

**COOPERATIVE RESEARCH REPORT
RAPPORT DES RECHERCHES COLLECTIVES
NO. 180**

REVIEW OF CONTAMINANTS IN BALTIC SEDIMENTS

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<https://doi.org/10.17895/ices.pub.7967>

ISBN 978-87-7482-640-8

ISSN 2707-7144

International Council for the Exploration of the Sea
Palægade 2-4, DK-1261 Copenhagen K
DENMARK

February 1992

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CHAPTER 1 - CONCLUSIONS

Matti Perttilä

The sediments offer a tremendous potential for the follow-up of the relative changes in the concentrations of the inorganic and persistent organic contaminants in the marine environment. Concentrations of harmful substances in water are known to be variable, depending on water exchange, season and hydrographical factors, while concentrations in biomaterial depend, among other things, on species, tissue type, age of the specimen, and the migration habits of the species. In peaceful net sedimentation areas, the sediments represent the local hydrodynamic regime, integrating the changes in the concentrations of persistent substances over a period of time, the length of which depends on the sedimentation rate. While the rate of sedimentation depends on the season, it has a great tendency to remain constant over the years.

In the Baltic Sea, the use of biota as a pollution indicator suffers from the drawback that, because of the strongly varying environmental conditions, only very few, if any, species are represented in all the subareas in at least roughly equal abundances. Due to the harsh conditions and low salinities in the northern areas, the species distribution and abundances differ greatly from those encountered in the southern parts of the Baltic Sea. This may affect the comparability of the results.

If certain hydrochemical and biological conditions are met concerning, e.g., stability of sedimentation, redox and bioturbation, the sediments also offer a possibility to analyse the long-term changes in these concentrations. This possibility is offered by means of measuring changes in the concentration of the radioactive ^{210}Pb in the sediment core.

However, the mathematical analysis, taking into account the typical instrument detection level, the mean sedimentation rate and the depth of the typical bioturbation, indicates that several years may pass before a change in the environmental conditions (e.g., increase or decrease of discharges) can reliably be detected in the sediments.

The presently available data are very fragmentary. This holds true especially for the chlorinated hydrocarbons and petroleum hydrocarbons, but also for many trace elements.

Because of the above reasons, treated in the following chapters in more detail, it is suggested that sediments should be taken up as a follow-up medium for studies of contaminants in the Baltic marine environment. However, ordinary monitoring on an annual basis is not recommended, but rather a Baseline Study should be conducted with the aim of obtaining reliable data on contaminant levels in the various sub-areas of the Baltic Sea.

The sediments provide an exceptional possibility to measure in a consistent way the differences and changes in environmental contaminants. This is so because of the possibility to study not only the present-day concentrations, but also at the same time the history of the sampling site with regard to the contaminant in question. The sediments thus yield a great deal of information for the periodic assessments of the state of the Baltic Sea, which are produced at five-year intervals under the Baltic Marine Environment Protection Commission (Helsinki Commission). The second periodic assessment was completed in 1990, and the third assessment is scheduled for 1995. In order to take full advantage of the repeated baseline studies in sediments, the first study should be carried out not later than in 1993.

The data collected so far on contaminants in Baltic Sea sediments are very fragmentary. The chemical methods, including the digestion, extraction, analysis and data evaluation, vary even though reliable reference materials are available for both organic and inorganic analyses. An account is given in the Review on the recommended chemical methods for analysing inorganic and organic constituents in the sediments, together with other characterizing information (grain size, normalization, etc.).

An intercomparison exercise on the chemical methodology has been carried out, and the results indicate serious discrepancies among the participating laboratories' experimental methods. For the organic contaminants, no methodological intercomparison has been carried out. It is also known that different devices are used for sediment sampling, and that the method of sampling may have an effect on the stability of the layering of the sediment core, thus disturbing the actual concentrations as well as the history of the sample. The first baseline study on contaminants in sediments should thus be carried out as a joint experiment.

The expedition should be conducted by one ship and should cover all the important sedimentation areas in the Baltic Sea, with scientists from all the countries participating in the Baltic Monitoring Programme. The exact sampling positions, while taking into account the recommendations given in the following chapters, should be determined on board, using accurate bottom mapping and satellite positioning.

In order to ensure the fruitful outcome of the first baseline study, a Steering Group has been set up at the 1990 ICES Statutory Meeting, with experts from all the participating countries. The participation in this group should follow the recommendations of the 1990 report of the ICES Working Group on the Baltic Marine Environment.

The primary task of the Steering Group is to organize the first sediment baseline study in the Baltic Sea. To support the Third Periodic Assessment of the Helsinki Commission, due in 1995, the study should be undertaken not later than in 1993. The sampling and the types of chemical analyses should be decided upon by the group, with the help of the subsequent chapters of this Review, where the most reliable methods are discussed. It is known that in practically all laboratories, modifications have been developed of the standard textbook methods, and the effects on the results, due to changes in analytical methods, have not always been thoroughly evaluated. This is almost certainly one of the reasons for the present scarcity of reliable data. In order to produce reliable data during the sediment baseline study, it is recommended that only a small number of dedicated sediment laboratories take the responsibility of analysing the samples. This sharing of the work should be decided by the Steering Group.

The Baltic Sea bottom and the sediment types, as described in detail in the subsequent chapters, are very variable. There are very few articles giving emphasis to the representativeness of the sediment stations. Mainly for reasons such as the frequency of earlier sampling, and the seemingly probable representativeness, in this Review a selection of sites is given. This selection should, however, serve only as a basis for further site analysis, to be carried out by the group. In sediment sampling, not only the selection of a particular subarea, but also the accurate location of the site is important. In many cases, the variability in the bottom type and topography is such that shifts of a few hundred meters can produce largely different results. Therefore much of the site selection work can only be undertaken during the expedition itself, and the best available technology should be used for determining the exact coordinates of the sites. It is also expected that a visual inspection of the bottom can in many cases yield valuable information as to the

usefulness of a particular site for sediment sampling. The ship to be used for the expedition should thus be equipped with suitable technology for visual inspection of the bottom.

This Steering Group should start its work immediately with the following terms of reference:

1. The group is expected to organize the first baseline study of contaminants in sediments in the Baltic Sea in 1993.
2. The group should make a selection of the number and positions of the sedimentation stations to be visited during the baseline study.
3. The elements and substances to be analysed in the samples, and the chemical methods to be used, should be selected with a view to the results indicated by the sediment intercalibration organized by ICES, and the data referred to in the Sediment Review.
4. As much as possible, the chemical analyses should be carried out by dedicated marine laboratories, possibly dividing the work among only a few laboratories, in order to ensure the data quality.
5. The ICES reporting format for contaminants in sediments should be used, in order to ensure that all relevant background information is also collected.
6. The group should report the data and results of the first baseline study so that they can be included in the third assessment of the Baltic Sea, to be compiled by the Helsinki Commission.

CHAPTER 2 - GENERAL DESCRIPTION OF THE BALTIC SEA BASINS

2.1 THE GULF OF BOTHNIA

Lauri Niemistö

Geological structure

The Baltic Proper is connected with the Gulf of Bothnia by a number of deep channels running both through the Archipelago Sea between the Åland Islands and the SW mainland of Finland and connecting the deep of the Åland Sea. The channels have formed at least partly by exaration along fracture zones that probably formed during the Precambrian. A set of very prominent channels links the Åland Deep with the Bothnian Sea. All the channels are characterized by very steep sides.

In the southern part of the Bothnian Sea the sea floor is very rugged, but further north the Paleozoic sedimentary rocks cover the crystalline rocks and change the bottom into gently undulating forms with thick post-glacial sediment filling the Eastern Basin. The northern boundary of this gentle topography runs NW from Pori in Finland to Härnösand in Sweden along a major fracture zone. Further north the sea floor has again a more rugged nature. The sea floor around the Härnösand Deep is characterized by large-scale drift forms, sometimes exceeding 100 m in height (Winterhalter, 1972). There is a rather sharp contrast between the bottom morphology off the Finnish coast as compared to that off the Swedish coast. The Finnish side is largely rather flat whilst the Swedish side of the coastline is governed by a series of faults and fractures which make the bottom morphology highly irregular, even near the coast. Large shallow-water areas occur in the central and southern parts of the Bothnian Sea.

In the north, the Bothnian Sea has a shallow connection, called the Quark, with the Bothnian Bay. The same general features, asymmetrical morphology, rugged on the Swedish side and gentle on the Finnish side, typical of the Bothnian Sea also hold true in the Bothnian Bay. The uneven sea floor in the central and northeastern part of the Bay is mainly caused by deposits of glacial drift of variable thickness and by channels running mainly NW-SE (Tulkki, 1977).

The Åland Sea is dominated by soft bottoms in the depression. The deepest and narrowest parts are eroded by bottom currents, hence the top surface consists of coarse-grained lag sediments. The area northeast of the depression is characterized by a rough bedrock topography with consequently associated alternation of hard and soft bottoms.

In the Bothnian Sea, west of the basin area that links the Åland Deep with the Härnösand Deep, large areas are dominated by hard bottoms. Along the coast of Sweden, as well as that of Finland, hard bottoms separated by minor soft bottom areas are present. From the coast off the town of Pori in Finland, a broad esker extends northwestwards almost across the entire sea. The reason why it is not visible on more than a part of the map is that it is covered in the central parts by thick soft deposits. Near the shore, coastal processes have destroyed the original ridgelike form of the esker. A more typical esker system exists in the southwestern part of the Bothnian Sea where the Uppsala Esker (Hoppe, 1961) extends as an underwater ridge approximately 100 km towards the NNE, illustrating well how complex the sediment distribution appears when detailed information is available.

Very extensive deposits of glacial drift occur in the northwestern part of the Bothnian Sea just off the coast of Sweden. Further to the east there is a large drumlin field. All of these drift forms are more or less exposed, with soft sediments in between and sometimes on the flanks. A more comprehensive description of the Quaternary sediments of the Bothnian Sea is given by Winterhalter (1972).

The conditions in the Bothnian Bay, constituting the northernmost part the Baltic Sea, are dominated by resedimentation of material derived from shallower areas. This dominance is due to the very rapid land uplift in the region and the vast shallow areas exposed to wave erosion. Sand waves are very common in the northeastern part of the Bay. Several of the eskers along the Bothnian Bay coast have submarine extensions. A review of the geomorphology and the sediments of the area has been prepared by Tulkki (1977).

The hydrography of the Gulf of Bothnia differs from that of other parts of the Baltic Sea. The relative amount of the more saline water annually flowing into the Gulf is larger than that in the Baltic Proper. Since the water flowing into the Gulf is mainly surface water of the Baltic Proper, its salinity is only slightly higher than that of the water body in the area. Therefore no sharp halocline can be formed. Under these circumstances, thermal winter convection takes place throughout practically the whole water column. Consequently, oxygen saturation seldom decreases below 60-80 per cent and anoxic conditions have never been recorded in the water.

The surface layers of the sediments are always oxidized, the redox potential exceeding + 250 mV (Bågander & Niemistö, 1978). The excellent conditions for the removal of phosphorus from the water phase are further enhanced by the considerable amount of iron transported into the Bothnian Sea.

Another special feature is the rapid land upheaval which, in the Northern Quark, attains as much as 0.9 cm per year and in the Archipelago Sea 0.3 cm yr⁻¹. New sea bottom areas are continuously revealed for wave erosion, and the water below 50-60 metres is almost continuously turbid (cf. e.g., Fukuda, 1960).

Types of sediments and sedimentation rates

Compiled by Matti Perttilä

Main source: Paavo Tulkki (1977)

Although autochthonous biological production is weak in the Bothnian Bay, there is abundant discharge of organic matter by rivers (Gripenberg, 1934). As a result the content of organic material in the silt is up to 7 %, which is of the same order of magnitude as in the biologically more productive southern Baltic Sea (7.3 % - 9.5 %) (Kolp, 1958).

Between the central sedimentation basin and the coast are restricted areas that are located in separate depressions sheltered by islands and shallows occupied by soft sediments. The upper boundary of the silt is at a depth of 15 to 20 m. These discrete accumulation depressions are most common in the northern Bothnian Bay into which the largest rivers transport sedimentary material. Near the coast of Sweden the sedimentation rate is intensified by the great depth of the fjord-like bays and the submarine extensions of the river valleys. In the same area the bottoms are soft, even in shallow regions (<20 m). The discrete accumulation areas are most sparse in the Quark and in the sea north of it (south of 64°N).

A description of the Bothnian Bay sedimentation areas is shown in Fig. 2.5.1.

Near the coast the bottom of the depressions is composed of material close in quality to the clayey silt in the central basin. The abundance of organic material is high, 4 % - 7 %. The depressions off Oulu are occupied by well-sorted silt and fine sand fractions. In the depressions farthest out the abundance of organic material decreases to 2 % or less. Thus the nearshore depressions act as effective collectors of the finest sediments and organic material, even though they are markedly shallower than the central Bothnian Bay.

On the basis of echograms and bottom samples, the sediments on the sea floor were classified into three main types: silts, sands and till. The silt sediments can be subdivided into two subtypes that do not differ much from each other in composition: the extensive silts in the central basin and the silts with small surface area in the littoral depressions. The deepest till occurrences, overlain by silt and abundant iron manganese concretions, are considered as a till subtype. Silt sediments covered by sand also abound in the Bothnian Bay.

The Bothnian Bay is free from the pure clay bottoms that prevail elsewhere in the Baltic Sea. Nowhere in the Bothnian Bay is the water so stagnant as to allow the pure clay fraction to deposit permanently.

The typical black or dark colour of the silts is caused by the relatively large amount of allochthonous organic matter, which undergoes decomposition in the deposits.

The till is not of the common type but partly sorted and recognisable as till primarily on account of the topography typical of till. The sand-covered silt bottoms occur often between the silt areas and the till zones, and were formed through the erosional action and transport of moving water. The sand bottoms, which are connected with sand occurrences on the mainland, derive often from numerous eskers levelled by littoral forces and from which the sand spreads out around the original esker. The Lohtaja esker is the only indisputably glacial formation; it has levelled on the coast and in the shallow water but, deeper down, it continues as a well-defined esker on the floor of the Bothnian Bay.

About one-half of the floor of the Bothnian Bay is under the influence of erosion. As a rule, the erosion zone extends to a depth of 60 to 70 m, but locally down to a depth of 80 m. The material discharged by rivers from the mainland and the minerogenic matter ground by the action of waves on the shallow bottoms are transported to the central parts of the sea and to the littoral depressions where the silt fraction may deposit permanently. Some of the finer matter migrates with the net southerly flow of water to south of the Quark. The shallow bottoms between the accumulation area and the littoral zone are areas of weaker erosion. The coarser matter deposits here and it is thus a transitory zone for fine-grained matter. The Quark and the areas north of it, as well as the bottoms of the eastern Bothnian Bay, form large, uninterrupted erosional areas, partly because of the shallowness of the area and partly because the energy of the currents flowing through the Quark to the Bothnian Bay is directed to the bottoms of these areas. The macrotopography of the sea floor controls these currents in such a way that the counterclockwise flow typical of the Bothnian Bay turns westwards at the ridge between Lohtaja and Rödkallen and only the surface current reaches the northern Bothnian Bay. This is a partial explanation for the lack of sediment deposition at the ridge. At the same time, the ridge is the principal site of iron manganese concretions. North of the ridge the area is subject to intense sedimentation, because the movements of water are less vigorous and the big rivers discharge abundant depositing material.

The effect of the energy released by waves in the shallowest parts of the Bothnian Bay is demonstrated in the levelling of the Lohtaja esker in waters shallower than about 10 m. Internal waves may have an effect on the sedimentation in the deepest depressions. Even though the internal waves have not been studied in the Bothnian Bay, their occurrence at depths of 40 to 70 m is highly probable, particularly in the autumn, when the turbulence in the water and the flow associated with waves may prevent the finest sediments from depositing.

Depending on the methods employed and the location, the rate of sedimentation in the Bothnian Bay has been estimated at 0.6 to 1.9 mm yr⁻¹. The rate is of the same order of magnitude as elsewhere in the Baltic Sea. Echo-sounding data indicate that since the Ice Age, about 150×10^9 t of silt sediments have deposited in the areas of active accumulation in the Bothnian Bay. This amount is 10 to 15 times as high as it would be if rivers were the only source of suspended solids, as computed on the basis of the contents of suspended solids in present-day rivers. Winterhalter (1972) reached a similar conclusion in his study of the Bothnian Sea. The "surplus" of sediments in the Bothnian Bay may be attributed to redeposition due to land uplift and to the formation of fine-grained sediments through the action of littoral processes. The profiles of the rivers running to the Bothnian Bay have been levelled as a result of land uplift and so some of the solids suspended in rivers have deposited in present-day inland lakes. The construction of dams in rivers in the past few decades has had the same effect and solids have started to deposit in the basins rather than reach the Bothnian Bay.

In the eastern basin of the Bothnian Sea, which is the largest accumulation area here, the sedimentation rate measured on one station is about 2.4 mm yr⁻¹ (Niemistö and Voipio, 1972). The distribution of the sediment types in the Bothnian Sea is depicted in Fig. 2.5.1 (Emelyanov, 1988).

2.2 THE GULF OF FINLAND

Jaan-Mati Punning

Geological structure

The Gulf of Finland is the easternmost gulf of the Baltic Sea, extending approximately 400 km in length and 50-120 km in width, with an area of about 30 000 km². The water regime of the Gulf is greatly influenced by the large catchment area of about 420 000 km². The inflow regime is determined by the large lakes of Onega and Ladoga. The drainage basin of these lakes, located on the middle Taiga hill and the ridge plain, constitutes about 73 % of the gulf's catchment area. The Neva river, flowing into the 10-28 km wide Neva Bay in the eastern end of the Gulf of Finland, gives 18-20 % of the total amount of river water flowing into the Baltic Sea.

The calculations by Nilsson (1986) show that the input of suspended material to the Gulf of Finland (estimation based on data from the period July 1975 - December 1976) is rather low, only 138 000 t. This is caused by the flat character of the drainage area and the big lakes, which act as traps, and the small erosion energy of the inflowing waters.

