTRODUCTION

The sediments contain differing amounts of natural organic substances depending on the type of the sediment and the hydrographic and environmental conditions. Because of the toxicity, persistence and lipid-solubility of most of the man-made organic contaminants, they are classified as harmful substances, and must be analytically separated from the naturally occurring compounds. This calls for dedicated personnel and sophisticated laboratory work. Because of the rapid development in the number of organic substances discharged into the environment during recent decades, and because of the rapid development in the chemical instrumentation, most of the available data are still fragmentary and there is a need for conclusive results for many compounds.

Pesticides are used for the protection of agricultural and forestry production in order to combat occurring pests. Insecticides, fungicides and herbicides serve this purpose. These deliberately designed "toxic substances" reach the Baltic Sea via rivers and from the atmosphere.

Except for their toxicity, the other characteristics of pesticides are not general for the entire substance class. However, to a certain extent they apply to the chlorinated hydrocarbons, for example: DDT, lindane ( $\gamma$ -HCH), dieldrin, chlordane, heptachlor, mirex and the substance mixture of chlorinated camphenes (toxaphene).

Polar and non-polar substances are adsorbed onto fine organic detritus, and thus carried to the bottom and trapped in marine sediments. For organic compounds under aerobic conditions, chemical (oxidation) and microbial decay takes place. Under anoxic conditions, different chemical changes may occur (e.g., DDT to DDD); however, a complete mineralization is extremely slow. In order to be able to compare the toxic substance concentrations measured in different types of sediment, a normalization to the share of organic carbon (TOC) in the sediment is necessary (Andrulewicz & al. 1979). This normalization of the data has been non-existent thus far. Over and above that, the comparability of the data has not been ensured because an intercalibration has not yet taken place. The concentrations reported thus far (Perttilä & Haahti 1984) for lipophilic substances in the sediments are several orders of magnitude higher than those in water. However, in the evaluation one must take into account the bioavailability of material adsorbed in the sediments.

The usefulness of the sum parameters extractable organic chlorine (EOCl) and extractable organic halogen (EOX) to describe the influence areas of discharges from pulp mills has frequently been disputed in different contexts. The parameters can be measured using rapid and straight-forward chemical methods, which provide data for assessment of the presence of pulp mill pollution.

Like most sum parameters EOCl and EOX include a large number of different species of substances, which may hamper their use when it comes to detecting specific discharge sources. For example, the contribution of natural organohalogens to the total EOCl and EOX may be significant (Asplund & Grimvall 1991, Gribble 1994, Kankaanpää & al. 1997, Neidelman & Geigert 1986). Therefore, best possible evidence for past or present pulp mill pollution can be obtained by combining the results of sum parameter and specific organochlorine analyses.

EOCl gradient studies including specific substances like chloroguaiacols, PCDD/Fs and alkyl-CDFs (Jonsson & al. 1993) have revealed high correlations to substances undoubtedly released from the mills. Also mercury (Borg & Jonsson 1996) showed a high linear relationship with EOCl in the southern Bothnian Sea and Northern Baltic proper, which most likely is due to the localisation of chloralkali industries close to the pulp mills in this region (Jonsson 1992).

A mass balance study for the entire Baltic Sea (Wulff & al. 1993) identified the pulp mills as being the largest source of the input of EOC<sub>l</sub> to the Baltic Sea ecosystem. These results were based on data from the Bothnian Sea and the Baltic Proper; data from the Gulf of Finland were not available. On the basis of these results, Jonsson (1992) suggested that EOC<sub>l</sub> in surficial sediments can be used as a tracer of pulp mill discharges not only locally but also on a large-scale basis. It should be noted that the possibility of the natural production of halogenated material (Kankaanpää & Tissari 1994, Kankaanpää 1997) was not included in the model.

Sediment investigations of EOC<sub>l</sub>, representing the mid and late 1980s, revealed an overall distribution pattern with very high concentrations close to the pulp mills in the Bothnian Sea, decreasing towards the open sea (Håkanson & al. 1988, Södergren & al. 1988 and 1993, Jonsson 1992).

In the Gulf of Finland, local pulp mill pollution was observed (Kankaanpää & al. 1997). In the open Gulf of Finland, however, the distinction between non-polluted and industrially polluted sediments using EOX becomes difficult since the EOX material from spring blooms is dominant (Kankaanpää 1997).

The perhaps best known record of anthropogenic discharges to the Baltic Sea during the 20th century has been obtained using sediment cores that showed distinct changes in vertical EOC<sub>l</sub> distribution and concentrations higher than those in natural sediments. Such cores showed clearly the temporal changes of chlorinated compounds from pulp mill discharges.

From knowing when important internal process changes were introduced within the pulp industry, a rather good estimate of the discharge record has been obtained (Wulff & al. 1993). The discharges to the Baltic from mainly Swedish and Finnish pulp mills started to increase from less than 100 tonnes per year in the 1940s. During the 1950-60s discharges increased, and, in the 1970-80s, 600-800 tonnes EOC<sub>l</sub> were discharged annually. During the past ten years, the pulp mill discharges of organochlorines to the Baltic Sea have decreased dramatically.

For EOC<sub>l</sub>, Jonsson (1992) found that the annual burial of EOC<sub>l</sub> in the offshore sediments of the Baltic proper showed background situation until the early 1950s. During the 1960-70s the sediment burial increased rapidly, reaching peak values (6 times the background) in the mid 1980s, thereafter somewhat decreasing.

Until this study, only a few sediment cores from the open Baltic Sea have been analyzed for PCBs. Pertilä & Hahti (1986) found about the same total PCB and total DDT concentrations (20-60 and 10-40 ng/g ds respectively) in the surficial sediments as Niemistö & Voipio (1981) did. de Wit & al. (1990) and Nylund & al. (1992) found substantially lower surficial sediment concentrations of total PCB (3-10 ng/g ds) in two laminated cores from the northwestern Baltic proper and the Bornholm Deep.

## 6.2 ANALYTICAL METHODS AND QUALITY ASSURANCE

### 6.2.1 Extractable organic chlorine (EOCl), extractable persistent organic chlorine (EPOCl), extractable organic halogen (EOX), extractable organic bromine (EOBr) and extractable persistent organic bromine (EPOBr)

The determination of sum parameters EOC<sub>l</sub> and EOBr for halogenated organic compounds was performed by the Center for Industrial Research (SI) in Oslo, Norway using neutron activation analysis (NAA) according to Martinsen & al. (1988). The sediment sample was homogenized and approximately 20 g wet material was transferred to an extraction vessel. The sample was extracted twice with a mixture of isopropanol and cyclohexane (1:1), using an ultrasonic bath and a mechanical shaker. The extracts were combined, and the cyclohexane phase was isolated by repeated washings of the extract with distilled water (pH 2), and an acidified ammonium nitrate solution. The cyclohexane phase was dried with anhydrous sodium sulphate. The chlorine and bromine content in the cyclohexane extract was determined by Neutron activation analysis (NAA).



Extractable organic halogen (EOX) measurements were carried out at the Finnish Institute of Marine Research in Helsinki, Finland. EOX was determined using a method modified from the original by Martinsen & al. (1988) as described by Kankaanpää & Tissari (1994). For extraction 5-10 grams of dried sediment was extracted with 70 ml of cyclohexane/isopropanol (80%/20%). The extract were washed two times with aqueous nitrate solution (pH 2). The organic phase was concentrated *in vacuo* to 0.5-2 ml final volume and analysed, in triplicate, with Euroglas ECS 2000 microcoulometric halogen analyser.

Analytical blanks were prepared along with the samples. Blank values were subtracted to give the correct sample values. All chemicals, solvents, etc were controlled to give no background levels of chlorine and bromine prior to use. The uncertainty of the EOCl and EOBr methods was about 10%, increasing to about 30% at levels near the detection limits of the method. The EOX method has an uncertainty about 30% with levels approaching the detection limit, otherwise about 15%.

### 6.2.2 Polybrominated diphenylethers (PBDE)

Polybrominated diphenyl ethers were analysed according to the method described by Nylund & al. (1992) with some modifications. CB-189 (2,3,3',4,4',5,5'-heptachlorobiphenyl), was used as standard, added to the sediment.

Elemental sulphur was removed by shaking the sample extract with a mixture of 2-propanol (2 ml) and tetrabutylammonium -sulfite reagent.

Dry weight was determined after heating an aliquot of the centrifuged sample at 105 °C overnight. The loss on ignition (the content of organic material) was determined after heating the dried sample at 550 °C for two hours.