The rocky northern coast of the Gulf of Finland is rich in skerries; on the slightly indented southern coast the cliff at places extends to the sea.

The bathymetry, relief and sediments have been rather poorly studied. The average depth is low. On the southern coast of Finland there is a 20-30 km wide area with a mean depth of less than 40 m. Mostly the depth varies between 40 and 100 m. The Gulf is deeper at its south coast and also in its eastern part where the bottom relief is also more indented.

In the shallow bottom areas the dominating Quaternary deposits are soft- and hard-bottom types. Together with the increase of depth, there is a transition from soft bottom with minor hard bottom outcrops to a soft bottom type consisting of silt, clay and mud.

In the section of bottom deposits, the lacustrine (Ancyclus phase) and the subsequent marine sediment complexes can well be distinguished by lithological and geochemical composition as well as colour. The Ancyclus deposits are typically dark grey pelites with distinguishable layering. Hydrogen sulphide can often be found. The transition from the deeper Ancyclus lake sediments to the more recent marine sediments is usually sharp, at which an interruption surface may occur. Greenish-grey pelite to aleurite pelite is typical of the marine deposits. Deposit gaps and off-carriage of deposits may often occur, which requires the use of the ^{210}Pb method in determining the age of the recent sediments.

Several maps of the Baltic Sea bottom deposits have been compiled and published. The material gathered has served as the basis for a geological map of the Baltic Sea bottom (1:500 000) containing sufficient information for planning further detailed geological work as well as determining suitable areas for special studies (pollution, contouring of concretion fields, search for building materials, etc.). The map-set still lacks the lithological map of bottom sediments (the surface layer of bottom sediments) which is especially important for identifying regions with active sedimentation. Relying on published material as well as material still under processing, several opinions are presented here which should be considered when planning special studies in the Gulf of Finland.

Types of sediments and sedimentation rates

The types of sedimentation areas in the Gulf of Finland are shown in Fig. 2.5.1.

Recent sediments (formed during the last 4000 years) are rather widely distributed in the axial part of the Gulf of Finland. It must be borne in mind that the morphometric axis (deeper areas) has been shifted somewhat to the south of the geographical central line of the Gulf, and especially in the areas deeper than 70 m. The zone of pelitic sediments penetrates the Gulf of Finland from the estuary and extends to I. Naissaar as a constant 20-25 km wide zone (tongue). To the east, from I. Naissaar to I. Aksi this zone becomes narrower (10-15 km) but continues. To the east of I. Aksi the axial zone of recent sediments reaches its initial width and extends practically to 26°30'E. Still more to the east the general picture of sediments becomes rather mosaic and geomorphological preconditions must be borne in mind while looking for suitable areas. Deeper bays penetrating into the mainland (the bays of Tallinn, Kolga, Eru, Hara) may be considered quite suitable polygons for special studies. The Käsnu Bay is less useful. It is not very probable to find extensive and noticeably thick areas of recent sediments between Vergi and Sillamäe at depths less than 60 m. A rather extensive area of recent sediments is situated in the central part of the Narva Bay (to the NW of Narva-Jõesuu, at a water depth of 20 m and more, between 27°30'E and 28°00'E; also around the islands of Suur- and Väike-Tütarsaar, at a depth of over 55 m).

The rate of sedimentation in the Gulf of Finland, especially in the eastern part, is higher than that in the Gulf of Bothnia. Niemistö and Voipio (1981) report the value of 7.4 mm yr^{-1} for a nearshore station in the eastern Gulf of Finland, which is the highest rate measured in their studies of the northern parts of the Baltic Sea.

2.3 THE GULF OF RIGA

V.V. Gordeyev and V.M. Kuptsov

The Gulf of Riga is situated in the eastern part of the Baltic Sea. The area of the gulf is $16\,330 \text{ km}^2$, or ca. 4.2 % of the overall Baltic Sea area.

The bottom forms a cup-like deep, in the center of which there is a meridianally running rise with the Ruhnu island elevating on it. Generally, the depth of the bottom in the Gulf of Riga slightly exceeds 40 m, the maximum depth of 56 m being located eastward from the central rise.

Geological structure

In the basement of the sediment mass of the Gulf of Riga bottom, the most pronounced are Silurian (in the northern part) and Devonian (in the central and southern areas) rocks (Blazhchishin et al., 1977). Silurian rocks have a predominantly calcareous composition, while the Devonian ones are terrigenous - calcareous. The thickness of Silurian deposits may attain 500 m, while Devonian rocks may attain 800 m thickness (Sviridov, 1981).

The Quaternary mass is represented by Pleistocene and Holocene deposits. Among the Pleistocene deposits one can distinguish glacial, lake glacial and marine glacial deposits (moraines, varved clays, loams, homogeneous clays); among early and middle Holocene deposits are clays (muds), sand and gravel sediments; among the present deposits pelitic muds, mudstone, sand-gravel and boulder-gravel can be distinguished.

The moraine thickness in the Gulf of Riga attains 30-50 m. Soft deposits include weakly consolidated and unconsolidated sediment (varved clays, muds, mudstone). Their thickness extends up to 30-35 m, the maximum values being located in a furrow east of the Ruhnu island.

The expedition on R/V "Akademik Kurchatov" (cruise 26a, 1978) operating in the southern part of the Gulf of Riga managed to obtain for the first time a complete Holocene profile (at st. 2595, Fig. 2.3.1). The cores successively penetrate medium and upper Holocene marine oozes and aleurites, followed by freshwater *Ancylus strata* overlying, after a hiatus, late-glacial sediments. The latter are represented by homogeneous clays, varved clays and aleurites.

In the western deep the thickness of the marine Holocene layer (8000 yrs) is 3.9 m, whereas in the eastern deep it varies between 3.4 and 4 m. Similar thickness values of the marine Holocene layer were observed off the Daugava mouth area.

An important feature of the Holocene masses in the Gulf of Riga is a powerful gas formation. The muds have a notably high cavernosity with the smell of H_2S discernable in some cases; in other cases the smell is absent, the gas being represented by methane. The cavernosity of muds may be attributed to the fact that gases, which had formerly been present in the form of crystallohydrates, then passed into their original form with a dropping pressure and increased the volume of sediment.

Types of bottom sediments and sedimentation rates

The distribution of the various types of bottom sediments in the Gulf of Riga is shown in Fig. 2.3.1 (see also Fig. 2.5.1).

The sediments are represented by terrigenous sediments, from sands to pelitic muds, the replacement of granulometric types occurring gradually: sands are deposited in the near-shore zone, whereas the pelitic muds cover the central parts of deeps. Soft sediments, which are of interest for pollution studies, occupy the central areas of the gulf and include terrigenous muds of fine-aleuritic, aleuritic-pelitic and pelitic size. An oxidized layer is present in the sediments nearly all over the gulf, but with a thickness varying from parts of mm to 10-15 cm. Ferro-manganese nodules (spheroidal, discoidal and crust-like) are confined to gently sloping sides of the deeps with low sedimentation rates (Varentsov and Blazhchishin, 1976).

The distribution of linear sedimentation rates in the gulf is shown in Fig. 2.3.2. Determinations were performed by two different procedures: most data were obtained by use of the ^{210}Pb method, and some by the radiocarbon (^{14}C) method (Kuptsov et al., 1984). Corresponding mass accumulation rates are given in Fig. 2.3.3.

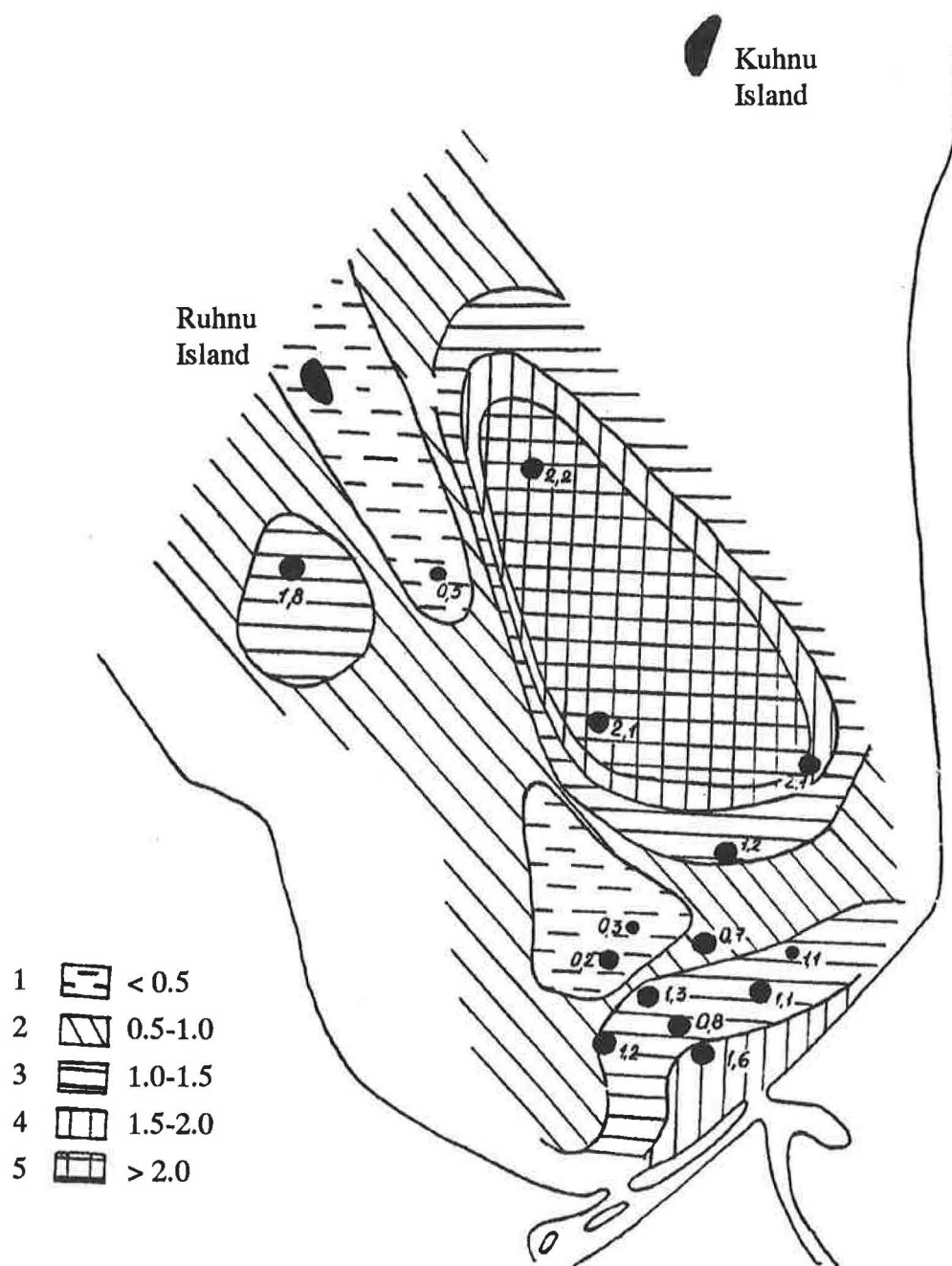


Fig. 2.3.2 Linear sedimentation rates (in mm yr^{-1}) in the Gulf of Riga.

2.4 THE GDANSK BASIN

S. Uscinowicz

The Gdansk Basin is in the SE part of the Baltic Sea. To the Gdansk Basin belong the Gdansk Deep and the Gulf of Gdansk. The SW, S, SE and E boundaries of the Basin are formed by the Polish and Lithuanian coastlines. In the NW the Gdansk Basin is connected with the Gotland Basin, from which it is divided by a protrusion of the sea bottom in the form of a ridge running from SW to NE at a depth of about 80 m. The maximum depth in the Gdansk Basin is 117 m.

Geological structure

The direct substratum of Quaternary deposits at the Gulf of Gdansk coast are upper Cretaceous and Tertiary deposits. The upper Cretaceous layer consists of marls, sands and glauconitic sandstone of marine origin. The Tertiary is represented by marine Oligocene and land Miocene deposits.

The Oligocene deposits are in the form of quartz-glauconitic sand and sandy clay with glauconite, phosphatic concretions and pieces of amber. Miocene deposits appear in the form of clays, silts and very fine quartz sands with mica, coal dust and layers of brown coal.

Upper Cretaceous deposits represented by silty sands with glauconite were found in two bores located in the NW part of the Gdansk Deep.

The top of the substratum of the Quaternary is at a depth of about 90-100 m below surface level in the southern and northern part of the Gdansk Basin to about 140 m below surface level in the central part (ca. 50 km E of Rozewie).

The Quaternary is represented by Pleistocene and Holocene deposits. At the southern coast of the Gdansk Basin, the Pleistocene appears as glacial till, fluvioglacial sediments and sediments of marginal lakes of the South Polish, Middle Polish and North Polish glaciations and as marine sediments of the Eem Interglaciace. The thickness of these sediments is between about 50 and 120 m (Mojski and Sylwestrzak, 1978; Makowska, 1978).

Within the Gdansk Deep the thickness of Pleistocene sediments ranges from about 10 to about 20 m. These sediments are represented by glacial till, varved, microvarved and homogeneous clays.

As a rule the glacial tills form one layer of 1 to 10 m thickness deposited during the North Polish glaciation. Varved, microvarved and homogeneous clays were formed during the Late Glacial in the Baltic Ice Lake. The thickness of the Late Glacial Baltic Ice Lake deposits ranges from 0 m, at the ridge dividing the Gdansk and Gotland Basins, to about 10-15 m in the central part of the Gdansk Deep.

Holocene deposits are represented by grey-brown and light grey Yoldia Sea and Ancyclus Lake clays, deposited during the Preboreal and Boreal Periods, and by olive-grey and dark grey and sometimes black Litorina Sea and Post-Litorina Sea clays and muds deposited during the Atlantic, Subboreal and Subatlantic periods.

The thickness of the Yoldia Sea and Ancylus Lake deposits ranges from 0 to 4-5 m, with an average of 2-3 m. Recent sediments of the Litorina and Postlitorina Sea form a layer with an average thickness of 6 m, reaching a maximum of 9-10 m.

The recent sediments covering the bottom of the Gdansk Deep, as with the Yoldia Sea and Ancylus Lake sediments, are at their thickest in the central part of the Deep. At the border of the Gdansk Deep their thickness is only 0.5-1.0 m. Locally, for instance in the ridge dividing the Gdansk and Gotland Basins, they are totally absent.

Sandy sediments cover the coastal zones of the Gdansk Basin, reaching into the sea to the 40-50 m isobaths in the west and 60-70 m isobaths in the eastern part of the Gulf of Gdansk.

Types of sediments and sedimentation rates

The distribution of the sediment types in the Gdansk Bay is shown in Fig. 2.5.1.

The source of the suspended matter from which recent muds of the Gdansk Deep are formed is the Pleistocene till and clay from eroded cliffs of the Rozewie region, the western part of the Gulf of Gdansk and the Sambian Peninsula. The eroded coast of the Sambian Peninsula supplies annually about 2.37 million tonnes of material (Emelyanov and Wypych, 1987). Rivers are an important source of suspended matter. The Vistula supplies annually about 1.5 million tonnes of suspended matter and 10 million tonnes of material in solution (Stoch et al., 1980); the Njemen (through Klaipeda Straits) supplies 0.23 million tonnes of suspended matter. Much suspended material, about 1.25 million tonnes per year, comes to the Gdansk Basin from the amber mines of the Sambian Peninsula (Emelyanov and Wypych, 1987). The annual rate of sedimentation, as obtained from ^{14}C and ^{210}Pb dating, varies from 0.5 to 4.0 mm.

Recent muds of the Gdansk Basin bottom are represented, with regard to grain size distribution, by silts, clayey silts, silty clays and clays. Most often, these sediments are olive-grey to black. The basic components of the Gdansk Deep muds are quartz, the percentage of which by weight is 30-40 %, and clay minerals. The most important of the clay minerals is illite, the second in order of importance is chlorite. Of less importance are kaolinite, smectite and mixed-layer minerals.

The organic matter content is, depending on the granulometric type of the sediment, between about 5 and 15 %. As regards chemical composition, silica dominates. The range and mean contents of selected elements are as follows (data from chemical analyses of 20 samples) (Pieczka, 1980).

Table 2.4.1 Major constituents in Gdansk Bay sediments.

SiO ₂	=	46.04 % - 79.71 %	mean	58.18 %
Al ₂ O ₃	=	6.68 % - 14.23 %	mean	11.19 %
Fe ₂ O ₃	=	2.18 % - 7.67 %	mean	4.57 %
CaO	=	0.87 % - 2.36 %	mean	1.46 %
MnO	=	0.02 % - 0.45 %	mean	0.26 %
P ₂ O ₅	=	0.10 % - 0.27 %	mean	0.18 %
SO ₃	=	0.38 % - 3.49 %	mean	2.05 %

2.5 THE BALTIC PROPER

E.M. Emelyanov

Geological structure

The Baltic Sea is comparatively shallow: the depth does not exceed 100 m for most parts of the area. However, there are basins with depths up to 249 m (Gotland Deep) and even 459 m (Landsort Deep). These deeps and others, e.g., Bornholm, Gdansk, Fårö, are good traps of mud: in just these basins green-grey sapropelitic-clayey muds began to accumulate from the moment when the Baltic Sea joined the Atlantic Ocean.

The first maps of bottom sediments were published by Gripenberg (1934), Pratje (1948) and Gorshkova (1960). Recently, about 3000 sediment samples were collected from the Baltic Proper, the Gulfs of Finland and Riga and from the Arkona Basin. Nearly all of them were studied granulometrically. About 1500 samples were analysed for CaCO_3 , SiO_2 terr, SiO_2 am, Corg, Al, Ti, Fe, Mn, K, Na, Cu, Zn, Ni, Co, Cr, Ba, V, Mo, Sn, Li, Rb, W, and for their bulk mineralogical composition. According to these data, new maps of the Baltic Sea were compiled, including the map on "surface" sediments (0.5 cm) (Fig. 2.5.1).

Types of sediments and sedimentation rates

The Baltic Sea is a young sea; it was formed on the place of a glacial lake. Its bottom is the latest morainic substrate. This determined the character of the main part of the sediment material reaching the floor. The main sources of this material are the shores and bottom, which are abraded and eroded very actively. By these processes, 17 million tonnes of solid material a year are supplied to the sea (without counting the Gulf of Bothnia) (Blazhchishin, 1984_b). Rivers supply only 4.6 million tonnes of solid material a year (Blazhchishin, 1984_a; Tulkki, 1977). That is approximately 3.5 times less than the shores and eroded parts of the sea bottom supply. According to the average annual primary production of 100 g C m^{-2} (Koblentz-Mishke and Konovalov, 1981), the Baltic Sea produces $77 \times 10^6 \text{ t}$ of organic matter or $115 \times 10^6 \text{ t}$ of the whole biogenic material. Only 1.5 %, or 1.7 million tonnes, of biogenic material is buried in sediments (Blazhchishin and Pustelnikov, 1977). From all material buried in the bottom, the share of abrasional and erosional (bottom material) is 73 %, the share of rivers is 19 %, and the share of organogenic is 7-8 %. This composition of pre-sediments formed on the bottom defines the four most important peculiarities in the distribution of bottom sediments in the Baltic Sea: 1) the wide-spread regions with an absence of recent (late-Holocene or even Holocene) sediments on the floor; 2) the wide-spread outcrops of late Quaternary moraines and products of their erosion (gravelly-pebbled sediments, relict sands) on the surface of the bottom; 3) the extent of exclusively terrigenous sediments with no biogenic component; and 4) in sediments there is a predominance of products of moraines (tills) erosion and more ancient sedimentary rocks outcropping on the shore cliffs, but not the products of the erosion of soils and of weathering. The following types of bottom sediments were defined (Fig. 2.5.1):

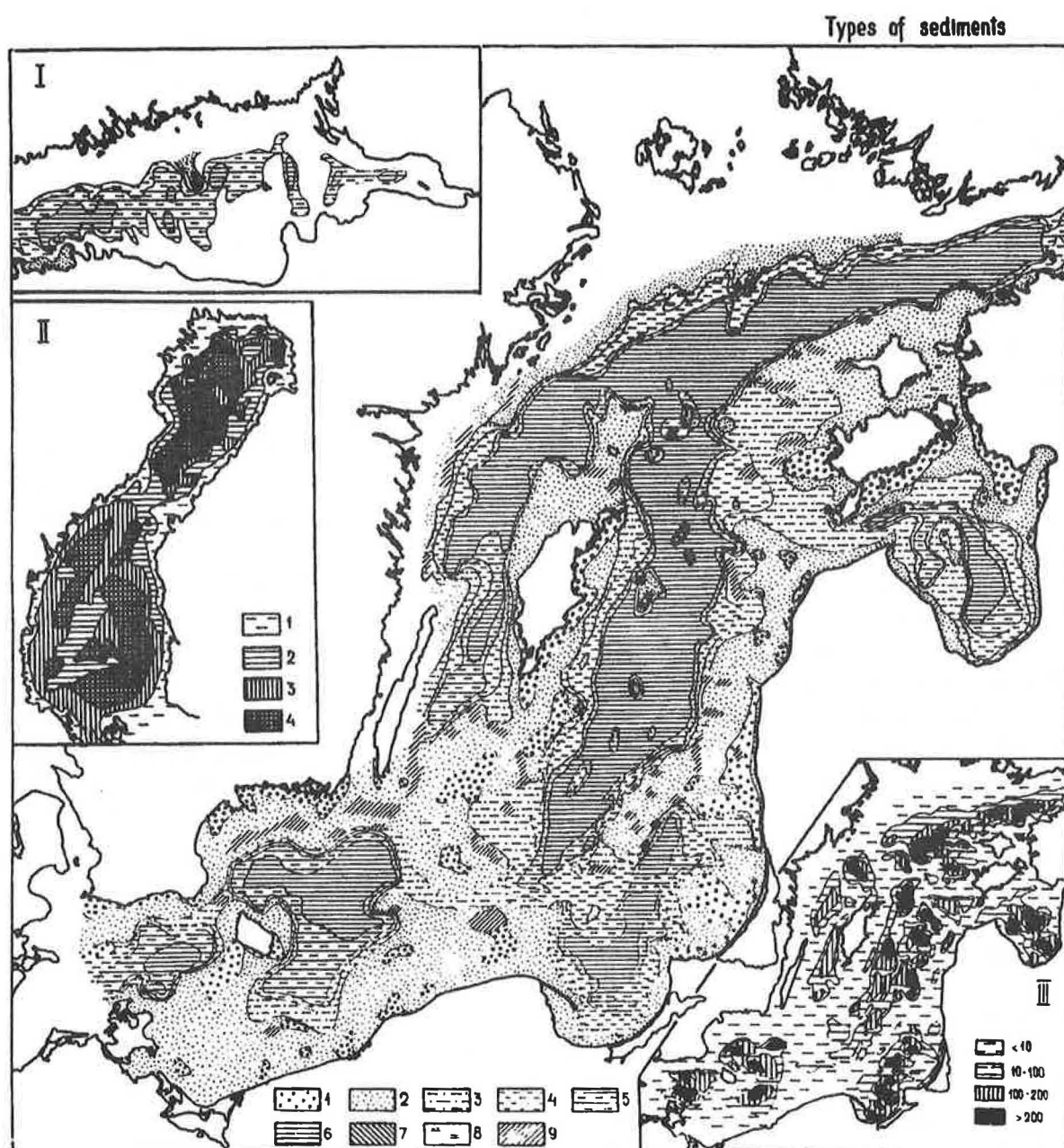


Fig. 2.5.1 After Emelyanov (1988). Types of bottom sediment in the upper layer (0-5 cm):

1 - pebble-gravel deposits;	2 - sands;
3 - coarse aleurites;	4 - fine-aleurite muds;
5 - aleurite-pelitic muds;	6 - pelitic muds;
7 - homogeneous (lake) clays;	8 - varved clays;
9 - moraine deposits.	

I - Gulf of Finland
 II - Gulf of Bothnia
 III - Baltic Proper

1) rubbly-pebbled and gravelly sediments (material which is more than 1 mm predominates, i.e., makes up > 50 % of the whole sediment; 2) sands (material predominates which size is 1.0-0.1 mm, usually 0.25-0.1 mm); 3) silts (fraction 0.1-0.05 mm predominates). If, in the fraction 0.1-0.01 mm, the fraction 0.1-0.05 mm predominates it is defined as coarse silts (coarse aleurites); if the fraction 0.05-0.01 mm predominates, it is fine silt. 4) Aleuritic-pelitic mud (amount of fraction < 0.01 mm is 50-70 %); according to terminology which is used in many countries this corresponds mostly to the term "mud". 5) Pelitic (clayey) mud, the amount of the fraction < 0.01 mm is more than 70 %. According to the terminology usually in use this corresponds to the term "clay".

As seen from Fig. 2.5.1, the two types of sediments most common in the Baltic Sea are sand and clayey muds. The first is confined to littoral sections or banks, the second nearly exclusively to deeps. Aleuritic-pelitic muds usually border clayey muds with narrow strips, which are disposed along external (upper) sides of the basins. Aleuritic sediments are distributed in the form of narrow strips, which are disposed between aleuritic-pelitic muds and sands. Wide fields of outcrops on the surface of the bottom of morainic sediments are observed in medium and shallow depths (100-10 m). In some regions these sediments are covered with a layer of residual sands with a thickness of 1-10 cm only. If we take off this layer, the areas of outcrops on the surface of the bottom of morainic deposits (tills) increase noticeably, and sands become smaller (Emelyanov, 1988). Recent sands are distributed mostly at depths down to 30-40 m, i.e., in the area of sea wave processing. They are reworked and redeposited during hard storms. Relict sands are distributed deeper. Usually, the upper border of clayey (pelitic), aleuritic-pelitic and fine aleuritic muds is situated under the layer of the pycnocline. In connection with that, as far as advancing from the Danish straits to the north-east, the pycnocline dips and the upper border of muds deepens in this direction, too. In the Arkona Basin muds lie at a depth of 35-40 m, in the Gdansk Basin at 60-70 m, and in the Gotland Basin at 80-100 m. When the pycnocline disappears (during the strong mixture of upper and deep layers of water), muds are removed much below the level of the pycnocline. Above or at the level of the pycnocline, muds lie only on the deeps of the floor, which are the hydrodynamic traps. Thus, a clear bathymetric location of muds and clastic sediments (sands and silts) is observed in the Baltic Sea. This division is conditioned by stratification of the water strata into an upper, hydrodynamically active and a deep, hydrodynamically less active layer.

There are exceptions to this rule. They are expressed by those relict sands which have been formed during the initial stages of Holocene transgression and which now can be situated below the pycnocline. In this case, below the pycnocline we can find strong near-bottom currents. In the central parts of the Gotland Deep, regions with the absence of holocene muds are found. This absence is explained by the presence of a near-bottom current, which is directed from the south to the north. This current is formed by the "intrusion" of salty North Sea waters into the Gotland Basin whereby two deep-water currents are formed: one is a contour current, which is directed along the isobaths on the eastern slope of the Gotland Basin, the second is near-bottom, and is directed to the deeper part of this basin from the south to the north (Grisenko et al., 1988).

Clayey muds of the Baltic Sea are hydronomical illitic and montmorillonitic-hydronomical in general. Only in the Gdansk Basin are they vermiculite and montmorillonitic-hydronomical. On the whole, muds of the sea consist of clayey minerals (30-45 %), quartz and feldspars (15-30 %), calcite and dolomite (3-10 %, sometimes more) (Table 2.4.1, p. 15). More detailed information about the mineral composition of bottom sediments has been listed in the literature (Lisitzin and Emelyanov, 1981; Emelyanov and Wypych, 1987).

In general, the chemical composition of bottom sediments is determined by their grain size distribution. We can separate three groups: I - SiO_2 total and Sn; II - CaCO_3 , Zr, W; III - all the other elements studied (Al, K, Na, Fe, Mn, Ti, P, Cu, Zn, Ni, Cr, Co, Ba, V, Mo, C_{org}). The first group of elements concentrates in high contents in the littoral zone, i.e., where the sands are distributed (fraction < 1.0 - 0.1 mm), the third concentrates in the deeps, i.e., where pelites are collecting (fraction < 0.01 mm) (Emelyanov, 1981, 1982, 1986b). This determines a clear confinement of chemical elements of the third group exclusively to deeps of the Baltic Sea (Blazhchishin and Emelyanov, 1977; Emelyanov, 1976, 1981, 1986a,b, 1988). Thus, the character of the distribution of elements, according to the granulometric types of sediments and the bottom area as a whole, is determined by processes of mechanical separation of sediments, i.e., it depends completely on the hydrodynamic regime of the sea. However, chemical elements are concentrated in the basins in different ways in spite of the approximately identical granulometric and mineralogical composition of muds. In the first place, it depends on the appearance and persistence of hydrogen sulphide in the near-bottom waters, and on the periodicity of the cycles of stagnation and aeration changes. More clearly periodicity of stagnation of littoral waters is expressed in the Gotland, Fårö, and Landsort Deep. Here the deep water below the pycnocline is divided into two layers: oxygen- and hydrogen sulphide-containing layers. On bottom sections which are washed by oxygen-containing water, the concentration of chemical elements is the same as in basins where hydrogen sulphide practically never appears (for example, in the outlying regions of the Gdansk basin (Emelyanov and Wypych, 1987)). In deeper parts of the basins with a constant periodicity of stagnation, muds of another composition accumulate on their slopes, i.e., above the O_2 - H_2S barrier. In stagnation zones, muds are usually microlaminated sapropelitic (3-5 % C_{org}) or sapropelic (5-10 % C_{org}). In separate microlayers 5-7 % of SiO_2 am was found.

In the upper layer (0-5 cm), contents of C_{org} exceeding 4 % are found in the muds of all studied basins: Arkona 5.64 %, Gdansk 5.16 %, Gotland 5.14 %, Fårö, Northern Baltic Proper and Landsort 4 %, the Gulf of Finland 4.25 % (Emelyanov, 1988). In shallow regions with sands and coarse-silts, and in morainic deposits the content of C_{org} does not exceed 1 %. Thus, the sea basins are effective accumulators of organic matter. In the microlayered muds of the Gotland Basin, a maximum content of C_{org} of 9.81 % was found for the Holocene layer.

2.6 WESTERN BALTIC SEA

Compiled by Lutz Brüggemann, Dieter Lange and Th. Leipe

Geological structure

As to their geological classification, the Belt Sea and the Arkona Sea are part of the transitional area between the Central or West-European table and the eastbound East-European table. The structural-tectonic-palaeogeographical development during the Caledonian and Alpidic epoch resulted in the formation of a complex block fault structure characterized by Hercynic, Rheinisch or East-West directed disturbance system, which showed considerable variations in the intensity of its mobility during the geological periods.

The regional disturbance system has left its traces on the relief of the sea floor in form of the course of isobaths, the coastal configuration, as well as the succession of late-glacial ice marginal positions. The thickness of the Palaeozoic-Cenozoic sedimentary basin may amount to 10 km

or even more. The present-day forms of the sea floor of the western Baltic have been decisively shaped by repeated alternating advances and retreats of ice during the Pleistocene Period as well as through late-glacial ice break-down and the Holocene transgression process. The forward pushing ice masses dug basins, valleys and troughs (trenches) depositing glacial debris as ground, end and lateral moraine.

The process of ice retreat began in the investigated area between 15 000 and 14 000 years before present (yr B.P.). Ice break-down was no continuous process; it was interrupted by several phases of stagnation and recurrently returning ice, which deepened the existing trough systems and basins. In the course of the next ice retreat, these depressions between ice marginal positions were filled with deposits of melt-waters such as stratified clays, muds, sludges and sands. Depending on the relief of the ground moraines, the thicknesses of the melt-water deposits varied from 2 to 6 m in the central part of the Mecklenburg Bay and from 2 to 12 m in the central part of the Arkona Basin. At the turn of Boreal/Atlanticum sometime before 8 000 yr B.P. the level of the ocean started to rise so rapidly that the sill regions in the Danish Straits were flooded within a short time, and in the course of the beginning Litorina transgression there was a salt-water intrusion into the western part of the Baltic. Depending on the Pleistocene relief the sea level reached at different times the individual parts of the investigated area. During this process sea water flooded local limnic waters (Mecklenburg Bay and Lübeck Bay) or forced its way to areas not covered by water before. For this reason littoral deposits cover varying pre-littoral sequences. Relative deep-water conditions dominated from time to time during the Litorina transgression, whereby the salinity was more than 10 ppt higher than the present salinity in the western Baltic. Already a short time after the beginning of the transgression, mud sedimentation started in the deeper basins and troughs of the investigated area. With the advancing transgression process the mud deposits took over bigger and bigger areas. Today, mud takes up nearly the entire area of the Mecklenburg Bay below the 22 m isobath. On the western edge of the Mecklenburg Bay the mud limit rises locally to 18 m, while in the southern part the mud sedimentation starts only at water depths of 24 to 27 m. In the Arkona Basin, the mud sediments are spread almost over the entire area up to the 40 m isobath. The only exception is the trough east of the Island Rügen, where mud rises to the 20 m isobath. The mud thickness may amount to 7 m in the southern part of the Lübeck Bay and 14 m in the southern part of the Arkona Basin. In general the thicknesses of the Holocene muds are clearly increasing in the basins in a direction from north to south.

The mud regions are connected at the edges to areas, in which the sand components are increasingly influencing the character of the grain mixture. The transition zone from the muddy-clayish basin sediments into the sandy marginal sediments varies considerably depending on the coastal configuration, the formation of the underwater relief and the intensity of the processes going on both in the composition of grain and in the region-wise expansion.

Near-bottom water stratum

The bottom water stratum is characterized by interactions between the surface layer of the sediment (turbulences, remobilization) and fluctuations in salinity, oxygen content, nutrient content, etc. in correspondence to dynamic conditions of currents and waves.

The seston amounts measured in the near-bottom water stratum of the Mecklenburg Bay and the Arkona Sea have been on average 3 to 4 mg l⁻¹ (Niedermeyer, 1987). Measurements by light scattering photometer (Prandke, 1986) have given for this suspension-rich layer a thickness of

2 to 5 m. Under stagnant conditions this near-bottom water stratum is characterized already by a reduction in oxygen and redox potential values. The share of organic matter in the seston of the bottom water stratum has risen during the past 20 years from 10 % to 40 % (Zeitzschel, 1965; Niedermeyer, 1987), which shows clearly the effects of increasing eutrophication. The suspended material of the sedimentation process consists of organic substances (30 to 40 %), biogenic gravel-like and carbonatic particles (20 to 40 %) and terrigenous, detritic material (quartz, feldspar, mica, clay minerals, 30 to 50 %).

Sediment types and sedimentation rates

The distribution of sediment types in the area of the Mecklenburg Bay is depicted in Fig. 2.6.1.