The samples were analysed by GC/MS using the negative ions formed at chemical ionisation (MS-ECNI). The gas chromatograph was a Carlo Erba MEGA MFC 500 equipped with a 30 m DB5-MS capillary column (J&W, 0.25 mm i.d., 0.25 mm film thickness). The samples were injected splitless at an injector temperature of 270 °C. Helium was used as carrier gas. The mass spectrometer was a Fisons Trio-1000. The ion source temperature was kept at 200 °C and the electron energy was 70eV. Ammonia was used as reagent gas. The ions monitored were *m/z* -79, -81 for the brominated compounds and -394, -396 for CB-189. For the injection standard, CB-207, *m/z* -462 and -464 were used. The samples were quantified against a technical product, Bromkal@70-5DE (Chemische Fabrik Kalk, GmbH).

The recovery of TeBDE, Pe1BDE and Pe2BDE have been determined to be 108, 101 and 106% respectively (relative to the surrogate standard). The concentrations reported have not been corrected for the recovery. CB-207 (2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl) was used as injection standard and the absolute recovery of the surrogate standard was 56%.

Solvent blanks followed the sediment samples through the extraction, clean-up and GC/MS analysis, in order to check for contamination. The samples were analysed randomly together with the quantification reference solutions. Hexane and acetone were glass distilled at the laboratory and tested for interferences before use. All other solvents used were of analytical grade. The limit of quantitation was set to five times the blank value. Samples containing less are reported as less than this limit of quantitation.

### 6.2.3 Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)

PAHs and PCBs were analyzed at the Institute of Zoology, Stockholm University.

After addition of internal PAH standards (2-methylanthracene, picene, *d*<sub>12</sub>-perylene, dibenzo[*a,i*]pyrene) and <sup>13</sup>C<sub>12</sub>-labelled PCB standards (2,2',5,5'-TCB, 2,2',4,5,5'-PnCB, 2,2',4,4',5,5'-, 2,2',3,4,4',5-HxCB, 2,2',3,4,4',5,5'-HpCB (IUPAC# 52, 101, 153, 138 and 180 respectively), the

samples were Soxhlet extracted (wet) with toluene for 24 h. After extraction the samples were volume reduced and then divided into two equal parts for PCB and PAH analysis, respectively.

The PAH extracts were subjected to dimethylformamide (DMF) clean-up extractions followed by elution through 100x10 mm columns packed with 10% deactivated silica (Näf & al. 1992).

The PCB extracts were volume reduced to approximately 15 ml and 5 g of copper powder was added to each extract to reduce the sulfur content. Further, the PCB samples were purified on a silica column composed of a mixture of three different layers of modified silica (Zebühr & al. 1993).

Analyses of the PAHs were made using a Hewlett-Packard (HP) 5890 Series II GC (with a Chrompack 25 m x 0.22 mm Cp-Sil-8 fused silica capillary column) equipped with a HP 5971A mass selective detector operating in SIM mode. Injections were made in splitless mode (2 min) while the GC oven temperature was held constant at 100 °C, after which the temperature was raised to 290 °C with 7 °C/min. This final temperature (290 °C) was held for 10 min.

The mono- to tetra-ortho PCBs were analyzed using the same HP GC/MS system as for the PAHs or a Fisons' MD800 system (with column as above) operating in SIM mode. Injections on the HP system were made in splitless mode and on the Fisons system using cold on-column injection.

For the PCB analyses, standard bottles were weighed before and after taking aliquots to control changes in standard concentrations. Stable isotope ( $^{13}\text{C}_{12}$ ) analogues of five of the PCBs were used as internal quantification standards (IQSs). IQSs were added to the samples at the earliest possible stage, here, the extraction of the samples. At least one IQS was used for each PCB homologue in which PCB congeners were to be analysed. An additional  $^{13}\text{C}_{12}$ -labelled PCB congener (IUPAC #118) was added to the final extract before analysis as a recovery standard (RS). The recoveries of the IQSs were between 60-105%. The two most abundant ions in the molecular ion cluster of each homologue and IQS were monitored. The isotope ratios between the measured molecular ions should be within  $\pm 10\%$  of the theoretical values. A solution containing Aroclor 1254 and  $^{13}\text{C}_{12}$ -labelled PCB standards (#52, #101, #118, #153, #138, #180) were run through the GC/MS to check the chromatographic resolution and the retention times of the compounds. An instrument blank, a solution of the IQSs and the RS, was analysed to verify that the GC/MS was not contaminated with a background of analytes. Procedural blanks were processed with each set of samples (in general one blank per ten samples) to check all of the material and equipment used for the samples and to confirm the absence of carry-over between samples

For the PAH analyses, standard bottles were weighed before and after taking aliquots to control changes in standard concentrations. Four IQSs were added to the samples at the earliest possible stage, here, the extraction of the samples (see Extraction, clean-up and Analysis). d12-chrysene was added to the final extract before analysis as a recovery standard (RS). A reference solution containing the PAH compounds to be analysed and IQSs was run through the procedure in the same way as the samples. This reference solution was used as an external standard (ES) for the calculation of relative response factors (RRFs) as well as a column check of the chromatographic resolution and retention times. An instrument blank, a solution of the IQSs, was analysed to verify that the GC/MS is not contaminated with a background of analytes. Procedural blanks were processed with each set of samples (in general a ratio of one blank per ten samples) to check all of the material and equipment used for the samples and to confirm the absence of carry-over between samples.

## 6.3 SPATIAL DISTRIBUTION

### 6.3.1 Sum parameters EOC1 and EOX

The surface EOC1 concentrations are generally lower in the Baltic proper than in the Gulf of Bothnia and the Gulf of Finland, except for two peak values (Fig 6.1). One of the extremes in the Baltic proper is East Gotland Deep (station F81, 32  $\mu\text{g Cl/g ds}$ ) where many specific compounds/elements show high concentrations. The second highest concentration, 24  $\mu\text{g EOC1/g ds}$ , which is almost 10 times the

background, is obtained in the Gdansk Bay, possibly indicating chlorinated compounds discharges in this region.

The Gulf of Finland, Gulf of Bothnia and Åland Sea areas were further studied for a more detailed distribution pattern of extractable organic halogen (EOX) (Kankaanpää 1996). The total halogen content in the surface layers varied between 2.2-10.1  $\mu\text{g Cl/g ds}$  at eleven stations, showing background levels (Kankaanpää 1997). Only the sediment sample from station XV1, 30 km off the point sources in the Finnish town of Kotka (eastern Gulf of Finland), contained slightly elevated EOX levels of 12.7  $\mu\text{g Cl/g ds}$ .

No large spatial variations in EOX distribution was observed (Fig. 6.2); the levels were somewhat higher in the Gulf of Finland (3.9-12.7  $\mu\text{g Cl/g ds}$ ) than in the Gulf of Bothnia and the Åland Sea (2.2-4.5  $\mu\text{g Cl/g ds}$ ). The difference can be due to the different character, e.g varying content of organic material, algal material, etc in the surface sediments. The sediments were sampled in June 1993, slightly before the Sediment Baseline cruise, immediately after the spring bloom, which means that substantial amounts of fresh planktonic material was present in the surface. EOX and water depth did not correlate.

Although the discharges of chlorinated compounds since the mid 1980s have been reduced substantially due to measures taken within the Swedish and Finnish pulp industry, this reduction has not yet changed the EOC1 concentrations in contaminated offshore surficial sediments. Jonsson & al. (1996) considered that resuspension of chlorinated organic matter may remain a substantial source for a long time, especially in the Gulf of Bothnia, where land uplift due to the former glaciation of Scandinavia may cause erosion of contaminated sediments. If also the large areas of transportation and erosion bottoms in the Baltic Sea are considered, representing approximately 2/3 of the bottom area, one should not expect to see any fast concentration responses to the changed input of contaminants. The response time may well be in the order of some ten years.

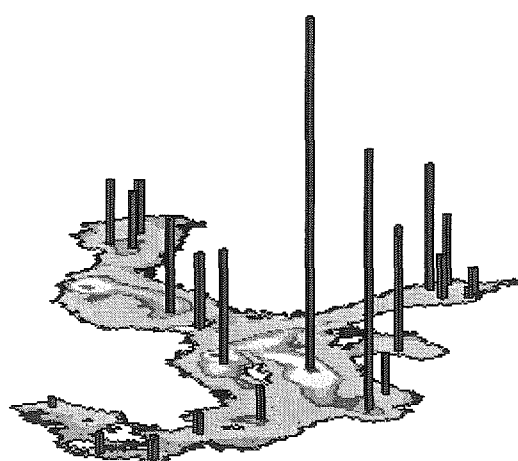


Fig. 6.1. Distribution pattern of extractable organic chlorine (EOCl) in surficial (0-2 cm) sediments (0.94-32.0  $\mu\text{g Cl/g ds}$ ).