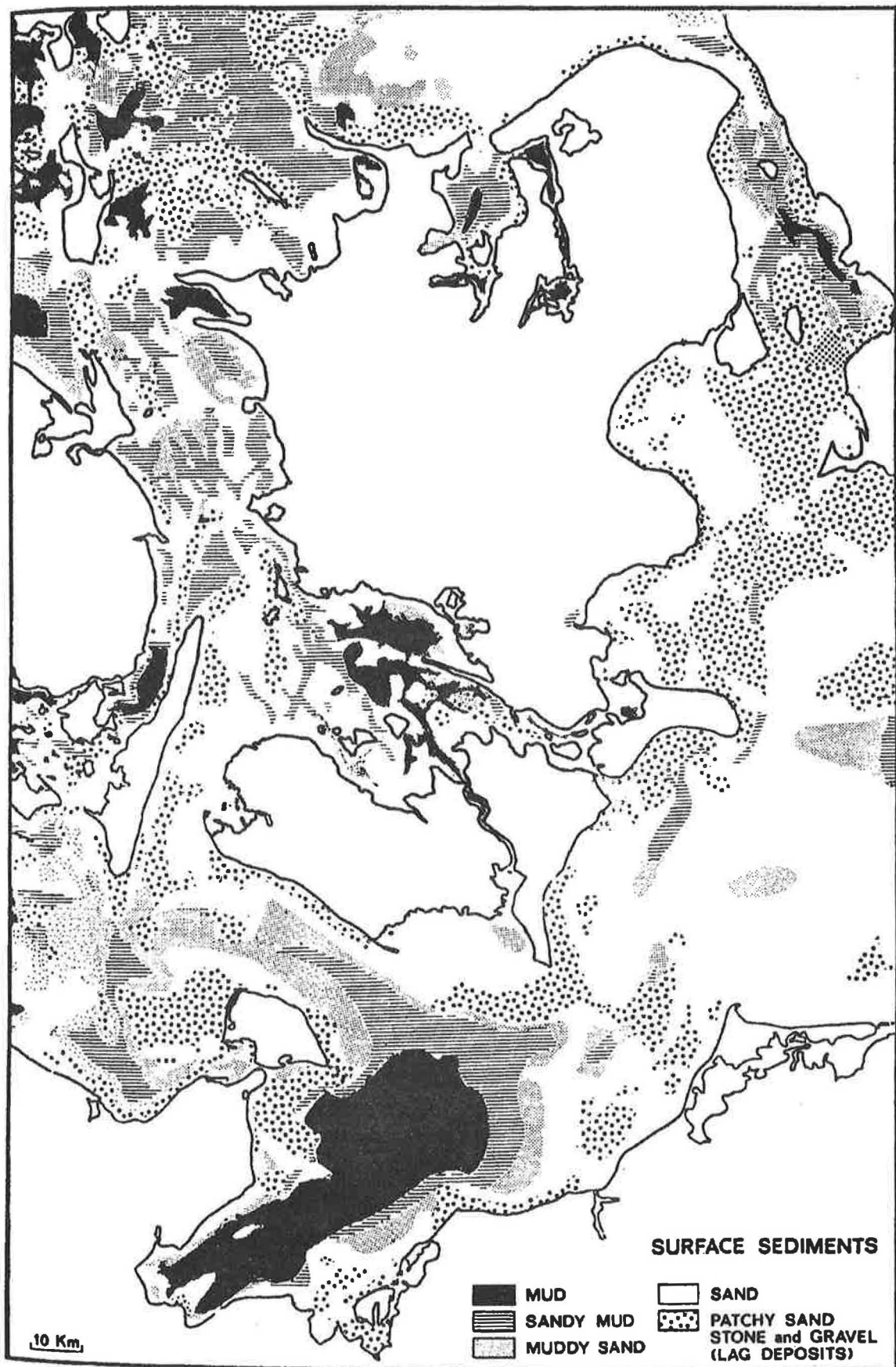


Fig. 2.6.1 Distribution of sediment types in the Mecklenburg Bay area. (After Pheiffer-Madsen and Larsen 1986.)

Although having various thicknesses and distributions, the muds of the three partial basins (Kiel Bay, Mecklenburg Bay and Arkona Sea, see also Figs. 2.7.1 and 2.7.2) show similar compositions. The mineralogical composition of the mud sediments corresponds to the composition reported by Rudolph (1968) for the Mecklenburg Bay.

The mud sediments of the three partial basins of the southwestern Baltic Sea reflect in their terrigenous components the composition of glacial and post-glacial deposits of the geological frame (supply regions). (This connection was suggested already by Müller (1971) for the area of the Mecklenburg Bay and the continent bordered on the south.)

The sedimentation rates in the mud regions of the Baltic Sea are on average 1 to 2 mm per year (different authors; for a review, see Brüggmann and Lange, 1981). The data on sedimentation rates may vary considerably from region to region.

Data on accumulation of organic carbon in sediments (mud) of the Kiel Bay are reported by Balzer et al. (In Rumohr et al. (1987)). The values are somewhere around 20 to 30 g C per m² and year. For the Belt Sea, Pfeiffer-Madsen and Larsen (1986) suggest recent accumulation rates for mud sediments ranging from 300 to 800 g m⁻² yr⁻¹ on average. These authors also report detailed data on individual mud regions (size, accumulation rate, absolute values of sediments in tonnes yr⁻¹).

The total organic carbon content (TOC) of the 5 cm mud surface layer might serve, in case of corresponding thickness of sample, as an excellent parameter for the characterization of mud sediments and sedimentation conditions.

The TOC varies from 2 % to 12 % (in dry matter) and ranges on average from 5 % to 7 %, the trend being increasing from the west to the south.

In the central parts of the basins and in current-sheltered localities, the accumulation of organic materials may reach extreme values in the presence of high plankton biomass. The predominantly anaerobic decomposition of the deposited organic matter can hardly cause reduction in the TOC values of the sediment profile (below the sediment-water contact zone) in the central parts of the basins. This reflects the equilibrium between methane and carbon dioxide liberation on the one hand, and between compaction and diagenetic "incarbonation" on the other hand. At the edges of basins there is to be seen a rapid reduction in the profile downward in the bottom due to predominantly aerobic decomposition of organic material. The share of inorganic mineral components is bigger, the pore water permeability higher.

Having a very high porosity, the muds show a low permeability. The organic material (also that of microbiogenic type) cements and wraps up inorganic sediment components and forms an aqueous plastic "framework" of the mud sediments. The often observed pellet structure of the muds represents a special form of such cementing. It goes back to sediment-eating benthos organisms "coprolites", but may also be hydrodynamically conditioned.

The grain size of the muds (inorganic part) is in the medium mud range (on average 15 to 20 µm). The mean grain size is slightly decreasing. Niedermeyer (1987) notes a relative uniformity in the grain size distribution of the sediment profile (0 to 40 cm). The clay fraction may amount to 30 % at most in the Arkona basin.

Apart from organic matter the sediment structure includes biogenic (opal, bio-calcite) and detritic (terrigenous) mineral phases (quartz, feldspar, mica, heavy minerals, etc.) as well as diagenetic new formations (pyrite, glauconite, dolomite, siderite, limonite etc.).

Numerous mineral new formations are of special interest due to their milieu indications and element accumulation: Fe Mn crusts, glauconite, pyrite (Greigit), FeOOH, dolomite, plaster, quartz (new formation!) (Dahmke et al., 1986; Rumohr et al., 1987; Suess, 1979; Moenke-Blankenburg et al., 1989).

Pore water and sediment milieu

Studies on pore water have been undertaken by Dahmke et al. (1986), Suess (1976), Blomquist (1977), but also Dietrich (1981) and Niedermeyer (1987). The pore waters are characterized as chlorite-alkali type and show partly Mg/Ca ratios exceeding 2 (2) (dolomite formation area). Mn and Fe are clearly accumulated in the pore water (reductive mobilization).

Oxygen, sulphate, and nitrate are reduced in the muds. Their contents are strongly decreased in the pore water; methane, CO₂ and H₂S are liberated and dissolved partly in the pore water. In the muds of the Belt Sea area, the redoxcline is only a few centimeters below the sediment/water contact zone. In the Arkona Basin and basins in the Belt Sea including the SW part of the Mecklenburg Bay, it may coincide with this zone in stagnation periods.

Benthic community

Schultz (1966) reported for the Mecklenburg Bay the highest biomass values for macrozoobenthos in muddy sand, and likewise in the transition area from sand-to-mud-accumulation. The community is clearly diminishing in direction towards both extremes (see also Rumohr et al., 1987). These interfaces are, however, subject to long-term fluctuations and trends (effects of eutrophication; water exchange). Also in the Arkona Basin, studies on benthos are very few. There were locally some increases in the benthos biomass due to eutrophication in the 1960s and 1970s (Gosselck, 1985) but this applies only to flat and well-aerated margin areas of the sediment basins. The rapid oxygen consumption in the muds of the Belt Sea and Arkona Sea has resulted in reduction of the benthic community in large parts of these areas. For instance, Ostracoda, Foraminifera and other representatives of the meiofauna can reach significant abundances only in case of sufficient aeration (mud surface stratum 0 to 3 cm). The life of macrobenthic organisms is linked to a well-developed sediment/water contact zone. The substratum raw density of the muds (on average 1.2 g cm⁻³), their low oxygen content and the wide "transition area from water-saturated mud to suspension-saturated water" all stand in the way of such a community.

Monitoring stations in mud areas of the western Baltic

One of the characteristic features of the southwestern Baltic Sea is that the Pleistocene ice marginal positions pass through the sedimentation areas. They have a segmented form and run NW/SE or E/W. These ice marginal positions consist mostly of several successive short banks of boulder clay, stone and block. They are 20 meters high at most and are positioned slightly against each other. They penetrate in several places the Holocene mud sediments. The monitoring stations should be placed in sea areas with high mud thicknesses (> 4.0 m), and they should

show the lowest possible anthropogenic disturbance of the sediment surface. The latter does not apply to all areas of the southwestern Baltic Sea because the surface of the sea floor is strongly affected by fishing with otter boards. Sidescan sonar photos show that undisturbed deposition conditions are hardly to be found in the surface sediments of the southwestern Baltic Sea. It is absolutely necessary that this fact be taken into account as the assembled data are interpreted. The following monitoring stations are suggested in consideration of the above-reported aspects:

Mecklenburg Bay: 54°18.0' N; 11°30.0' E
(Mud thickness 4.5 m, water depth = 23.8 m)

Arkona Sea: 54°18.0' N; 13°30.0' E
(GRD 113) (Mud thickness > 6.0 m, water depth = 47.0 m)

2.7 KATTEGAT AND BELT SEA

Compiled by Lutz Brüggemann and Matti Perttilä

Source: Pheiffer-Madsen and Larsen, 1986

Geological setting

The Kattegat and the Belt Sea are underlain by the eastern margin of the North Sea sedimentary basin. Basement occurs along the Swedish coast towards the Kattegat. The pre-quaternary surface consists mostly of Tertiary clays, marks and danian limestones in the Belt Sea and mainly of Cretaceous limestones with minor areas of Iuranic and Triassic sandstones in the Kattegat area.

The submarine landscape of the seas around Denmark is largely derived from a submerged glacial landscape shaped by the ice cover some 40 000 - 20 000 years ago. The Dybe Rende (Deep Channel) in the eastern Kattegat may be a glacially eroded "marginal channel" in the old sediments just off the basement rocks of Sweden. The rest of the area seems to be more or less eroded accumulations of clayey tills and meltwater sediments derived herefrom, much like the adjacent land.

During the deglaciation, large amounts of fine-grained (fine sand - clay) meltwater deposits were deposited in valleys and basins in the Kattegat and the Belt Sea, smoothing the glacial topography a great deal. This is especially important in the Western Kattegat, but also the basins in the Belt Sea are often underlain by thick meltwater deposits characterized by a layering conformable to the base. Today many submarine meltwater deposits are covered by younger sediments.

As an effect of low absolute sea and different isostatic uplift of the formerly glaciated areas, relative sea level was considerably lower in the Danish area ca. 9500 years BP to ca. 8000 years BP. Most of the present-day sea floor outside the "Dybe Rende" was land with extensive lakes, bogs and streams in the lower parts.

After a period of relatively low sea level in the early Postglacial time, the sea level rose comparatively quickly by ca. 30 m between 9000 years BP and 7000 years BP. Most of the present-day sea floor in the Western Kattegat and the Belt Sea was transgressed by the sea, and

the marine sedimentation commenced. The base of the marine muddy sediment is often clearly observable on echograms. Thus the thickness of the mud deposited since the transgression can be determined. The local age of the start of the marine sedimentation and the depth changes through time differ from place to place, but may be predicted fairly accurately. In the Belt Sea the oldest marine sediments are deposited close to 7500 ± 500 years BP.

Introduction

The purpose of the present sediment mapping (Figs. 2.6.1 and 2.7.1-2) is to delineate the areas where the sea floor consists of fine-grained sediments, mud, and where the geological circumstances seem to indicate that a net deposition takes place today. Accordingly no details as to the type of sand bottoms or erosional areas have been considered. The maps are compilations of existing data only. They have been compiled from various sediment maps and data collections made by various authors for various purposes.

In general the maps of the German areas and the Swedish part of the Sound are based on a dense network of sediment samples, while the maps of the Danish Straits are based on a ca. 2 km grid of seismic lines calibrated from comparatively few samples. The map of most of the Kattegat is chiefly based on rather sparse data.

The bottom sediments comprise several types of components. One is mineral grains derived from erosion of the sea floor, or brought into the sea by rivers and wind. Other important components are organic matter, iron oxides, sulphides, shells, etc., which to a great extent are produced or modified in the sea. The light organic matter is preferably deposited as a part of the muddy sediments.

The grain size of the bottom sediments is chiefly determined by the local sources of the sediments and the fastest bottom currents at the locality in question. Most of the investigated areas are rather shallow, with extensive areas of depths less than 20 m. Judged by the extent of clean sand bottoms, currents set up by the waves are the dominant factor determining the grain size of the bottom sediments in roughly half of the investigated area. The depth of effective wave action and the direction of sediment movement are thus determined by the wind strengths and directions in conjunction with the size and form of the individual sea areas. Sediment boundaries often locally parallel isobaths unless fetch or bottom morphology changes suddenly (Seibold et al., 1971).

During storms the sand grains are moved around and the detritus components, deposited in calmer weather, are washed away. Eventually they are deposited in more quiet environments, often in deeper waters, forming the mud deposits.

In narrow straits, in channels between banks, and in the deep basins, the sediment distribution is determined by the topography and the velocity of the sea water currents.

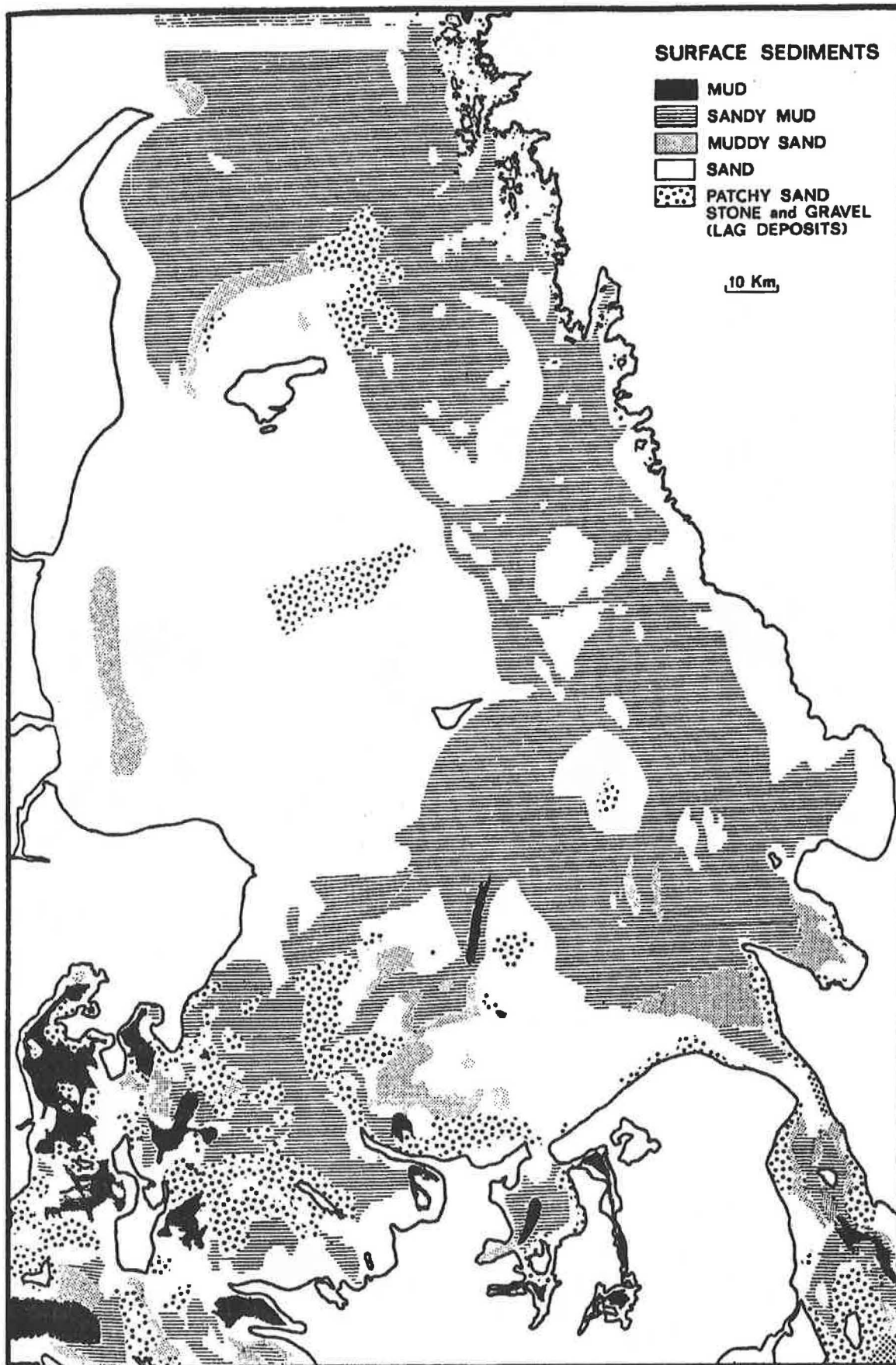


Fig. 2.7.1 Distribution of sediment types in the Kattegat area. (After Pfeiffer-Madsen and Larsen, 1986.)