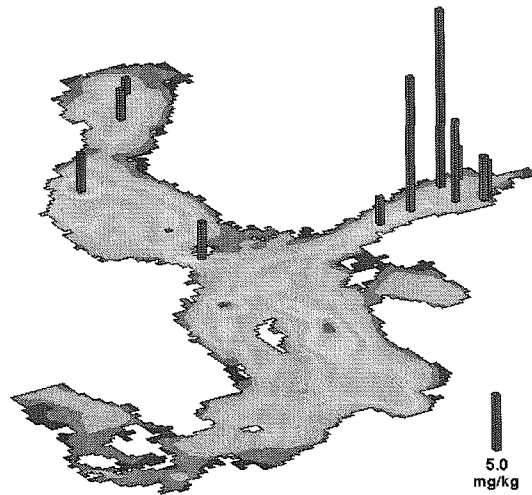


Fig. 6.2. Spatial distribution of extractable organic halogen (EOX) in surficial (0-2 cm) sediments (2.2-12.7  $\mu\text{g Cl/g dw}$ ).

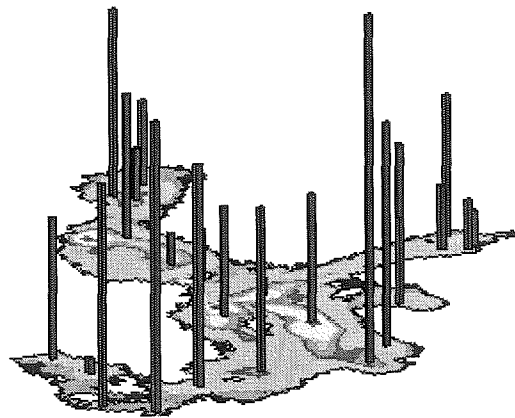


Fig. 6.3. Distribution pattern of polyaromatic hydrocarbons (PAH; 18 cong.) in surficial (0-1 cm) sediments (0.88-35.2  $\mu\text{g/g dry matter}$ ).

### 6.3.2 Specific substances

For the polycyclic aromatic hydrocarbons (PAHs) concentrations are shown related to carbon content (Fig. 6.3) for 18 congeners ranging from fenantrene to coronene.

The highest concentrations are found in the southernmost Baltic Sea, with lower values in the central Baltic proper and somewhat higher values in the Gulf of Finland and northern Gulf of Bothnia.

Also concerning the sPCBs (Fig. 6.4), there are complications in comparing our data with other investigations since the sum PCBs often are based on different congeners.

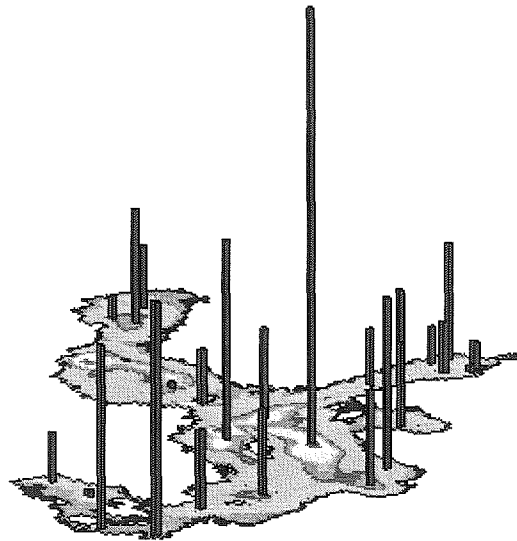


Fig. 6.4. Distribution pattern of sPCB (7 cong.) in surficial (0-1 cm) sediments (3.51-54.7  $\mu\text{g/g dw}$ ).

## 6.4 TEMPORAL CHANGES OF CHLORINATED HYDROCARBONS IN SEDIMENTS

### 6.4.1 General features

In the upper 2 centimeters of the sediment column decreases of many contaminants are observed in those cores where the sedimentation rates are so high that the upper centimeters represent the early 1990s. This could partly be due to diagenetic processes within the highly dynamic surficial sediment. However, since the concentrations in the upper parts commonly are 25-50% lower than in the deeper sediments, representing the 1980s, this could hardly be explained by concentration processes due to mineralization of the organic matter, which as an average constitutes some 15-20% of the dry matter. In contrast to the surficial decrease of other parameters measured, EOX shows increasing concentrations toward the sediment surface in most of the cores analysed, which can be explained better by natural production.

Contaminant concentrations, expressed in relation to dry matter, are highly affected by changes in deposition of dry matter and the content of organic carbon. Erosion of old sediments, caused by crustal rebound after the last glaciation of Scandinavia has been suggested to be an important factor for the sedimentation process in the Baltic (Blazhchishin 1984). A major part of the sedimented dry matter in the Baltic basin probably originates from resuspension of uplifted glacial and postglacial sediments (Jonsson & al. 1990). On the other hand, the decreasing rate of crustal uplift reduces the erosion and sedimentation of minerogenic material from coastal areas. Thus, temporal changes in deposition of eroded material should affect the down-core concentration pattern significantly.

Recent investigations in an offshore area in the NW Baltic proper (Jonsson & al. pers. comm.) show quite high deposition rates during the 1960-70s. During the 1980s the deposition rates were reduced to about 50% of the rates in the 1960-70s, thereafter, in the early 1990s, increasing to similar deposition rates as in the 1960-70s. The deposition rates were well correlated to annual means of the duration of wind speeds exceeding 15 m/s, confirming the importance of erosion/resuspension for the deposition rates in the offshore Baltic proper depositional areas for fine material.

Until good estimates of variations in deposition rates have been obtained for the Baltic Sea, detailed interpretation of down-core trends are not possible. Therefore, the discussions below are only aiming at interpretations of the large and obvious changes in concentrations and deposition of contaminants.

### 6.4.2 Sum parameters

For the extractable organic chlorine, EOCl, Jonsson (1992) compiled a “mean core“ for the Baltic proper representing 5 sediment depth intervals from 8 cores. In Fig. 6.5 this is compared with a similarly compiled core from the Sediment Baseline Study. The concentration changes with time are similar although the core from late 1980s generally shows lower concentrations. The distribution pattern is characterized by background concentrations (3-6  $\mu\text{g Cl/g ds}$ ; Håkanson & al. 1988) up to the 1940s; thereafter increasing with peak values corresponding to the early 1980s. In both mean cores decreases occur in the upper part.

The increasing EOX toward the sediment-water interface in several cores in the Gulf of Finland (Kankaanpää 1997), suggests that the EOX concentrations in sediments cannot be attributed solely to the discharges of AOX from the pulp mills in the area, as the production of AOX decreased from about 2600 t AOX  $\text{a}^{-1}$  in 1989 to about 1000 t AOX  $\text{a}^{-1}$  in 1992, and in 1993 the output was already down to approx. 600 t AOX  $\text{a}^{-1}$ . If discharges were the main contributors, rather a downward trends of EOX in the cores would be expected, at least in a long perspective.

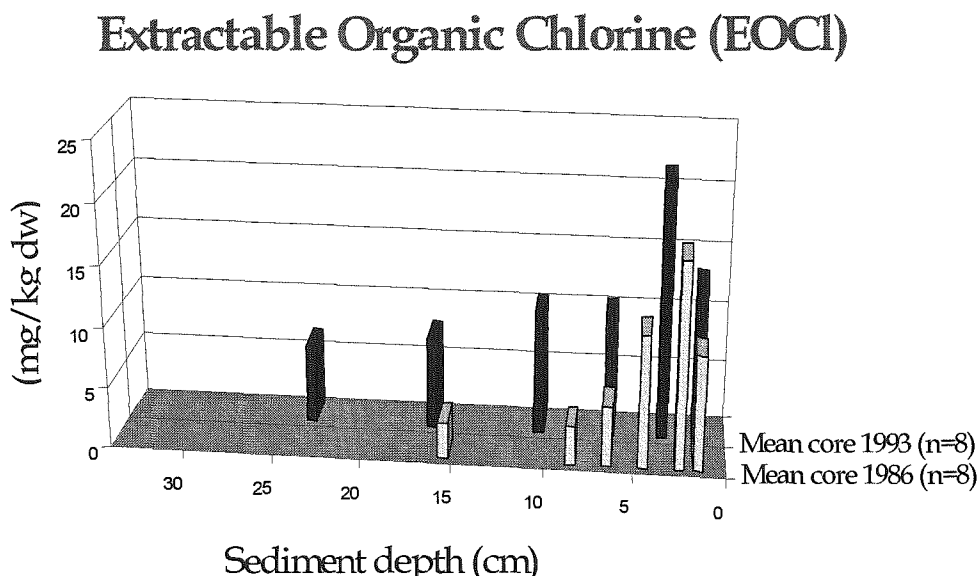


Fig. 6.5. Mean EOCl distribution in cores for the Baltic proper sampled in 1986 and 1993.