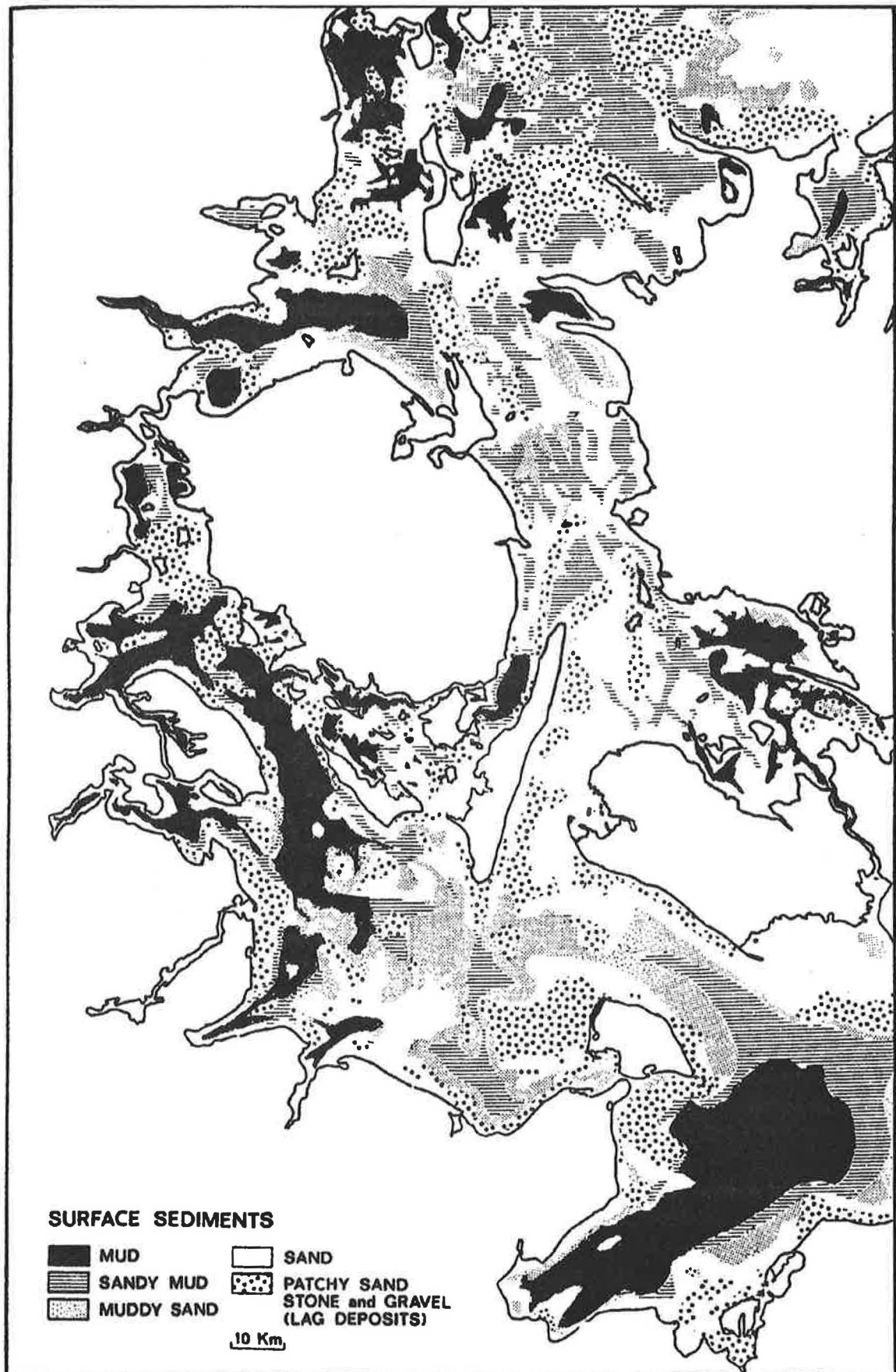


Fig. 2.7.2 Distribution of sediment types in the Belt Sea area. (After Pheiffer-Madsen and Larsen, 1986.)

Sediment types and sedimentary environments

The most distinctive properties of the sediments are the grain size and the consistency, which mirrors the water content.

The grain size is described using the following terms.

		<u>diameter mm</u>
Stone		20
Gravel		20 - 2
Sand	coarse	2 - 0.6
	medium	0.6 - 0.2
	fine	0.2 - 0.06
Silt		0.06 - 0.002
Clay-grade		0.002 = 2 μ m

Mud sediment

"Mud" denotes here soft coherent fine-grained marine sediment consisting of water with 10-20 percent solid matter by volume. Mud may be regarded as deposited detritus. The solid matter consists of 10-40 % (by weight) clay minerals, 50-70 % silt and 0-20 % sand. It is characteristic that the individual silt grades are of almost the same size, giving an almost straight curve in an "accumulated grain size" diagram. The mud contains ca. 3-20 % finely divided organic matter. Only in sheltered bays do layers with macroscopic plant remnants occur. The mud contains variable amounts of shell remnants.

The uppermost part of the mud is often composed of 0.1 mm - 0.7 mm long ellipsoid pellets, especially in more sheltered bottoms. The pellets are formed as faeces when suspended detritus or single particles of bottom material are gathered and digested by pelagic or benthic animals, chiefly bivalves and copepods. The pellets are very porous and of low density. They are easily suspended by the currents, but their settling velocity is considerably faster than that of the fine grains of which they consist. Judged from the amount of pellets on the mud bottom surfaces and in sediment traps set above the sea floor, the sedimentation of sediment pellets dominates in sheltered bays, and is possibly also of importance in the more open Kattegat. The pellets are comparatively physically resistant. Thus redeposition does not seem to cause a significant sorting of the components of the mud bottom, but for the sand grains which are not built into the pellets. A few cm down in the bottom the pellets gradually combine to a coherent gel structure. This is considerably more resistant to erosion than the pellets (Postma, 1967).

The accumulated organic matter on the mud bottom is decomposed by benthic animals and bacteria. Where the supply of oxygen is sufficient, the surface of the sediment is oxidized. This is often shown by a light rusty brown zone coloured by Fe-Mn hydroxides on top of the mud. A few mm to a few cm below the surface, the consumption of oxygen equals the supply. Below this level anoxic reducing conditions prevail, and the organic matter is decomposed by sulphate-reducing bacteria producing hydrogen sulphide. This reacts with iron from the sediment, if available, precipitating black FeS, and by further reaction the grey FeS₂ pyrite is formed. Based on estimates in the Little Belt area (Lillebæltkommittéen, 1983) only a few percent of the organic matter supplied is actually stored in the sediment. The often very limited decrease in organic

content observed from the surface downwards indicates that most of the organic matter decomposes very close to the sea floor.

The combination of many small grains (with collectively a very large internal surface, 10^4 - 10^5 $\text{cm}^2 \text{g}^{-1}$) of ion-exchanging clays, iron oxides, organic matter and the precipitation of sulphides provides the mud sediments with a very high and diverse binding capacity for trace metals and other substances.

Mud deposits

The minimum water depth for mud deposition is probably the depth where the currents seldom exceed 10-20 cm/s.

The surface of the mud deposit is very even, but seldom horizontal. It slopes less than 1.5 m per km in areas with no special restriction to the flow. It is suggested that the supplied sediment material is fairly evenly distributed over the surface of a flat mud basin in the Little Belt almost like water in a lake (Lillebæltkomitéen, 1983). Thus the spot determination of accumulation rate by ^{210}Pb may be considered reasonably representative for a large flat area with an even bottom.

In places where the bottom currents accelerate, for example in narrow straits and channels, or near banks and projections on the coastal slope, the average mud deposition decreases and often complicated patterns of moats, channels and localized deposits develop (Werner, 1978). In valleys like basins it is often observed that the mud deposits lie as "shoulders" making one or both slopes of the valley. They are developed in narrow fjords as well as the huge deposits on the western slope of "Dybe Rende" in the Kattegat and the adjacent Skagerrak (Fält, 1982). Often the mud shoulders merge with the gently sloping mud plains described above.

Sandy mud and muddy sand

These sediment types form the transition between the pure sand transported chiefly by traction along the bottom, and the coherent mud deposited chiefly from suspended matter. Even an admixture of 5-15 % by weight of mud to a pure sand causes an increase in porosity from ca. 33 % by volume to 66 % by volume, a marked decrease in density and a softening of the sediment.

According to Seibold et al. (1971) muddy sand contains between 50 % and 95 %, and sandy mud between 10 % and 50 %, material of grain sizes greater than 0.04 mm. In individual sea areas it is possible to identify mud, sandy mud or muddy sand reasonably well by the loss on ignition.

Sand

The sand bottom consists of grains with a diameter between 2 mm and 0.06 mm; thus, each grain is visible to the unaided eye. Medium- to fine-grained sands with grains less than 0.5 mm are most common. The porosity of the sand is in the order of 20-30 % by volume, corresponding to a water content of ca. 20 % of dry weight. The comparatively wide, unclogged pores between the grains facilitates the flow of water and oxygen through the bottom. The individual grains are loose and moved one by one in contrast to the coherent, flocculated mud. Due to the rather fast

settling of the sand grains, they are chiefly transported close to the sea floor. The bottom is shaped into currents or wave ripples by this mode of transport. The upper 0-50 cm of the sand are frequently redeposited in much of the wave-dominated depositional environments (Kolp, 1958; Seibold et al., 1971).

The transported sands are normally very well sorted with respect to grain size. A part of the detritus, deposited on the sand in quiet periods, is washed out during redeposition. However, some detritus including the organic matter is eventually mixed down into the sand by physical or active biological processes. Even in areas with no net deposition some recent detritus (mud) is present in the bottom (Eisma, 1981) giving a loss on ignition of 0.2-0.8 % by weight on most clean sands.

The content of detritus, in addition to the material bound in mineral grains and rust, or organic coatings on the sand grains, or in shells, means that also the sand bottom contains some trace metals. It is probable that the concentration of trace metals is much higher in the biologically important detritus component than in the sand as a whole.

Lag deposits (residual bottom)

Sea floor areas, where the substratum is almost uncovered and occasionally subject to erosion, are widespread in the seas around Denmark. They may appear as wave-cut platforms along the coasts, or on the upper parts of banks, or at the bottom of channels with strong currents, or in areas with low net sedimentation often along the rim of the mud basins. Due to the thin sand cover, it is often difficult to delineate the erosional areas.

Often they are covered by a veneer of mixed sediment including grain sizes left behind by the erosion, so-called lag deposits. If the substratum is till, coarse meltwater deposits or rock, the erosional areas are recognized by the patchy occurrence of stones and gravel. However, these may be missing on erosion in late glacial meltwater clays or pure sand. Detailed studies in the southern part of the Belt Sea demonstrate a very complex pattern of sediment types in erosional areas. Floderus (1989) has recently shown that a significant part of the turn-over of organic matter and nutrients takes place in thin moving mud blankets on the lag deposits and sand bottom areas of the Kattegat.

Sediment accumulation

In the Belt Sea and the fjords, mud rich in organic matter accumulates mostly in small basins in the deeper parts of the area (see Figs. 2.6.1 and 2.7.1-2). The western Kattegat is so shallow that the redistribution of sand by the waves prevents mud deposition (Floderus, 1989). Muds with a rather low content of organic matter (Olausson, 1975b) are deposited on the flanks of the deep channel in the Kattegat. A very significant part of the sediments is brought in from the North Sea and deposited in the northernmost Kattegat (Kuijpers et al., 1990). The accumulation rates have been estimated on a regional scale using the thickness of marine mud deposited since the Littorina transgression (Larsen and Pheiffer Madsen, 1986) and using ^{210}Pb dating. Fig. 2.7.3 shows the variation in local recent (~ last 20 years) accumulation rates of mud in mud basins in the western Baltic and the Belt Sea as determined by ^{210}Pb . It appears that the rate is frequently $200\text{-}500\text{ g m}^{-2}\text{ yr}^{-1}$, but much higher rates are locally met in areas where sandy mud accumulates.

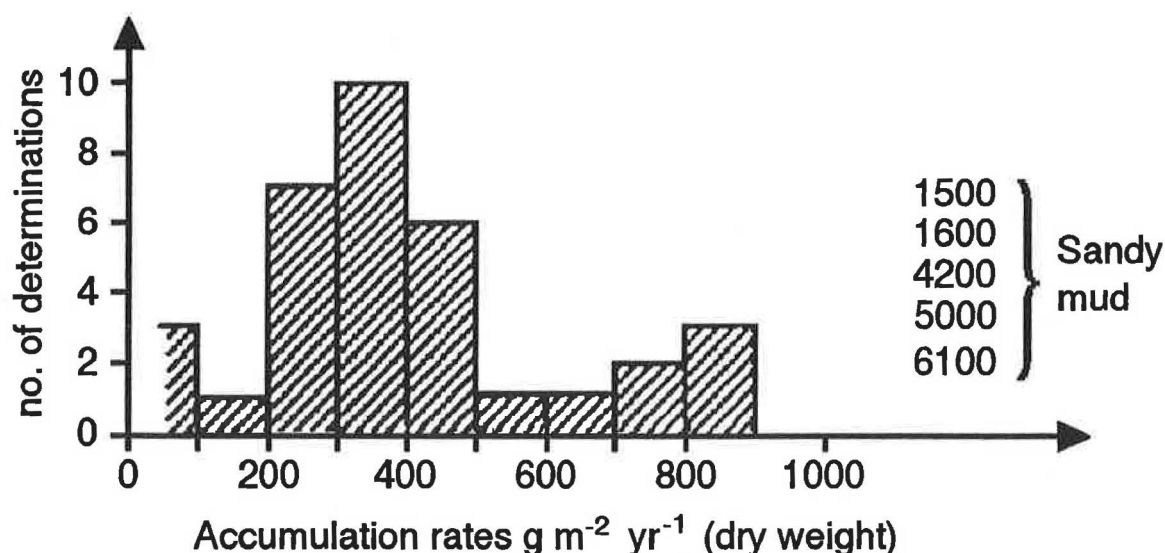


Fig. 2.7.3 Local accumulation ranges of mud dry weight from the southern Baltic and the Danish Straits determined by ^{210}Pb . Non-deposit areas have been avoided.

Accumulated amounts

The amount of mud sediment is estimated for each area. The average accumulation rate of dry sediment is estimated from the dating results. Multiplying this rate by the size of the mud area obtained from the geological mapping gives the amount of mud accumulated per year in each subarea. The number of sediment cores available indicates that there is a lack of data for approximately half of the subareas shown in Fig. 5.1 (especially the Kattegat area). In areas where no dating results (see Table 5.3) are available, the accumulation rate has been estimated by comparison with adjacent and similar areas. In most cases, the 50 % fractile, i.e., $385 \text{ g m}^{-2} \text{ yr}^{-1}$, has been used. By summation of the figures for the subareas, the amounts of the main areas are obtained (Table 2.7.1).

Bearing in mind the scarcity of data from certain areas, these best estimates should however be considered primarily as orders of magnitude. This is especially true for the Kattegat and Western Baltic areas.

Table 2.7.1 Accumulated amounts of mud and organic matter in the sea areas around Denmark.

Main area	Total area km^2	Mud area km^2	mud 10^9 kg yr^{-1}	organic matter 10^8 kg yr^{-1}
Kattegat	22200	8940	9.8	6.3
Belt Sea	14350	5340	2.2	2.1
Western Baltic Sea	11550	2104	1.2	1.0

For comparison, the sediment transport into the north of the Kattegat area via the Jutland current was estimated to be of the order of $8 \times 10^9 \text{ kg yr}^{-1}$ (Rodhe, 1973).

2.8 LAMINATED SEDIMENTS IN THE BALTIC PROPER

Per Jonsson

Introduction

The occurrence of laminated surficial sediments is a well-known phenomenon in lakes (Renberg, 1986; Anderson and Dean, 1988), in coastal areas of the Bothnian Bay (Heikkilä, 1986) and the Bothnian Sea (Cato, 1987; Axelsson, 1983), in coastal (Morris et al., 1988) as well as in open parts of the Baltic proper (Axelsson, 1987; Jonsson and Jonsson, 1988; Suess, 1979). Ignatius (1958) argues that recent Baltic deep-bottom sediments generally consist of "homogeneous clay or clay gyttja, which is sometimes characterized by a distinct, exceedingly thin lamination, possibly an annual varve microstructure with 0.1-2-mm layers".

Climatic variations throughout the year form the basic condition for the formation of annually laminated sediments in Swedish lakes (Renberg, 1981). Normally, differences in sedimentation rate and in the composition of sedimenting material, in combination with alterations in diagenetic processes, are the most important factors leading to the creation of annually laminated sediments. If macroscopic benthic fauna are present, the sediment will be mixed due to bioturbation, and a sediment without lamination will be formed. During the post-glacial period, deposition of this type of homogeneous clay or clay gyttja predominated in all the different basins of the Baltic. In the deepest parts of the Baltic proper, laminated sediments have been formed periodically during the post-glacial period (Ignatius, 1958). The present large-scale distribution of different sediment types in the Baltic proper is shown in Fig. 2.8.1 (Emelyanov, 1988).

There are many indications that the prerequisites for lamination of sediments are now favourable for large areas. Several studies have shown that the macrobenthic fauna has become almost extinct in the periodically anoxic basins below the halocline, an area of almost 100 000 km² in the Baltic proper (Cederwall and Elmgren, 1980; Melvasalo et al. (eds.), 1981).

Distribution of laminated sediments in the Baltic proper

Of the total of 69 stations visited in the open Baltic proper, 50 were characterized as accumulation bottoms for fine material (i.e. < medium silt); 48 of these showed clearly visible lamination in the surficial sediments. Because of the consistency in the area extension of the laminated sediments, the probable extension of laminated sediments in the open parts of the Baltic proper, excluding the Gulf of Finland and the Gulf of Riga, can be outlined (Fig. 2.8.1). This map was drawn by compiling the bottom dynamic map of Emelyanov (1988) and our own results. The area of laminated sediments covers 70 000 km².

The physical and chemical properties have been studied in 29 and 8 cores, respectively. The average thickness of the recently laminated layer was 4.5 cm with an average thickness of 2.5 mm for each lamina. At some stations the entire cores were laminated with more than 100 laminae. As an average for the 21 examined cores, the level 4.5-cm below the sediment surface is 19 years old, i.e. deposited in 1968-1969 if each lamina represents one year.