Another interesting thing to note is the relative increase in the persistent part of EOCl. Opposite to what one might expect, due to degradation of EOCl with time, the portion of EPOCl increases towards the sediment surface. Certainly, there is room for several possible interpretations for this. One of the most likely is that the input of persistent organic pollutants, as measured by EPOCl, has increased in relation to more easily degraded compounds during the 20th century. This interpretation is supported by sediment investigations from the Baltic proper concerning PCBs (Pertilä & Haahti 1986, de Wit & al. 1990, Nylund & al. 1992, Axelman & al. 1995, Kjeller & Rappe 1995, this investigation), DDTs (Pertilä & Haahti 1986, Nylund & al. 1992) and PCDD/Fs (de Wit & al. 1990, Kjeller & Rappe 1995) in general showing increasing concentrations during recent decades.

However, whatever interpretation is chosen, the increase of EPOCl, both quantitatively and in relation to EOCl, should be looked upon as an indication of impaired contaminant situation in the sediments.

### 6.4.3 Polyaromatic hydrocarbons (PAHs)

The down-core PAH concentrations (Fig. 6.6) show in general peak concentrations in the 1970s and early 1980s thereafter somewhat decreasing. This is in agreement with Axelman & al. (1995), using

varve-counting as dating methods. Renberg & Wik (1985) showed high correlation between soot particle deposition in lake Grånästjärn and oil and coal combustion in Sweden with peak values around 1970. Thus, the decreased deposition of PAHs in the Baltic during recent decades is probably a result of decreasing discharges of PAHs from combustion.

The degradation of PAHs is probably insignificant in these, at most stations, laminated sediments. This is demonstrated by hardly no changes in the relative congener composition going with sediment depth in the cores (Fig. 6.7).

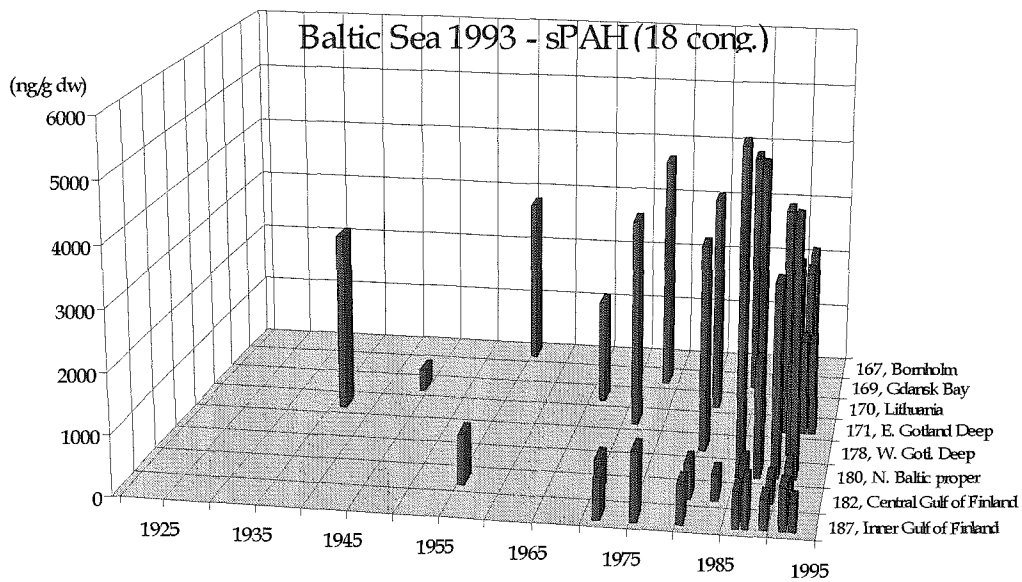


Fig. 6.6 sPAH (18 cong.) concentrations in 8 dated sediment cores from the Baltic proper and Gulf of Finland.

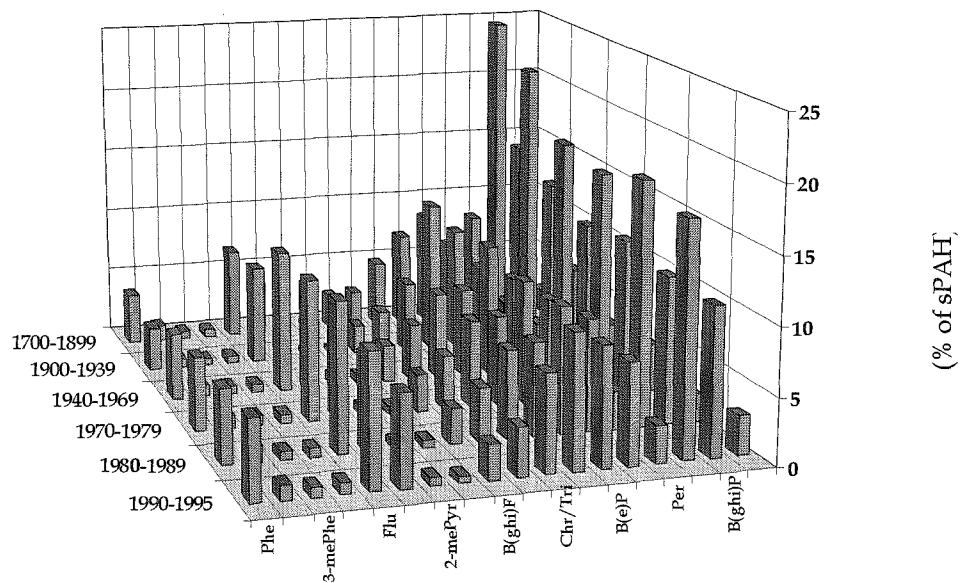


Fig. 6.7. PAH congener composition (% sPAH) in 8 dated sediment cores from the Baltic proper and Gulf of Finland.

#### 6.4.4 Polychlorinated biphenyls (PCBs)

The comparison with previous PCB data may to some extent be hampered by a different number of congeners analyzed and included in the total amounts in this study. However, the vertical distribution patterns are similar with substantially higher concentrations in the upper sediment layers, corresponding to the period after 1960. In the core from the northwestern Baltic proper, the sum of PCBs was correlated to the Nordic toxicity equivalents for PCDD/Fs (NTEQ;  $r^2=0.78$ ), as well as to EOC1 ( $r^2=0.90$ ) and most of the specific PCDD/F isomers analyzed (e.g., 2,3,7,8-TCDF;  $r^2=0.76$ ).

The down-core concentration profiles of the PCBs are different from the PAHs, showing no decreases from the 1970s and onwards (Fig. 6.8), except for the Gulf of Finland, where concentrations are slightly lower in the early 1990s than in the 1970s. The general concentration trend for the Baltic proper is however an increase from the early 1970s and onwards, which is in controversy with the decreasing concentrations trends for PCBs in pelagic biota from the Baltic proper. The possible reasons are discussed below.

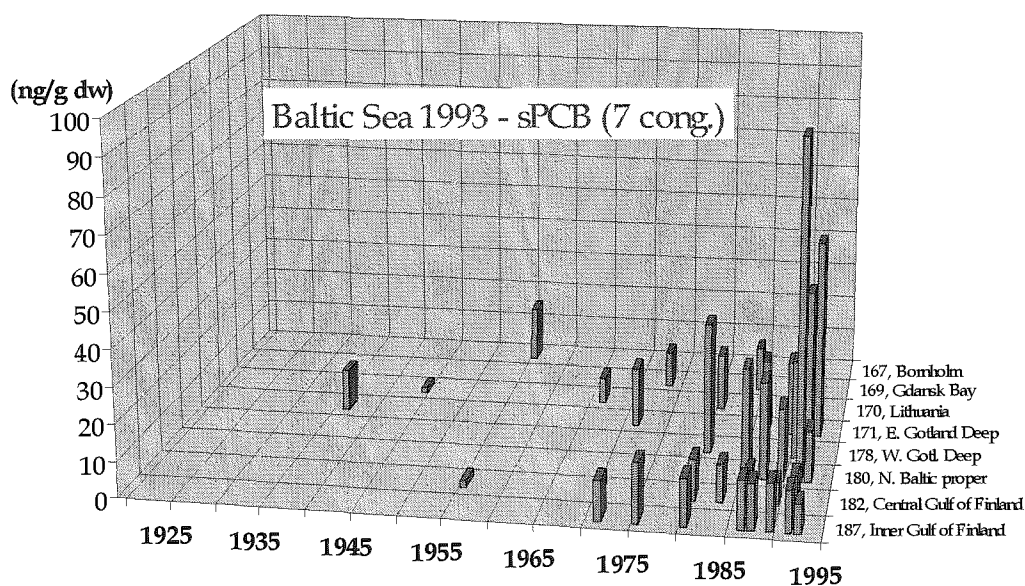


Fig. 6.8. sPCB (7 congeners) concentrations in 8 dated sediment cores from the Baltic proper and Gulf of Finland.

Also for PCBs, the almost constant relative congener composition with increasing sediment depth indicates very slow, or no degradation at all, of PCBs in the reduced and laminated sediments (Fig. 6.9).



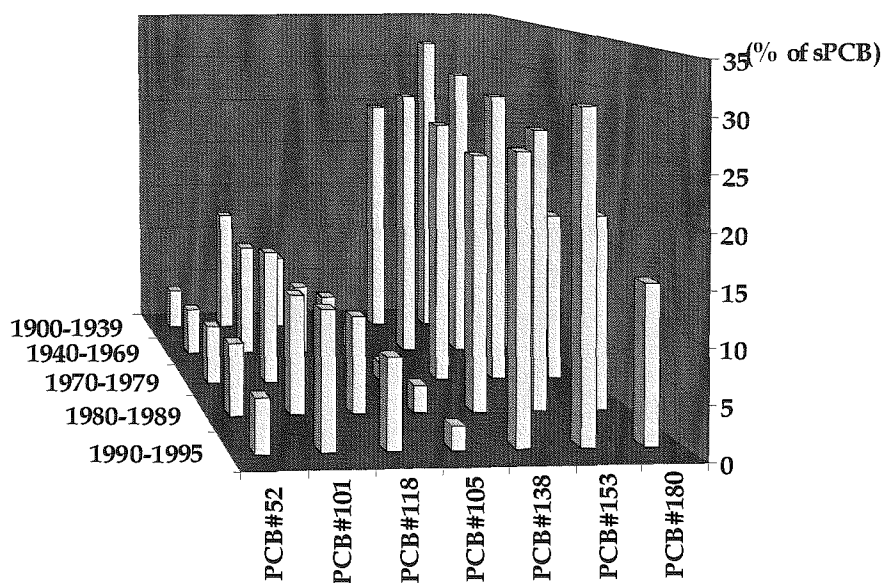


Fig. 6.9. The relative PCB congener composition (% sPCB) in 8 dated sediment cores from the Baltic proper and Gulf of Finland.

## 6.5 Contaminant sources

Since the the ban of DDT and restrictions on the use of PCBs in the early 1970s, considerable attention has been devoted to possible trends in the levels of organic pollutants in the marine environment. In the Baltic Sea, substantial downward trends has been observed for DDTs and PCBs in biota during the last 15-25 years (Odsjö & Olsson 1987, Olsson & Reutergårdh 1986, Bignert & al. 1993). sDDT and sPCB in herring from the Baltic proper decreased with approximately a factor 8 and 4, respectively. Also in guillemot eggs substantial decreases concentrations have been. The decreases have been assumed to be due to the restricted use of these contaminants in the Baltic area, although this conclusion has been questioned by Jonsson (1992), who suggested that the downward trend of sPCB in herring, at least partly, may be an effect of changed distribution of PCB within the ecosystem due to eutrophication.

In a mass balance study, using data from the Baltic Proper and the Bothnian Sea, Wulff & al. (1993) demonstrated that the discharges from pulp mills clearly dominated the input (75 %) of EOC1 to the Baltic Sea in the mid 1980s. The atmospheric input was estimated to 23 % of the total, while the input via rivers was negligible (< 2 %). More than 50 % of the input since the early 1940s was still stored in the Baltic system, although a substantial part must have left the Baltic through the Danish Sounds. The main part (80 %) of the store is found in the sediments and the rest in the water mass.

Although the main input of chlorinated compounds was to the Bothnian Sea, showing very high concentrations close to the mills, these coastal sediments contain only some 10 % percent of the total sediment store. About 90 % was dispersed from the discharges into the open sea areas, and the main part (ca. 60 %) of the sediment store was found in the Baltic proper, indicating a large-scale transport of EOC1. This mass balance is also a clear indication of a more efficient trapping in the anoxic/hypoxic sediments of the Baltic proper.

In Table 6.1, an attempt is made to estimate the annual sediment burial of sPCBs (7 cong.) in the 1990s based on analyses on sPCB in surficial (0-2 cm) sediment and estimates of dry matter accumulation rates in different parts of the Baltic Sea. Almost one ton sPCB is buried in the sediments every year which is about the same figure as the annual input to the Baltic Sea from rivers, direct discharges and atmosphere. This indicates that the Baltic Sea is an efficient trap of PCB, and that the Baltic proper sediments are the main sinks for PCBs in the Baltic. The estimated annual PCB burial of approx. 40 kg a<sup>-1</sup> compares rather well with a recent estimation of 20.6 kg a<sup>-1</sup> from sediment trap studies of

1996 (Kankaanpää & al. 1997). The mean concentration of sPCBs was 8.0 ng/g ds in 1996, which compares very well with the 10.2 ng/g value of 1993.

Table 6.1 Sediment burial of sPCB (7 cong.) in the Baltic Sea in the early 1990s based on estimates of dry matter accumulation rates from Borg & Jonsson (1996).

Area	Dry matter deposition (t a <sup>-1</sup> )	No. of samples	Average PCB concentration (ng/g dw)	Estimated PCB burial (kg a <sup>-1</sup> )
Baltic proper	31x10 <sup>6</sup>	n=10	23.7	735
Gulf of Finland	3,9x10 <sup>6</sup>	n=6	10.2	40
Gulf of Riga	3,2x10 <sup>6</sup>	n=2	13.3	43
Gulf of Bothnia	9,9x10 <sup>6</sup>	n=7	9.1	90
TOTAL BALTIC SEA				908

A totally different approach to the budget of halogenated compounds was adopted in a recent study by Kankaanpää (1997), indicating that natural production may be, at present, a substantial source of EOX in the Gulf of Finland. It has been suggested that industrial pollution from the pulp mills had only a local effect up to approx. 30 km off the sources, and further off industrial EOX could not be distinguished from the natural background. It was estimated that about 90% of the EOX sedimenting in the Gulf of Finland originated from natural sources (in 1997).

The EOX results from the Sediment Baseline Study of 1993 are well in accordance with the later observations: the EOX concentrations of this study (2.2-10.1, except station XV1; 12.7 µg Cl/g ds) were of the same order as in sediments (0.5-13 µg Cl/g ds) from 1993-1994, and the EOX levels increase toward the sediment-water interface. The correlation between the EOC1+EOBr (as EOC1 + 0.3 x EOBr) and EOX was low, which indicates that the two methods used by SI and FIMR produce different results from the same samples (parallel cores). This is not surprising since the extraction methods are different; SI used extraction from wet sediment using 1:1 cyclohexane – isopropanol and analysed only the cyclohexane phase while FIMR extracted dried samples with 4:1 cyclohexane – isopropanol. Therefore, probably much of the polar compounds that were included in the measurement (in the isopropanol phase) by FIMR were excluded in the analysis of SI. However, the EOX levels measured by FIMR were generally not higher than the EOC1 + 0.3 x EOBr measured by SI.

As there are two differing explanations for the source of EOC1 and EOX in the marine environment, it remains to be solved if the discrepancy is solely due to the two different chemical methods used. Obviously, the chemical methods should be uniformed and intercalibrated. The final explanation for the EOC1 and EOX levels in the marine environment may well be a synthesis of the two prevailing theories.