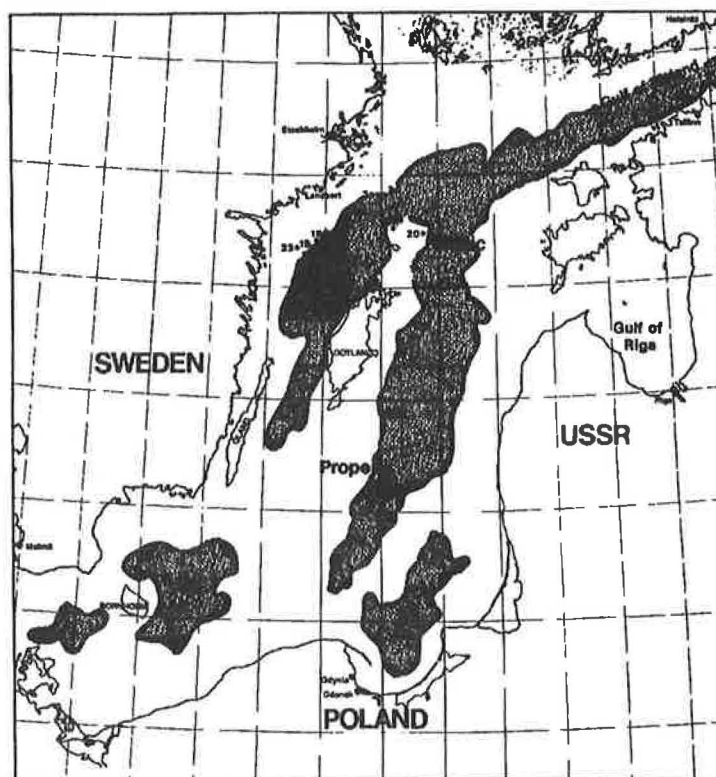


Fig. 2.8.1 Positions of the stations (1-35) where cores were taken for physical and chemical analysis. The probable extent of laminated surficial sediments in the Baltic proper is shown by the shaded area.

Is the area of laminated sediments in the Baltic proper expanding?

If the occurrence of laminated sediments only depends on the rising redoxcline in the Baltic during the 20th century (Melvasalo et al. (eds.), 1981), a correlation between water depth and number of laminas in the cores is to be expected. However, there is no such evident correlation. The correlation does not increase even if the material is treated separately for the different main basins. It is, therefore, suggested that due to the variable bottom topography and hydrography of the Baltic, a mosaic of more or less separated small basins exists with different oxygen conditions close to the bottom.

There are many indications that the area covered by laminated sediments has increased substantially during the last decades. In the deepest parts of the major basins of the open Baltic proper, laminated sediments have been deposited for more than one hundred years, indicating natural oxygen deficiency in these areas. At 7 sites out of 29, laminated sediments are found throughout the investigated cores down to 13-70 cm below the sediment surface, which is the maximum depth investigated.

It is also known that laminated sediments are currently being deposited on all accumulation bottoms for fine material, deeper than 75 m, in the open Baltic proper. No cores have been found with between 40 and 100 varves, which indicates that the recent expansion of the area of laminated sediments started in the late 1940s. This conclusion is supported by several reports from the 1950s concerning decreasing abundance of benthic macrofauna and oxygen concentrations below the halocline (Melvasalo et al. (eds.), 1981).

Fig. 2.8.2 visualizes the expansion of the laminated bottoms in the Baltic proper, assuming that each laminated core represents equal fractions of the total accumulation bottom area. This is an uncertain assumption and the number of cores is small. However, there is strong evidence that the major expansion took place between the end of the 1940s and the end of the 1980s. Therefore, it can be concluded that the expansion shown in Fig. 2.8.2 is at least a qualitative estimate. Expansion will, however, probably be halted, because the lamination has now reached the level of the halocline.

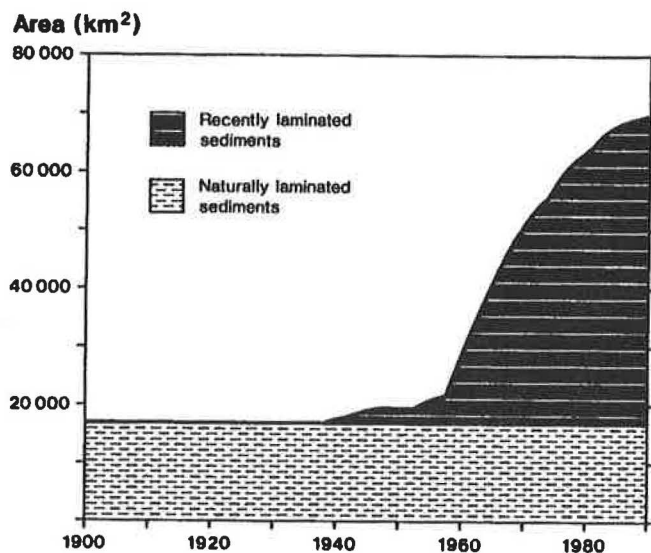


Fig. 2.8.2 Schematic illustration of the probable expansion of laminated surficial sediments during the 20th century in the Baltic proper.

Laminated sediments and mass balances

In estimating future mass balances and budgets for the Baltic, it is of major importance to discover methods that discriminate between the natural and the anthropogenic inputs of carbon, nutrients and contaminants. Sediments are excellent tools to help estimate the final output, including the sum of the natural relocation of substances and the anthropogenic load, from the pelagic Baltic ecosystem to the sediments. However, we must focus on studies aimed at gaining a better understanding of the erosion/transport bottom system in the shallow and coastal areas of the Baltic, where large relocations occur in the resuspension/transport/sedimentation zone above the halocline. It must be determined to what extent these pools of nutrients are available for biological production.

Thanks to the ease of datings of the laminated sediment cores, analyses of contaminants in these sediments may be valuable in estimating the total load of different contaminants to the Baltic. Lamination offers possibilities to determine changes in the load over time, with a better resolution than is possible in a bioturbated sediment. However, if the load to a large extent is due to erosion of post-glacial sediments, as is proposed to be the case for nutrients, the temporal variations will be obscured by a high "background". Use of tracer substances, like radionuclides, are other important tools to determine the time scales for the transport and relocation processes in the coastal areas, until the time when particles reach the true A-bottoms for fine material and finally leave the recent Baltic ecosystem for the long-term geological system.

CHAPTER 3 - EVALUATION OF THE SENSITIVITY OF SEDIMENT RESPONSE IN POLLUTION MONITORING

Birger Larsen and Anders Jensen

Introduction

Bottom sediments are often the best available medium for long-term monitoring of many contaminants in aquatic recipients. Sediment monitoring is carried out by measuring the concentration of the contaminant in surface sediment samples, often in the upper 0.5-1 cm. This is done at intervals of time in order to assess the present level of pollution and to detect changes in the flux of that contaminant. The sensitivity of a given monitoring site is the minimum change in flux recorded as a statistically significant change in concentration in the sediment detected by the sampling scheme and chemical methods used.

In some environments, such as current-swept estuaries and dumping grounds, renewal or redeposition of the upper sediment layer (< 10 cm) occurs frequently. Here sediment monitoring shows the changing compositions of the successive sediment "covers" through time. In environments with reasonably steady but moderate sediment accumulation rates (about 1 mm yr⁻¹) the time trend of the contamination flux is recorded as a concentration depth profile in the sea floor. A sample of, for example, the topmost 1 cm, will integrate the effects over a period of time depending on the accumulation rate of the sediment and the disturbances caused by the mixing processes. This is illustrated in Fig. 3.1, which shows that the same response in concentration change may cover a wide range of changes in flux. In such cases it is not easy to interpret the observed trend in concentration in terms of change in the flux of the contaminant and plan a satisfactory monitoring programme. The problems are due to differences in sediment accumulation rates and/or depth and intensity of mixing of the sediment. These parameters may be estimated at the site using the ²¹⁰Pb profile as described below.

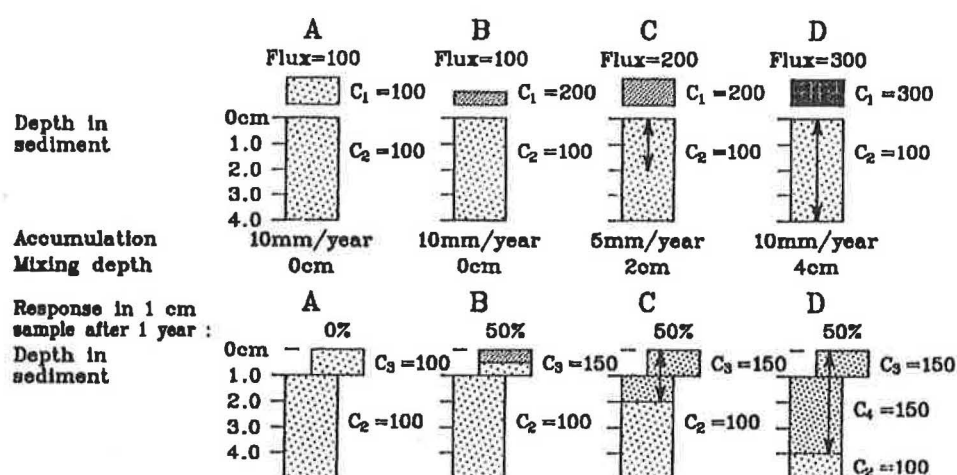


Fig. 3.1

Schematic models illustrating monitoring responses in sediments. In column C and D total mixing within a year to a depth as shown by arrows. Note the same concentration in top 1 cm sample B, C, and D in spite of differences in flux to the sediment surface in the preceding year.

TOP: Flux of contaminants in units in 1 year.

C₁: is concentration in sediment deposited through 1 year.

C₂: concentration in uncontaminated sediment (base-level).

C₃: is concentration in sample of the top 0-1 cm of sediment after 1 year of accumulation and in C and D mixing.

Response is $(C_3 - C_2) 100 / \text{Flux}$.

This model used the mixing parameters and accumulation rates evaluated from the ^{210}Pb profile to show how changes in the flux of a compound to the sediment surface affects its concentration in the surface sample.

Sediment parameters

A first step in the selection of a sediment monitoring station is to assure that the sediments are reasonably uniform and muddy in the uppermost 50 cm in the sampling area. Changing sediment type through time and thus changing affinity of the pollutants to the sediment (Förstner and Wittmann, 1983) almost excludes meaningful monitoring at moderate pollution levels. Basic sediment parameters, such as grain size distribution, content of organic matter, macrofauna and the variation in dry matter content (or water content), down a core should be available. Steady state is assumed for these parameters.

Determination of time-dependent sediment parameters is based on the vertical distribution of the natural radioactive isotope ^{210}Pb (for more details see Pheiffer-Madsen and Sørensen, 1979). The content of unsupported ^{210}Pb (that is ^{210}Pb not produced in the sediment) decreases regularly downwards in undisturbed and steadily deposited sediment owing to radioactive decay. Departures from this predictable ^{210}Pb profile in the topmost sediment column permits an assessment of mixing and/or intermittent erosion. A condition for a sensitive monitoring site is reasonably rapid and continuous sedimentation with little or no mixing. Such a sampling site may be recognized by a preliminary study of the ^{210}Pb profile, before expensive chemical analyses are carried out.

It is not possible to describe the mixing by bioturbation, etc., exhaustively. However, mixing that does not result in complete homogeneity, and which still can be treated as random mixing, is according to Berner (1980) best approximated by a "biodiffusion" coefficient, D . Fig. 3.2 illustrates the influence of the size of D on the ^{210}Pb profile, when other parameters are kept constant.

The observed depth profile of unsupported ^{210}Pb can be modelled by the advection-diffusion equation (Berner, 1980).

In Fig. 3.2, z (cm) is the depth below the sediment-water interface, D ($\text{cm}^2 \text{yr}^{-1}$) is the mixing coefficient, λ is the radioactive decay constant, C (dpm g^{-1}) is the concentration of the ^{210}Pb , w (cm yr^{-1}) is the accumulation rate and t (yr) is time.

In the present work it is assumed that the mixing coefficient is constant until mixing depth I , and equal to 0 below that level. This simplification seems to work well in mud sedimentation areas of the Danish Seas and the Baltic. However Christensen and Bhunia (1986) have presented a more realistic model which includes variable bulk density due to compaction and a variable biodiffusion coefficient in the mixing zone. Using the steady state solution for the advection-diffusion equation, the parameters W , D , I and the flux of ^{210}Pb to the sediment surface can be calculated. The range of variation of W , D and I is illustrated in Table 3.1 using data from approximately 100 stations. All samples are ^{210}Pb dated mud and muddy sand cores from the Danish Seas (Pheiffer-Madsen and Larsen, 1986). Most of the stations were carefully selected by marine geological mapping as locations judged to be rather undisturbed accumulation areas.

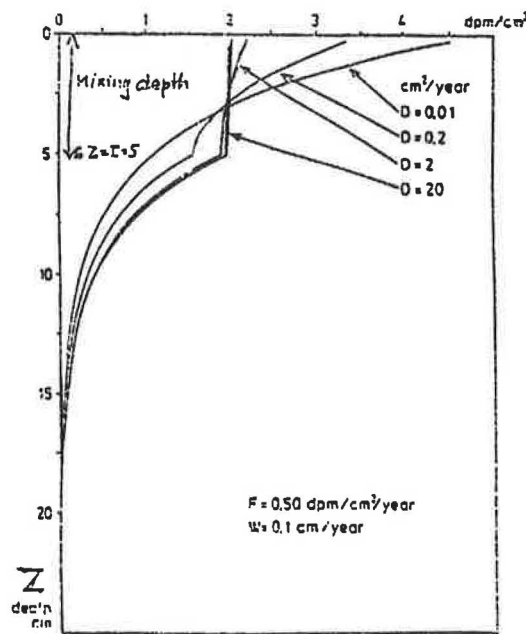


Fig. 3.2 Depth profile of unsupported ^{210}Pb , concentration decreasing downcore due to radioactive decay. The profile is deformed by random mixing in the top 5 cm, being uppermost at any time with an intensity described by "biodiffusion coefficient D ". For D exceeding $2 \text{ cm}^2 \text{ yr}^{-1}$ almost homogeneity is observed. In the examples the flux of ^{210}Pb is fixed at $0.50 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ and the accumulation rate of sediment at 1 mm yr^{-1} .

Table 3.1 Outline of sediment model parameters from approximately 100 sediment cores from Danish marine areas.

Fractile	Accumulation rates		Mixing depth I cm	Mixing coefficient D $\text{cm}^2 \text{ yr}^{-1}$
	R $\text{g m}^{-2} \text{ yr}^{-1}$	W cm yr^{-1}		
25 %	250	0.06	2.5	0.5
50 %	385	0.10	5.5	10
75 %	650	0.17	9.5	∞

It appears that the accumulation rates in the mud accumulation basins frequently are $200\text{--}500 \text{ g m}^{-2} \text{ yr}^{-1}$ or $0.5\text{--}1.5 \text{ mm yr}^{-1}$. Only 25 % of the cores show a mixing depth less than 2.5 cm corresponding to approximately 25 years of deposition and mixing coefficients less than $0.5 \text{ cm}^2 \text{ yr}^{-1}$. This indicates that most mud bottoms are disturbed in the surface layers even in these rather sheltered seas.

Concentrations in surface samples

The flux of a pollutant, in contrast to the flux of ^{210}Pb , is not constant with time. A non-steady state solution of the advection-diffusion equation can be obtained using the implicit finite differential equation (Crank-Nicholson) method (Christensen and Bhunia, 1986). The solution yields a concentration profile from a known or assumed input history. In sediment monitoring programmes, mostly the topmost 1 cm of the sea floor is sampled, but thinner samples may be

chosen for better resolution. The limit is the thickness of the annually resuspended layer, and the sampling technique. The model calculates the change in concentration in the topmost cm as a function of change in flux of the pollutant and the accumulation rate, the mixing depth and mixing intensity. As an example a sediment profile with fixed accumulation rate (1 mm yr^{-1}) and a fixed mixing depth ($I = 2 \text{ cm}$) has been calculated. Fig. 3.3 shows the relationship between flux (in percent of initial value = 100) increased over a period of 1 or 5 years and the resulting increased concentration in the topmost 0-1 cm sample (in percent of initial value) after that period.

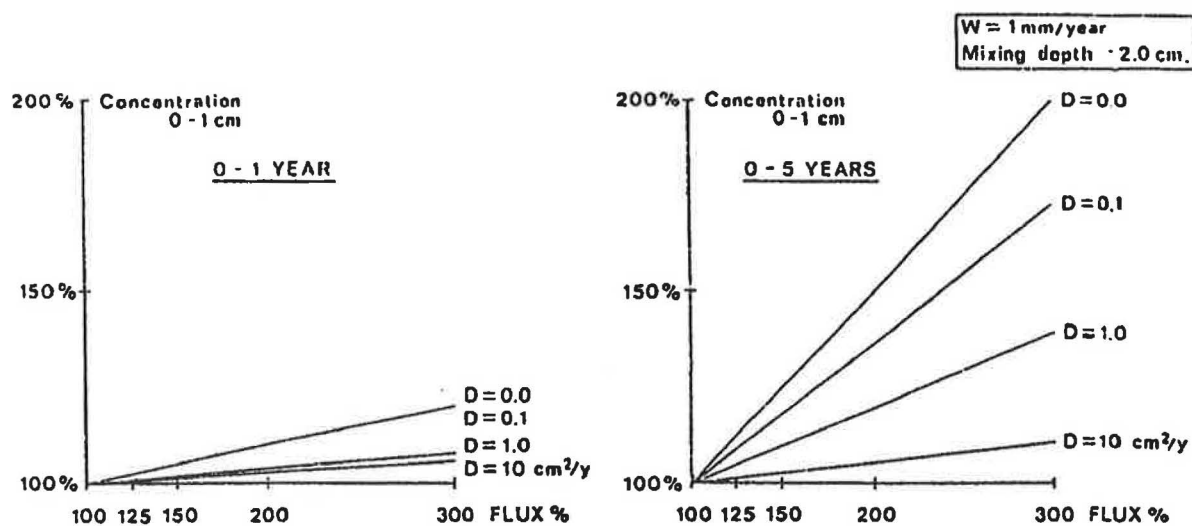


Fig. 3.3 Flux in percent of initial 100 increased for a period of 1 and 5 years, respectively, and the resulting concentration in the 0-1 cm sample (initial 100) with various values of mixing described by mixing coefficient D . Accumulation rate is constant at 1 mm per year and mixing depth 2 cm.