By calculating the record of annual burial of EOC1 in the offshore sediments of the Baltic proper and relating this to the annual discharges from the pulp mills Jonsson (1992) calculated the sediment burial efficiency. Until about 1970 the curves for load and sediment sequestering were well correlated, however, thereafter, a higher burial efficiency was indicated from the mid-1970s and onwards, coinciding well in time with the large-scale expansion of laminated sediments in the Baltic proper (Jonsson & al. 1990).

A similar time trend is indicated in the mean core from 1993. One important conclusion from this is that the burial efficiency of EOC1 is increased when altering the oxic and biotubated sediments into anoxic/hypoxic and laminated sediments, which occurred over large areas in the Baltic proper during the 1960s-1980s (Jonsson & al. 1990). Also our results concerning PCB burial in the sediments indicate increases with time during recent decades.

This interpretation is supported by former sediment investigations from the Baltic proper concerning persistent compounds like, e.g., PCBs (Pertilä & Hahti 1986, de Wit & al. 1990, Nylund & al. 1992,

Axelmann & al. 1995, Kjeller & Rappe 1995), DDTs (Perttilä & Haahti 1986, Nylund & al. 1992) and PCDD/Fs (de Wit & al. 1990, Kjeller & Rappe 1995) and sulphide-binding metals (Jonsson 1992, Borg & Jonsson 1996), in general showing increasing concentrations during recent decades in recently laminated Baltic proper sediments coinciding in time with the expansion of laminated sediments and clearly increasing organic content in the sediments (Jonsson 1992).

Assuming a dry matter deposition rate of  $31 \times 10^6$  tons/year (Jonsson & al. 1990) some 20 kg PBDE is buried annually in Baltic Sea sediments. This is approximately 50 times lower than the present burial of PCBs (cf. Table 6.1). However, in a core sampled in 1989 (Nylund & al. 1992), sPBDE showed a more rapid increase towards the sediment surface than sPCB and sDDT. This may be an indication of a recent substantially increased use of PBDE as flame retardants, but may also be an indication of different degradation rates and/or water solubility. In any case more interest should be focussed on PBDEs in the future to observe whether this is an increasing problem or not in the offshore Baltic Sea.

## 6.6 CONCLUSIONS

From the discussions above, it is indicated that we have a fairly good picture of the distribution patterns of many pollutants in the Baltic Sea, although the sources of EOCl and EOX may not only be industrial.

In the environmental administration, however, as in many other sectors of society, there is a clear tendency to consider only one problem at a time and thereby not realise the interactions between different problems.

The assumption that contaminants' sedimentation has been increasing partly due to the increased eutrophication is supported not only by the results from this investigation but also from several other studies showing substantial increases for many contaminants in Baltic sediments during recent decades. In time, these enhanced levels become correlated to the recent expansion of laminated sediments in the Baltic proper. Increased sediment burial efficiency is indicated for EOCl in relation to estimated load from pulp mills in recently laminated contaminated sediments.

For the Baltic there are indications that eutrophication processes has changed the fate of halogenated compounds in the ecosystem in a large-scale perspective. However, there are also reasons to underline that this may also be valid on a local level. This problem may serve as an example of the importance of a holistic approach, considering all the different environmental problems in the Baltic when remedial measures are to be defined.

Substantial parts of the contaminants were in 1993, when this investigation was carried out, buried in the mostly tranquil environment of the laminated sediments of the Baltic proper. As a result of an improved oxygen situation in the deep water, for example due to a major inflow of oxygen-rich water through The Danish Sounds, many contaminants may have been mobilized back into the water mass. We do not know at present whether the inflows during 1993 and 1994 has changed the situation.

Concerning the monitoring of sediments, it seems that EOCl and EOX alone, especially in open sea areas, are not suitable parameters for many of the stations studied. Long-term changes in pulp mill pollution can be traced only when data from chlorophenolics and possibly dioxins are combined with sum parameter data. However, close (approx. 0-20 km) to point sources EOCl and EOX are valuable parameters in evaluating organohalogen pollution.

## 7. SEDIMENT AGE DETERMINATION AND SENSITIVITY

Arne Jensen, Birger Larsen, Per Jonsson & Matti Pertilä

### 7.1 INTRODUCTION

During the Sediment baseline study the following techniques were used to date the sediment cores:

- $^{210}\text{Pb}$
- $^{137}\text{Cs}$
- X-ray
- Varve counting

The different techniques were useful in different parts of the investigation area and for different types of sediments. In general, all bioturbated cores were most accurately dated by the  $^{210}\text{Pb}$  method, which integrates the deposition rate over a number of years (Pheiffer-Madsen & Sørensen 1986).

In some deep areas of the Baltic proper, however, laminated sediments have been naturally formed during hundreds of years (Jonsson & al. 1990). In extensive areas of the Baltic proper and the Gulf of Finland bioturbated sediments were deposited until large-scale oxygen deficiency occurred during recent decades in the bottom water. Over vast areas, the benthic macrofauna was more or less wiped out causing structural turnover in the sediments from bioturbated to laminated conditions. For these recently laminated sediments the  $^{210}\text{Pb}$  method proved insufficient and resulted in clearly incorrect results, e.g., indicating a high mixing rate for obviously non-mixed sediments. These problems have recently been paid attention to by Carman & Rahm (1996) who consider  $^{137}\text{Cs}$ , plutonium and varve counting better adopted for dating of recently laminated sediments.

Therefore, in the sediment baseline study, we have chosen to adopt the dating results from  $^{210}\text{Pb}$  for the stations with clearly bioturbated sediments, whereas the other dating methods have been used, often in combination, for the laminated cores.

In chapter 7.1 the results from  $^{210}\text{Pb}$  dating are presented and discussed. The laminated areas are dealt with in chapter 7.2 and in 7.3 the final conclusions concerning which stations that are suitable as monitoring stations in the future.

### 7.2. BIOTURBATED SEDIMENTS – $^{210}\text{PB}$ DATING

$^{210}\text{Pb}$  (isotope of lead) in a sediment core originates partly from atmospheric deposition (unsupported  $^{210}\text{Pb}$ ) and partly from the decay of radon in the sediment core (supported  $^{210}\text{Pb}$ ). The background content of  $^{210}\text{Pb}$  is calculated from the concentration of supported  $^{210}\text{Pb}$  that is independent of the sedimentation, and estimated by measurement of supported  $^{210}\text{Pb}$  in the deeper parts of the sediment, where the concentration is constant since all unsupported  $^{210}\text{Pb}$  has decayed.

The  $^{210}\text{Pb}$  isotope has a half life of 22.3 years. The unsupported  $^{210}\text{Pb}$  is produced in the atmosphere through the decay of radon-222, which is spread by diffusion from the surface of the earth. These isotopes are part of the natural radioactive decay of uranium-238. The unsupported  $^{210}\text{Pb}$  enters the aquatic environment mostly via atmospheric deposition and descends, adsorbed to particles, to the sediments. The age of the sediments, and the average sedimentation rate can be determined by measurements of the  $^{210}\text{Pb}$  concentration in different sediment layers.

#### 7.2.2 Determination of $^{210}\text{Pb}$

In about ten slices (1 cm thickness) of the sediment core distributed down through the core the  $^{210}\text{Pb}$  concentration is measured indirectly by analyzing the concentration of  $^{210}\text{Po}$  (Polonium) with a-spectrometry (Pheiffer-Madsen & Sørensen 1979). The dried sediment samples (about 0.5 g) are

decomposed in a mixture of hydrochloric and nitric acid and  $^{210}\text{Po}$  is deposited on a silver plate at  $65^\circ\text{C}$ . The activity of  $^{210}\text{Po}$  is measured by  $\alpha$ -spectrometry. Samples are spiked with  $^{208}\text{Po}$  for determination of chemical yield and a  $^{210}\text{Pb}$  standard treated as the sediment samples is used for calibration.  $^{210}\text{Pb}$  activity is assumed to be equal to the measured  $^{210}\text{Po}$  activity.

### 7.2.3 Dating and estimation of the sediment accumulation rate

The age of the different layers of a sediment core is estimated from the activity profile of unsupported  $^{210}\text{Pb}$  in the sediment core under the condition that  $^{210}\text{Pb}$  is not mobile in the sediment. Different applied methods imply different assumptions. Besides, an estimate of the uncertainty of the datings is calculated. The dry sediment accumulation rate is calculated from the datings.

Details of the different methods of age calculation by means of the lead isotopes are published elsewhere (Jensen 1997). The first method (weighted linear regressions) assumes that the sediment accumulation rate as well as the  $^{210}\text{Pb}$  concentration in the new deposited sediment are constant. Besides, it implies that the flux of  $^{210}\text{Pb}$  is constant.