The relation is shown for varying values of the mixing rate. For no mixing ($D = 0$) the figures show the consequences of an annual adding of 1 mm sediment with the higher concentration to the sediment profile and simultaneous removal of the lowest 1 mm from the sampling interval by burial. With increasing mixing rates, greater amounts of the new added material are mixed below the sampling depth. Fig. 3.4 shows the development of the increase in concentration through time as a response to a doubling of the accumulation rate, with the same assumptions as in Fig. 3.3.

Fluxes of most trace metals have increased by a factor of between 2 and 7 in the period from 1950 until today in the Danish Seas (Pheiffer-Madsen and Larsen, 1986). This indicates that an increase of 10 % in flux from one year to the next should be considered large in this area. The next section addresses the problem of analytical ability to detect the responses predicted here.

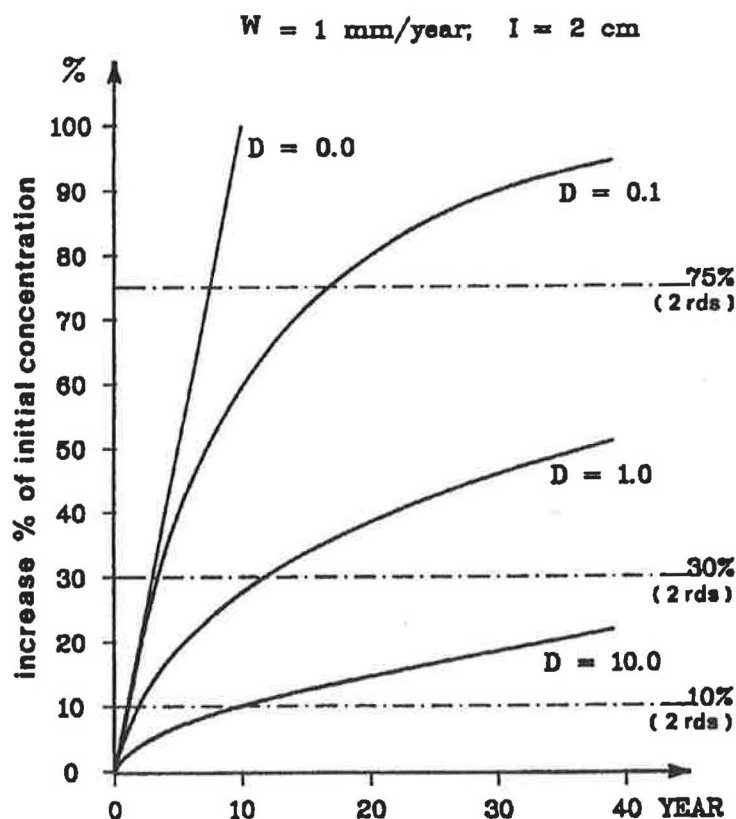


Fig. 3.4 Change in concentration in topmost 1 cm in percent of initial value as a function of time since the flux has been doubled, with various values of the biotransformation coefficient. Preconditions as in Fig. 3.2. Dotted lines indicate detection limits for analytical rsd 2x5, 2x15, 2x37.5, respectively.

The analytical uncertainty

Trend monitoring implies comparison of chemical determinations made at different points of time. The accuracy of the determinations through time - the reproducibility - of the laboratory or laboratories involved is thus essential when analytical results from different sources are to be compared in order to assess the trend of contamination (Nicholson, 1985).

The reproducibility of the chemical analyses (including reference sample variability) is at the moment best expressed by the relative standard deviation ($\text{rsd} = \text{sd in percent of the mean}$) for repeated determinations of concentrations of heavy metals in reference samples. The sediments in the examples are moderately contaminated muds. The concentration levels of the reference samples are shown in the first line in Table 3.2. I is the reproducibility (= intra-laboratory variability) achieved at one experienced laboratory through 2 years. II is the inter-laboratory reproducibility among 5 intercalibrated Danish laboratories, using 1 known and 1 unknown reference sample per analytical batch. III is an example from an international intercalibration involving about 20 laboratories, of which some were previously intercalibrated. IV is "achievable precision for reference materials" as suggested by MacDonald and Nelson (1984).

Table 3.2 Levels of metal concentrations (A) in ppm and I-IV relative standard deviations (rsd) in percent.

	Cd	Cr	Cu	Ni	Pb	Zn	Hg
A in ppm	0.4	20	30	30	20	150	1
I 1 laboratory	9	6	5	11	13	2	-
II 5 labs.	28	8	6	12	8	8	-
III ICEM-C, HF	53	29	18	34	38	8	39
IV "Achievable"	10-24	-	3-4		17-26	3-6	-

From Table 3.2 it appears that the rsd is substantial and increases considerably when more laboratories are involved. It is obvious that a close standardisation and intercalibration is needed when conducting international monitoring programmes. Based on an ICES intercalibration, Loring (1987) concludes that 10 % is an achievable intra-laboratory rsd for most elements in this type of sample, provided reference materials are used to avoid biased results. In order to assign statistical significance to an obtained difference in concentrations (a change), the difference should exceed 2 sd. When longer time series are available, trend analysis might be advantageous (Nicholson, 1985).

The sensitivity analysis

This comprises:

1. Determination of sediment parameters.
2. Selection of the increase of pollution flux of interest in the modelling. This may be based on a dated historical pollution record in the sediments at the site (Christensen and Goetz, 1987), ecotoxicological or statutory considerations.
3. Calculation of the response in the surface sample of determined thickness through a sequence of years from the start of the change in flux, as shown in Fig. 3.4.
4. The expected rate of change in the topmost sample interval is subsequently compared with the analytical reproducibility for the substance in question, and the number of years required to reach a detectable response is determined.

Table 3.3 shows the number of years required for a 100 % increase in the flux of a pollutant to the sediment surface to be detected as a 10, 30 or 75 % increase in concentration of the pollutant in the topmost 0-1 cm of the sediments. Values have been calculated first using the assumptions from Figs. 3.3 and 3.4 (no. 1-3) and secondly from data on 3 actual cores from the Baltic Sea.

Table 3.3 Number of years before a 100 % increase in flux of a pollutant to a sediment surface can be detected as a 10, 30 and 75 % increase in concentration of the pollutant in the uppermost 0-1 cm of the sediment.

	R $\text{g cm}^{-2} \text{ yr}^{-1}$	W cm yr^{-1}	D $\text{cm}^2 \text{ yr}^{-1}$	I cm	10 % years	30 % years	75 % years
1	-	0.1	0.1	0.2	< 2	4	>
2	-	0.1	1.0	2.0	2	12	> 40
3	-	0.1	10.0	2.0	10	50	> 100
B12	0.1115	0.38	0.0	0.0	< 1	1	3
B16	0.0129	0.049	2.5	6.0	10	39	> 50
B34	0.0117	0.035	0.06	4.5	3	12	50

A calculated example based on case 2 in Table 3.3 and Fig. 3.4 is as follows: An accumulation rate of 1 mm yr^{-1} corresponds approximately to $400 \text{ g m}^{-2} \text{ yr}^{-1}$ (water content 20 %, solid density 2.5); Cd concentration in the sediment is 0.25 mg/kg (flux $0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$). The question is how many years pass until a doubling of the flux causes an analytically significant ($2 \times \text{rsd}$) response in the upper 1 cm of sediment. The analytical reproducibility of Cd at this level is 15 % rsd so the Cd concentration should exceed 30 % rsd: $0.25 + 2 \times 0.038$ (0.33 mg/kg for detection). With the preconditions in case 2, Fig. 3.4 shows that a doubling of the flux to $0.2 \text{ mg m}^{-2} \text{ yr}^{-1}$ would show up as a detectable response after approximately 12 years.

Conclusion

These examples indicate that it is possible to make estimations of the sensitivity of a given sediment site for trend monitoring using parameters obtained by modelling ^{210}Pb profiles from the site. The sensitivity is not a constant but varies from one site to another due to differences in the sedimentation parameters. It is therefore very important that sediment sites for long-term monitoring are very carefully selected, and that the mixing is checked at each sampling of the station, as otherwise very substantial changes in the flux of contaminants may go undetected.

CHAPTER 4 - REVIEW OF METHODS FOR THE DETERMINATION OF CONTAMINANTS IN SEDIMENTS

4.1 GENERAL CONSIDERATIONS

Lutz Brüggemann

The following chapters have been written on the basis of methodological guidance provided by expert groups of international organizations, e.g., ICES, IOC, UNEP, FAO and IAEA. In addition, original papers have been consulted and the experience of the author's laboratory used.

Most of the methodological review outlined below refers to the determination of "heavy metal" contaminants. This takes into consideration the currently observed practice in monitoring laboratories. Taking into account the environmental relevance of contaminants, persistent organics will certainly in future need increasing attention.

Sampling strategy

Ideally, sampling strategy should be based on a knowledge of the sources of contaminants, the transport pathways of suspended matter and the approximate rates of sediment accumulation. Since contaminants mainly concentrate in the fine-grain size fractions, priority should be given to locating areas of fine sediment deposition. In the Baltic Sea, most of the central basins are areas where muddy sediments, mainly composed of silty and clayey material ($< 63 \mu\text{m}$), deposit. In the deep basins the (bio-)mechanical mixing rate is low due to anoxic conditions above and/or in the surface sediment layer. In the Bothnian Bay, Arkona Basin, Belt Sea and in the Kattegat, strong mixing occurs extensively (see Table 3.1), but favourable sites may be found.

Prior to sampling, the area should be surveyed by echosounder, at the least. A better survey would be obtained using a high-frequency seismic reflection profiler (e.g., 3.5 KHz system) as well, preferably with side-scan sonar. This allows identification both of regions with thicker sediment layers, where sampling may yield sequences with rapid and undisturbed accumulation, and of areas of outcrops of older sediments. Additionally, the results of such surveys would indicate whether or not single cores or surface samples can be expected to be representative for that area. Generally, sediments which look physically disturbed by man's activities (e.g., trawling or mooring grounds) are not suitable for trend monitoring purposes.

Where sampling for the spatial extent of contamination is intended, a gridded or statistically random sampling pattern is needed. Time trends (history of contamination load) may be obtained from single cores taken at well-determined spots, e.g., from central parts of the Baltic basins.

Sample collection

Tightly closing grab samplers with a minimum size 15x15 cm, e.g., of the Van Veen or Shipek type, are usually adequate for studies of the most recently deposited layers of sediments. These samplers may penetrate as deep as 15 cm, depending on the texture of the sediments. Initially, a visual inspection should be made of the samples to ensure that they have been collected with minimal disturbance. The recently deposited material, usually indicated by colour and texture, may be scraped with suitable tools from the mid-part of the grab area.

A box corer, e.g., of the Reineck type, can obtain almost undisturbed samples. Sub-sampling is necessary if sub-surface sediment layers shall be separated. This is done mainly by pressing tubes into the freshly taken box core sample. From these tubes slices of sediments in about the range 0.2 to 10 cm may be obtained after extruding the core.

Taking sediment cores which can be directly extruded from tubes for slicing is in very many cases an optimum choice if the sampling is done to reveal time trends of the contaminant load. For contaminant-related sediment studies in the Baltic Sea, the Niemistö gravity corer (Niemistö, 1974) is widely in use. The sediment core of 5 cm diameter and of a maximum length of about 50 cm is extruded from a plexiglas tube with a piston and 0.2 to 5 cm sub-sample slices can be obtained without contact to the air, with low contamination risks and without significant losses of pore water. In addition, immediately after sampling, redox potential measurements can be carried out with high reliability (Bågander and Niemistö, 1978). Sampling of the often extremely soft sediment surface layer may pose problems when using the Niemistö corer. Better results may be obtained with the help of a corer specially designed for obtaining undisturbed samples (Barnett et al., 1984).

Several problems limit the representativeness of sediment sampling with most types of corers (Blomquist, 1985). These limitations should always be kept in mind when interpreting stratigraphical records of contaminants and geochemical trends:

- a) Very soft and fine-grained material from the sediment surface with water contents up to 98 % may be pushed away during sampling due to the dynamic pressure ("shock wave") caused by lowering the sampling equipment. Therefore, large heavy weight box or piston corers are generally not suitable for use in contaminant monitoring. The losses of surface mud sediments from the Baltic Sea may be in the order of 10 cm and more.

It is possible to reduce those effects by lowering the equipment more slowly in the vicinity of the sediment surface or if sampling would be carried out by divers. However, the latter procedure is practicable only for shallower parts of the Baltic Sea, e.g., in the Mecklenburg or Kiel Bight.

- b) Surface sediments are stirred up and re-suspended during sampling, particularly when using instruments with narrow-mouthed coring tubes. A supporting frame is advantageous to reduce the tilting tendency of the corer. This is realized for instance with a modified Kajak-type gravity corer (Blomquist and Abrahamsson, 1985).
- c) In relation to the ambient sediment surface, the cores may be shortened by between about 5 and 45 % of their original length (Blomquist, 1985). This does not seem to depend very much on the sampler type if certain lower limits of core diameter (about 5 cm) are observed. Even when sampling is performed carefully by SCUBA divers, if sub-sampling of cores is done from large diameter box cores, nearly the same reduction in core length will occur. This shortening phenomenon is explained by both the effects of compaction and/or physical thinning caused by lateral extrusion in front of the lowered corer.
- d) A phenomenon has been identified whereby surface material may "contaminate" the lowest part of the core during coring. Therefore, it would be advisable to discard the bottom 2 to 5 cm of the cores.

Sampling frequency

A reasonable sampling frequency is determined by

- the mass accumulation rate (in mud areas of the Baltic Sea in the order of 50 to 400 g m⁻² yr⁻¹) and linear sedimentation rate (0.02 to 1 cm yr⁻¹, for many areas around 0.1 cm yr⁻¹),
- the sub-sampling (slice) thickness; often 1 cm is selected with respect to practicability (number of samples, handling, time, etc.),
- the mixing of the sediment which transfers part of the freshly deposited material in depths down to 15 or even 20 cm,
- the contents of the contaminants in question and the range of expected changes in their fluxes to the bottom, and
- the reproducibility of the analytical determinations.

Taking these variables together, in only some very selected cases is a sampling frequency of more than once per five years advisable.

Sample description

A "log book" should be used during sampling and sub-sampling where a visual description of the sample is made. This description should contain at least the following information (see Section 4.5):

- textural description (anomalies),
- homogeneity and indication of bioturbation or stratification, and
- colours (Munsell colour chart).

If possible, the sediment cores should be X-rayed before slicing to confirm the information on textural changes and biological mixing.

Sub-sampling

Preferably, sub-sampling of sediments should be performed immediately after coring. The best method of sub-sampling cores of soft sediments is to extrude the core upwards and slice off layers using a non-contaminating cutter. A screw-drive to the extruder with known pitch of screw allows very thin layers to be taken if required. For circular cores, a 1 cm deep box of diameter 1 cm less than the original core can be pushed over the extruded core and then sliced off. The smeared zone around the outside of the core is thus excluded.

Sample storage

In the field, the sub-samples should be stored frozen, or kept at a sufficiently low temperature (ca. +4 °C) to limit biological and chemical activity. For long-term storage samples should be frozen or freeze-dried. For very long-term storage (e.g., sample banking), gamma radiation or liquid nitrogen freezers may be used.

In most cases, it is advisable that separation (by centrifuging) and handling of pore water samples from cores be carried out in an oxygen-free atmosphere.

Table 4.1.1 Working material and storage temperatures for different determinands.

Determinand	Sub-sampling tool	Storage container	Storage temperature
Metals (other than Hg)	Plastic	Plastic	-20 °C (long-term) +4 °C (short-term)
Organic contaminants	Metal	Glass/metal	-20 °C
Mercury	Plastic	Plastic	-20 °C
Organic carbon	Metal/plastic	Glass/metal	-20 °C
Carbonate	Metal/plastic	Glass/metal/plastic	+4 °C

Necessary sedimentological and geochemical background information

Before the contaminants of concern may be analysed, it should be ensured that a basic amount of information will be provided about the deposit, its composition and environment. This includes the determination of

- water content,
- grain size characteristics,
- organic and inorganic carbon, phosphorus and nitrogen contents,
- content of Al, Fe and Mn.

The redox potential should be evaluated at least qualitatively (i.e., whether the surficial sediments are oxic, sub-oxic or anoxic and, if oxic, whether there exists a redoxcline within the core and where). For temporal trend monitoring, information on the accumulation rate is mandatory.

Compensation for grain size effects ("normalization")

The final analytical results on contaminant concentrations in sediments are most influenced by grain size effects, i.e., by the fact that coarse constituents (sand, > 63 µm) with normally very low contaminant concentrations will "dilute" the contaminant concentration of the total sample. Different methods have been proposed and are in use to correct for this effect, which may cause random variabilities in concentrations of heavy metals in neighbouring ("co-genetic") samples:

- a) Analysis of contaminants in the grain size fraction < 63 µm is mandatory. An analysis of reports out of 100 publications (1972 to 1984) in which contaminant data are given on various grain size fractions has clearly revealed that the majority of authors prefer the < 63 µm fraction for analysis (31 %, Literathy et al., 1987). Other fractions are only used in 13 % (< 2000 µm), 8 % (< 2 µm; < 100 µm), 7 % (< 175 µm), 3 % (< 4 µm; < 16 µm), 2 % (< 25 µm; < 57 µm) or 1 % of the papers (< 150 µm). This also follows the ICES guidelines for the monitoring of contaminants in sediments (ICES, 1987_a). Only in cases where contamination of the coarser fraction (> 63 µm) is suspected, should both fractions be analysed. The grain size separation

may be performed by dry sieving or wet sieving using uncontaminated de-ionized water, or sedimentation (Atterberg) methods.