The second method (the Constant Initial Concentration, C.I.C.) assumes that the concentration of unsupported  $^{210}\text{Pb}$  in the depositing material is constant in time for the same locality. This means that the sediment accumulation rate may vary in time.

The third method assumes that the flux of unsupported  $^{210}\text{Pb}$  is constant in time for the locality. It means that the sediment accumulation rate and the concentration of  $^{210}\text{Pb}$  in the depositing material may vary. The method is named the C.R.S. method (Constant Rate of Supply). The following equation is valid

A description of the C.I.C. and C.R.S. methods can be found in Pfeiffer Madsen & Sørensen 1979.

Each dating method is based on different assumptions which may conform more or less to reality.

The linear regression method will be the most accurate if the conditions of a constant sediment accumulation rate as well as a constant flux of  $^{210}\text{Pb}$  down through the core are fulfilled. It has the advantage of other methods that the measurements in all layers are used in the calculation of age in each layer and the estimated, weighted variance. Besides, the estimated variance contribution from other error sources is calculated in addition to the counting variance. The variance estimate in connection with the other methods is calculated only on the basis of the counting variance.

The C.I.C. or C.R.S. methods can be applied if one of the above requirements are met. The advantages of these methods are that they only require conformation with one of the two assumptions for the use of the linear regression model. In most circumstances, the assumption of a constant flux of  $^{210}\text{Pb}$  (the C.R.S. method) down through the core will be the most probable assumption as the  $^{210}\text{Pb}$  input from the atmosphere is constant. The C.R.S. method is therefore the most common used sediment dating method.

The modified C.R.S. method may correct for the systematic errors in the traditional C.R.S. method, but only under the condition that the estimate of the remaining integrated activity is reasonable. Further, this requires that the conditions for the use of the linear regression method are met approximately.

Generally, the available information about the sampling locality as well as the dating expertise may be used in each case in the selection of the appropriate dating method.

The average dry sediment accumulation rate is calculated between the mass depths  $M_i$  and  $M_{i+1}$ , when the age datings have been calculated (Jensen 1997).

All the above mentioned dating methods assume that  $^{210}\text{Pb}$  is immobile in the sediment, i.e. that neither diffusion nor mixing take place in the sediment. These assumptions can be tested by the mixing/diffusion model shown below. Further, the model estimates the linear sediment accumulation rate with the assumption of constant sediment accumulation rate at the particular locality. This is the same assumption as the linear regression model requires.

The distribution of unsupported  $^{210}\text{Pb}$  in a sediment core can be modelled by the advection-diffusion equation and using the steady state solution with the condition of constant rate of sediment accumulation, the parameters and the flux of  $^{210}\text{Pb}$  to the sediment surface can be calculated. The mixing intensity is assumed to follow a half Gaussian distribution, (Christensen 1982, Christensen & Bhunia 1986).

### 7.2.4 Results

The data has been used for calculating the models described in chapter 7.2.3. Each model result is evaluated in details based at the obtained model results as well as the knowledge concerning the sampling locality. The model results which most accurate describe the age and sediment accumulation rate are selected. These results are described and commented below. Several of the models give in many cases nearly identical results and only the result of the modified C.R.S. method is presented.

The age of the sediment was calculated in relation to the depth of the sediment layer. It was impossible to perform datings at the cores from station no. 156 (Kattegat), 184 (GF-5) and 189 (Åland Sea) due to intense mixing in the upper part of the sediment core (Jensen 1997).

Table 7.2.1 shows the optimized solution of equation (as described above) for the cores as a function of the dry mass depth ( $\text{g cm}^{-2}$ ). The solution of this equation is based on the number of slices, as indicated in Table 7.1.1 Frequently, the upper part of the sediment core is mixed by e.g. bioturbation, trawling and sometimes the mixing is caused by the sampling equipment. To obtain the most optimal model solution for estimation of the sediment accumulation rate, some slices might be excluded from the upper part of the core, as indicated in Table 7.2.1 This implies that the sediment accumulation rate has been calculated from the subsequent sediment slices by estimating the linear decrease below the mixing zone. The mixing coefficient,  $D_0$ , and the effective mixing depth is estimated by an iterative process over the whole sediment profile. The sediment accumulation rate estimated by this model gives practical the same result as for the modified C.R.S. method.

### 7.2.5 Discussion

The results for the different cores indicate normally a linear accumulation rate in the upper part of the sediment core with a very little standard deviation for the estimated ages. The inclination changes often at higher depth, and the standard deviation increases significantly. The upper part of the sediment are in many cases excluded from the age determination due to disturbances. The age of this part of a disturbed sediment core is shown in the figures by linear extrapolation from the surface (1993) to the first calculated age where the age is shown with a prediction interval.

With a constant sedimentation rate, the relation between the logarithm of unsupported  $^{210}\text{Pb}$  concentrations as a function of the mass depth will theoretically be linear. If this is the actual situation, the results of the dating can be evaluated with good accuracy which normally implies a fine correlation between the depth and age of the sediment. The age relation in the individual slices can be complicated due to mixing.

The optimal solution to the steady state model correlates mostly with the measured concentration of unsupported  $^{210}\text{Pb}$ . Because of this, the calculated accumulation rate describes the sedimentation during this period. Deviations from the linear trend in the upper part of these profiles are an indication of disturbances by bioturbation etc. Generally, a linear decrease of  $^{210}\text{Pb}$  is observed below the disturbed zone.

Table 7.2.2 gives a summary of the estimated parameters and with an indication of the quality of the dating. The calculated effective mixing depth (s cm) is equivalent to a real mixing depth of 2-3 times s, since the effective mixing depth is calculated as a half Gaussian distribution.

Some of the cores have had a sufficient length that the concentration of  $^{210}\text{Pb}$  in the deepest part is constant (Table 7.2.1 – supported  $^{210}\text{Pb}$  (SPB)). However, for several cores it has been necessary to use a value from a nearby sediment core as the core has not been long enough. For other cores which were

not deep enough and which have a high concentration of  $^{210}\text{Pb}$  down to 20-25 cm a SPB has been chosen giving the best fit to the model. This information is included in Table 7.2.1

Table 7.2.1 Number of sediment slices included in the model calculations for sediments from the Baltic Baseline Study.

Station name and no.	Supported $^{210}\text{Pb}$ - depth <sup>1</sup> dpm g <sup>-1</sup>	Number of slices included in model	Number of slices excluded in model optimization	Remarks
Kattegat, 156				Dating impossible
Kiel Bight, 157	1.02-25	20	10 (0-10 cm)	
Lübeck Bay, 160	1.01-21	19	5 (0-3, 10-11, 12-13 cm)	
Arkona Basin, 166	0.50	22	13 (0-13 cm)	
Bornholm Basin, 167	1.02 (157)	10	3 (0-3 cm)	
Gdansk Bay, 169	1.02 (157)	21	0	
Lithuanian Coast, 170	0.99-19	12	1 (0-1 cm)	
Gulf of Riga, 175	1.00	45	1 (0-1 cm)	
GF-1, 181	1.60-24	13	7 (0-7 cm)	
GF-4, 183	2.20-21	20	12 (0-12 cm)	Dating 12-20 cm.
GF-5, 184	12.6-14			Dating impossible
GF-6, 185	1.00	16	1 (0-1 cm)	Core not deep enough, only 25 cm deep
GF-3, 186	1.00	25	10 (0-10 cm)	
Åland Sea, 189	High $^{210}\text{Pb}$			Dating impossible
EB-1, 190	2.50	25	0	Core not deep enough, only 25 cm deep
Hamosand, 192	2.50	25	9 (0-9 cm)	Core not deep enough, only 25 cm deep
BO-3, 193	2.50	13	5 (0-5 cm)	
F2, 195	2.50	13	3 (0-3 cm)	

<sup>1</sup> The activity of supported  $^{210}\text{Pb}$  (SPB) is given as dpm g<sup>-1</sup> and at which depth it has been measured (cm). If the core has not been long enough the SPB from a nearby core has been used (indicated by the core number). In several cases another value of SPB have been chosen which gives the best fit in the model.

Table 7.2.2. Accumulation rate, mixing coefficient, and effective mixing depth for sediments from the Baltic Baseline Study.

Station name and no.	Accumulation rate		Mixing coefficient $\text{cm}^2\text{yr}^{-1}$	Mixing depth cm		Quality of dating
	Mass $\text{g m}^{-2}\text{yr}^{-1}$ $\pm$ s.d.	Linear $\text{mm yr}^{-1}$ (depth 0-2 cm)		Effective model	Real	
Kattegat, 156						Dating impossible
Kiel Bight, 157	313 $\pm$ 9	1.5	150	3.0	6-9	**
Lübeck Bay, 160	508 $\pm$ 18	2.3	1	2.1	4.2-6.3	**
Arkona Basin, 166	260 $\pm$ 58	1.4	150	4.1	8.2-12.3	*
Bornholm Basin, 167	250 $\pm$ 23	1.6	43	1.1	2.2-3.3	**
Gdansk Bay, 169	879 $\pm$ 91	7.5	12	0.1	0.2-0.3	***
Lithuanian Coast, 170	1,111 $\pm$ 241	5.3	43	0.4	0.8-1.2	***
Gulf of Riga, 175	1,512 $\pm$ 50	7.8	525	0.7	1.4-2.1	***
GF-1, 181	353 $\pm$ 88	1.7	535	2.1	4.2-6.3	*
GF-4, 183	391 $\pm$ 11	-	-	-	-	**
GF-5, 184						Dating impossible
GF-6, 185	1,851 $\pm$ 127	15.0	43	0.1	0.2-0.3	***
GF-3, 186	729 $\pm$ 81	5.0	525	3.3	6.6-9.9	**
Åland Sea, 189						Dating impossible
EB-1, 190	1,520 $\pm$ 96	6.0	150	0.5	1.0-1.5	***
Harnosand, 192	1,173 $\pm$ 74	4.6	525	2.6	5.2-7.8	***
BO-3, 193	325 $\pm$ 28	1.8	43	1.4	2.8-4.2	***
F2, 195	352 $\pm$ 30	1.9	12	1.4	2.8-4.2	**

s.d. = standard deviation

\*\*\* good dating, \*\* reasonable dating, \*poor dating

### 7.2.6 Sensitivity of the response for bioturbated sediment for pollution load changes

Another model calculation was performed on the basis of the datings of bioturbated cores. The purpose of this calculation was to evaluate the sensitivity of the sediment areas to measure changes in pollution input. The principle of this sensitivity analysis is described by Larsen & Jensen 1989.

The following input were used in the model calculations:

- depth of sediment surface sample (10 mm used)
- the sediment accumulation rate
- the mixing described by D and s
- the number of years between sampling: 3, 5, and 10 years
- the relative analytical standard deviations (% RSD) for the chemical analyses
- selected at 10%. These RSD are obtainable for the methods normally used, for example, atomic absorption spectroscopy used in heavy metal analysis. If a higher RSD is expected the per cent relative change in pollution input flux shall be multiplied by this factor (a RSD of 20% means that the flux shall be multiplied by two).

Table 7.2.3 shows the results of these model calculations and indicates that several locations are very useful in monitoring changes in pollution inputs.



Table 7.2.3. Sensitivity for pollution monitoring with a relative standard deviation of 10% for the chemical analysis.

Station name and no.	% change in input flux		
	Number of years between sampling		
	3	5	10
Kiel Bight, 157	235	155	85
Lübeck Bay, 160	40	30	20
Arkona Basin, 166	310	205	115
Bornholm Basin, 167	105	65	35
Gdansk Bay, 169	10	10	10
Lithuanian Coast, 170	15	15	10
Gulf of Riga, 175	25	15	10
GF-1, 181	295	180	95
GF-6, 185	10	10	10
GF-3, 186	135	85	50
EB-1, 190	20	15	10
Harnosand, 192	90	60	30
BO-3, 193	100	65	35
F2X, 195	75	50	30

The results have been the basis of the conclusions and recommendations (Chapter 2). If sediment samples are taken and analyzed every fifth year, it will be possible to detect changes in pollution input from 10-50 % for station no. 160 (Lübeck Bay), 169 (Gdansk Bay), 170 (Lithuanian Coast), 175 (Gulf of Riga), 185 (GF-6), 190 (EB-1) and 195 (F2). The differences are caused by the different accumulation rates and mixing in the upper part of the sediment cores. If sampling is only performed with a frequency of ten years the majority of localities where datings has been performed are very suitable to use in a pollution monitoring programme with changes in input flux of less than 50%. The exceptions are st. no. 157 (Kiel Bight), st. no. 166 (Arkona Basin) and 181 (GF-1).

### 7.3 LAMINATED SEDIMENTS – DATING WITH X-RAY AND VARVE-COUNTING

Laminated sediments are frequently found in lakes with low oxygen concentrations in the bottom water (see e.g. Renberg 1981, Renberg & Wik 1985, Renberg 1986 and in the Baltic proper offshore areas (Jonsson & al. 1990, Jonsson 1992) and archipelagoes (Morris & al. 1988). The lamination may either be due to natural morphological properties of the specific are, or to recently increased loading of organic matter and/or nutrients caused by Man. Without the bioturbating macrobenthic fauna, the normally occurring seasonal changes in the composition of sedimenting matter are preserved in the sediments as more or less distinct annual varves or lamina.

Due to the lack of macrobenthic fauna and the subsequently low bioturbation in the laminated sediments, we consider the time resolution for environmental changes to be very high in this type of sediment. Thus, also the sensitivity of the sediment response for pollution load changes may be considered higher in the laminated sediments than in the bioturbated.

In some of the cores clearly visible varves have been documented. This is most evident in the cores from Gotland Deep (171), West Gotland Deep (178), LL-19 (180), GF-2 (182) and XV-1 (187), but also the cores from GF-1 (181), GF-3 (186) and GF-4 (183) have clearly visible lamination in the upper parts of the cores. Preferably in the cores from the Gulf of Finland also the  $^{137}\text{Cs}$  profiles give good guidance in distinct dating of the sediment level corresponding to the Chernobyl fallout in 1986. The dating of these cores (Table 7.2.1) are therefore based on a combination of  $^{137}\text{Cs}$  dating and varve counting from CD images and x-ray photographs.

Table 7.3.1. Accumulation rate, mixing depth and estimated quality of dating for laminated sediment cores from the Baltic Baseline Study.

Station name and no.	Accumulation rate		Mixing depth (mm)	Remarks	Quality of dating
	(g m <sup>-2</sup> yr <sup>-1</sup> )	(mm yr <sup>-1</sup> )			
Gotland Deep (171)	310	2.9	< 2.9	Surf. fluffy layer	*
W. Gotl. Deep (178)	230	1.0	< 1.0		*****
LL-19 (180)	1500	21	< 21		*****
GF-2 (182)	1770	5.9	< 5.9		*****
XV-1 (187)	2000	12	< 12		*****

\*\*\*\*\*excellent dating, \*\*\*very good dating, \*\*good dating, \*reasonable dating, \*poor dating

In chapter 2, a discussion has been presented concerning the occurrence of a fluffy layer in the upper 5-10 cm of the core from the Gotland Deep. The uncertainties in dating due to this layer is the reason why the quality of dating has been judged to be poor in the core from the Gotland Deep. In the other four cores the very clear lamination indicating neglectible degree of bioturbation provides excellent conditions for precise dating.

#### 7.4 CONCLUSIONS CONCERNING STATIONS SUITABLE FOR FUTURE MONITORING

From the discussions in 7.2 and 7.3 conclusions may be drawn from the dating exercise concerning the different stations suitability for monitoring purposes. In Table 7.4.1 we have summarized the information in three classes, i.e. if sampling is performed 1/ every fifth year 2/ every tenth year and 3/ not suitable for monitoring.

Table 7.4.1. Characterization of the observation stations with respect to monitoring (overall conclusions).

Station name and no.	Sampling frequency		Not suitable for monitoring
	Every 5 years	Every 10 years	
Kiel Bight (157)			X
Lübeck Bay (160)	X	X	
Arkona Basin (166)			X
Bornholm Basin (167)		X	
Gdansk Bay (169)	X	X	
Lithuanian Coast (170)	X	X	
Gulf of Riga (175)	X	X	
Gotland Deep (171)			X
West Gotland Deep (178)	X	X	
LL-19 (180)	X	X	
GF-1 (181)			X
GF-2 (182)	X	X	
GF-3 (186)		X	
GF-4 (183)		X	
GF-6 (185)	X	X	
XV-1 (187)	X	X	
EB-1 (190)	X	X	
Hamosand (192)		X	
BO-3 (193)		X	
F2X (195)	X	X	

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