- b) "Normalization" of heavy metal concentrations by relating their "total" concentrations in non-fractionated (total) samples with the "total" concentrations of anthropogenically not influenced ("conservative") reference elements:

Si: Characteristic for the amount and distribution of metal-poor quartz which acts as a coarse-grained "diluter" of trace contaminant concentrations.

Al: Characteristic for the amount of Al-silicates, used to account for granular variations of metal-rich fine silt and clay size Al-silicates. A good chemical tracer for clay minerals (except in sediments derived from glacial erosion of igneous rocks, as is typical for the Baltic Sea sediments).

Fe: Characteristic for metal-rich silt and clay size Fe-bearing clay minerals, Fe-rich heavy minerals and hydrous Fe oxides; chemical tracer for Fe-rich clay minerals.

Sc: Structurally combined in clay minerals, used therefore as a tracer for clay minerals which are concentrators of trace metals.

Cs: Structurally combined in clay minerals and feldspars, used as tracer of clay minerals which are concentrators of trace metals.

Li: Structurally combined in clay minerals and micas, used as a tracer of clay minerals, particularly in sediment containing Al-silicates in all size fractions (as for the Baltic Sea, with glacially eroded igneous rock material in the sediments, see above).

C-org: Characteristic for fine-grained organic matter which is often an accumulator of trace metals such as Hg and Cd.

Loss on ignition (550 °C) is closely correlated with C-org, and clay content. Used extensively in Danish pollution monitoring normalization.

- c) Preparing regression curves between "total" contents of metals in non-fractionated samples and the percentage of the fraction < 63 µm (silt + clay), < 20 µm (medium silt and finer fractions) or < 2 µm (clay).

Background levels

It is necessary to establish natural background metal levels before the extent, if any, of heavy metal contamination can be estimated. Such background levels are subtracted from the "total" values to yield an estimate of the anthropogenic contribution.

Background levels can be estimated either by

- direct measurement of metal concentrations in texturally equivalent sub-surface core samples from depths below any possible contamination or biological mixing, with due consideration given to possible effects of early diagenesis (e.g., pore water mobilization and redistribution of metals), or

- if direct measurements are not available, average metal concentrations of texturally equivalent sediments reported in the recent literature may be used (with caution). For the conditions met in the Baltic Sea, the first possibility should be given preference.

The "metal excess" over background levels may be easily calculated by

$$Me_{\text{excess}} = Me_{\text{total}} - (Al_{\text{total}} * Me/Al\text{-background ratio}).$$

Similarly, "enrichment factors" (EF) may be obtained by

$$EF = Me/Al_{\text{sediment sample}} : Me/Al_{\text{background reference sample}}.$$

Typical total background concentrations of heavy metals in fine-grained Baltic mud sediments could be (in $\mu\text{g g}^{-1}$ dry substance) 0.03 (Hg), 0.2 (Cd), 10 (As), 20 (Cu), 25 (Pb), 30 (Ni), 80 (Cr) and 100 (Zn).

4.2 FURTHER TREATMENT OF SEDIMENTS PRIOR TO CHEMICAL ANALYSIS AND DETERMINATION OF BACKGROUND PARAMETERS

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Drying

Preferably, the (mud) samples should be freeze-dried. For analyses of inorganic constituents (metals), except volatile elements and their compounds (e.g., Hg), drying may be performed at 105 °C or 60 to 80 °C. (However, dry-sieving of such oven-dried samples is not recommended. In addition, the reduced surface area and the altered binding conditions at the sediment surface for contaminants are not advisable for the subsequent chemical attacks.)

Grain size determination

Preferably, from a sub-sample of the original sample and/or of the separated fraction for the chemical analysis ($< 63 \mu\text{m}$), the full mass spectrum of grain size fractions should be determined quantitatively. For sand ($> 63 \mu\text{m}$) and silt (2 to $63 \mu\text{m}$) fractionation using wet-(dry-)sieving would be equivalent for monitoring purposes. If finer material, such as the amount of the different clay size fractions, is to be determined, organic matter should be removed first with hydrogen peroxide, the soluble salts should be washed out with distilled water and the sample should be finally freeze-dried before the "pipette method" or settling cylinders are used with chemical dispersants to prevent aggregation.

Water content

The water content must be measured (weight loss of samples during freeze-drying or drying of sub-samples at 110 °C) because it is needed to relate to linear sedimentation rates (cm yr^{-1}) and/or mass accumulation rates ($\text{mg m}^{-2} \text{yr}^{-1}$). When sediments with a water content exceeding 90 % are analysed for chemical constituents, a "salt correction factor" should be introduced (dilution of solid sediment parts by dried sea salts).

Carbonates

The determination of carbonates is generally carried out by measuring the CO₂ released by 2 or 4 M HCl. In the most simple cases, this measure is by weight or volume (Bernard calcinometer). The analyses of "total carbon" mentioned below can provide this value by determining the difference between an untreated sample and a decarbonated sample. Moreover, the carbonates can be semi-quantitatively estimated by calcination at 1050 °C, after determination of the organic matter (through ignition loss, see below). This method is simple but not very specific and it depends very much on the temperature chosen and on the way this is regulated in the furnace.

Organic carbon

The methods currently most used follow different principles. These are in the order of prevalence:

- Total carbon determination by total combustion in a flow of oxygen in the presence of a catalyst. The resulting CO₂ is measured. The organic carbon will be obtained after subtraction of the inorganic carbon (see above). Specific instruments are available for this type of analysis.
- The organic matter content is estimated by difference weighing before and after combustion of the sample at 450 °C to 550 °C in a muffle furnace. By dividing by 1.8, a semi-quantitative number for "organic carbon" may be obtained.
- The organic matter is oxidized by K₂Cr₂O₇ in sulphuric acid, followed by back titration with iron sulphate and ammonia (Olausson, 1975_a).

The results obtained by these three methods are very well correlated with each other. Most specific for "organic carbon" is the first method mentioned.

4.3 INORGANIC CONSTITUENTS

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Total phosphorus

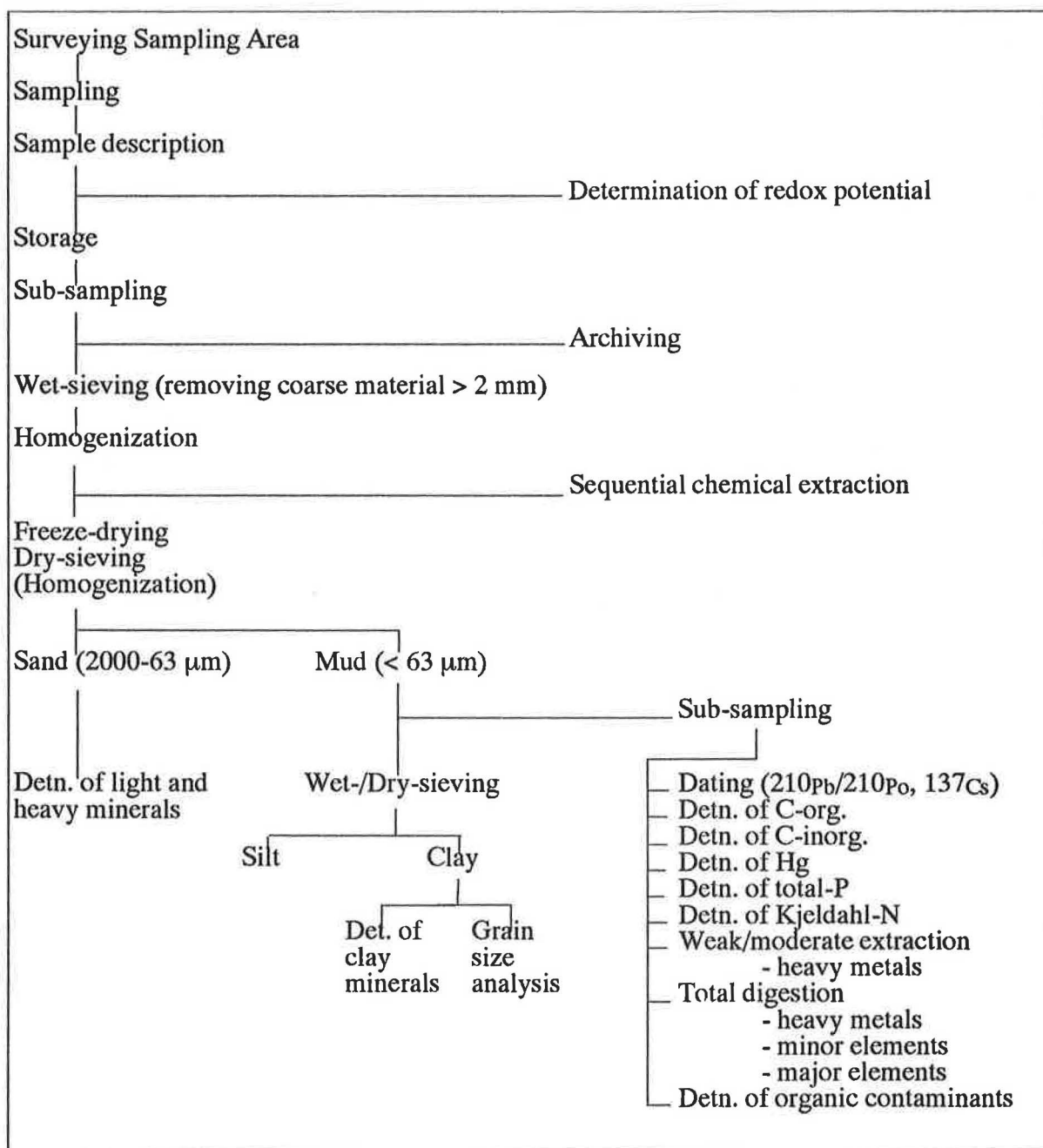
The sample is digested with HNO₃ and HClO₄ (both concentrated) in order to release organic phosphorus and to decompose inorganic forms. An acid ammonium-molybdate reagent is added to a suitable volume of the filtered, digested sample. The resulting phosphomolybdate complex is reduced to an intensive blue dye by ascorbic acid. The intensity of the colour is measured in a spectrophotometer at 882 nm. Samples with a P-content greater than 20 µg g⁻¹ can be measured (Olausson, 1975_a). For the extraction of the easily leachable fraction, see below.

Kjeldahl nitrogen

Kjeldahl nitrogen is the sum of organic and NH₄-N. The nitrogen compounds are converted to ammonium sulphate. The NH₃ is released and distilled off from this salt (in order to eliminate interfering substances) and determined as indophenol blue dye at 625 nm after addition of

sodium phenate and sodium hypochlorite solution. With the method described by Olausson (1975_a), $\text{NH}_3\text{-N}$ concentrations ranging from 400 to 7500 $\mu\text{g g}^{-1}$ can be measured.

Table 4.3.1 Typical approach for the determination of physical and chemical parameters in sediments.



"Total" and partial digestion/extraction methods

In order to determine the major, minor and trace metal concentrations in marine sediments by wet chemical methods, it is necessary to dissolve all or part of the sample. Sample digestion methods commonly used are:

- "total" decomposition,

- strong acid digestion,
- moderate or weak acid extraction,
- sequential extraction procedures, or
- specific procedures (e.g., Hg).

In the following paragraphs, methods will be mentioned which have been used successfully by experienced laboratories and/or in the course of intercalibration exercises (Loring, 1987; Loring and Rantala, 1990; ICES, 1987b).

"Total" decomposition methods use hydrofluoric acid (HF) in combination with concentrated oxidizing acids or their mixtures, such as aqua regia. In addition, to perform real decomposition, or alternatively, alkaline fusion followed by acid dissolution of the flux can be used.

HF decomposition has several advantages:

- (a) HF is the only acid that completely dissolves the silicate lattice and releases all the associated metals, such as Al, Fe, and Li, used for the grain size normalization of the data.
- (b) Accuracy can be assessed by analyzing reference materials certified for their total metal concentrations mainly determined after HF decomposition.

(Some laboratories have been reluctant to use HF due to its corrosive nature and health aspects. However, 28 years of experience has shown (Loring and Rantala, 1990) that the use of HF poses no greater danger than other strong acids when normal laboratory safety rules for handling acids are observed.)

Very often, HF and aqua regia are used together in a sealed teflon decomposition vessel ("teflon bomb") of about 20 to 50 ml capacity. The main advantages of the teflon bomb decomposition are (a) rapid decomposition, (b) reduced risk of contamination, (c) small volume of acid required, and (d) no loss of volatile elements. All teflon vessels with screw tops can be heated in a microwave oven or, very simple and also effective, submerged in boiling water. For heating the bombs by submersion in boiling water, suitable covered ceramic dishes on a hotplate are recommended. (For more details on necessary laboratory equipment, labware and reagents (49 % HF, 70 % HNO₃, 37 % HCl, boric acid; all of high quality) specific methodological guidelines (Loring and Rantala, 1990) should be consulted.)

As a rule, to 0.1 to 1 g of the dried sediment sample 1 ml aqua regia (HNO₃ : HCl = 1 : 3 v/v) and 6 ml HF are added. The carefully closed teflon bomb is heated for 1 min in a microwave oven or at least 1 hour in boiling water. After cooling in cold water, the digest is poured into a solution of 5.6 g H₃BO₃ in 20 ml H₂O and made up to 50 or 100 ml. (For samples with more than 0.5 g sediment/100 ml, gelatinous precipitates of borosilicates will occur. After 7 to 14 days those precipitates will settle and the atomic absorption spectroscopy (AAS) analyses can be performed.)

From UNEP (1985), a digestion of air-dried sediment samples with concentrated HNO₃ in open teflon beakers is conducted in order to destroy organic matter and evaporated to dryness at 80 °C. This is followed by treatment with 5 ml mixed HNO₃/HClO₄/HF in the ratio 3:2:1 and evaporating at 120 °C to dryness. The residue is taken up with HCl and diluted to 25 ml. The main disadvantage of this digestion version is the risk of losses of trace elements due to formation

of compounds of low solubility in HCl and evaporation losses. In addition, information on the concentrations of some elements necessary for the characterization of sediments and normalization, e.g., Al, cannot be obtained. The advantages in relation to the bomb digestion are reduced matrix problems in the subsequent AAS measurements and lower blanks by avoiding the addition of high amounts of boric acid, needed for the complexation of the excess fluoride.

For strong acid digestion without HF addition, many procedures are presently in use (ICES, 1987b) from which some dominate, e.g.,

- a) several hours' digestion of sediments with 1:1 diluted HNO₃ (about 1 g/20 ml),
- b) digestion of 0.5 g sediment with HCl (2 ml) and HNO₃ (5 ml) for 15 to 24 hours,
- c) digestion with hot concentrated HNO₃ (1 g/5 ml),
- d) digestion in closed plastic bottles in an autoclave at 120 °C for 0.5 h (1 g/20 ml 1:1 HNO₃).

Generally, compared to procedures which include HF, the strong acid digestions dissolve significantly lower amounts of Al, Cr and Ti. Depending on the nature of the samples and the specific digestion procedure, lower results will be obtained for many elements (Cd, Zn, Cu, Fe, Mn, Ni, Pb). Therefore, the use of such strong acid digestions seems only feasible for monitoring programmes on a national level for restricted local areas influenced by contamination from point sources, but not for programmes run on a multinational level in the Baltic Sea.

For a quick screening on the easily available (non-detrital) fraction of the metal content in sediments, some very simple extraction procedures using moderate or weak acids are in use:

- a) 18 hours' extraction of 0.5 g sediment sample with 25 ml 1 N HCl (ICES, 1987a);
- b) 6 hours' extraction of 2 g sediment sample with 25 ml 25 % acetic acid (Loring and Rantala, 1990).

The 1 N HCl removes significantly larger amounts of Cu, Mn, Pb and Zn from all sample materials and partly also Cd, Cr, Fe and Ni from some sample materials than the acetic acid treatment (Loring, 1987). This is not surprising due to the different strengths of both acids. (In no case should the extracted metal fraction be declared as the "bioavailable" or "true potentially available part" of the sediments! The term "bioavailable" should be used only specifically in relation to metal-accumulation experiments with selected organisms.) To simulate the "potentially available fraction" following changes of the natural background conditions of the sediments, a combination of different pre-treatment procedures may be applied (e.g., low temperature ashing (LTA) of the organic part/wet oxidation of sulphides and related compounds/reduction of Fe/Mn-oxides/hydroxides with hydroxylamine) before a very weak extraction with a diluted acid (0.01 to 0.05 N HCl) may follow. However, such type of "optimum procedure" would be extremely laborious and time consuming. Therefore, a one-step moderate to weak extraction could present a reasonable alternative.

Most studies dealing with contaminants in sediments concern "total" concentrations. Relatively few attempts have been made to evaluate their speciation, i.e. the partitioning among the various forms in which they might exist. Use of total concentrations as a criterion to assess the potential effects of sediment contamination implies that all forms of contaminants have an equal impact on the environment. Such an assumption is clearly untenable.

Conceptually, the sediment material can be partitioned into several portions which can be extracted by appropriate reagents. More elaborate methods make use of sequential extractions. The extraction procedures have been borrowed or adapted from the methods of soil chemical analysis.

The still limited use of sequential extraction (see, eg., Belzunce Segarra et al., 1987) procedures is due to

- time consumption,
- blank problems in connection with the use of many different reagents,
- no clear "cuts" are possible to be made with most extracting reagents between different binding forms,
- undesired changes of original natural binding phases occur during storage and sequential treatment of the samples.

Nevertheless, such procedures are recommended for use on a selected number of samples to furnish detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of contaminants (Tessier et al., 1979).

In the following, a suite of extraction procedures for metals from sediments are summarized by Salomons and Förstner (1980, see refs. therein).

Table 4.3.2 Extraction procedures for metals from sediments.

Method	Reference
<u>Adsorption and cation exchange</u>	
BaCl ₂ /triethanolamine at pH 8.1	Jackson, 1958
MgCl ₂ at pH 7.0	Gibbs, 1973
NH ₄ HOAc, pH 7.0	Jackson, 1958
<u>Carbonate phases</u>	
CO ₂ -C treatment of suspension	Patchineelam, 1975
Acidic cation exchange resin	Deurer et al., 1978
NaOAc/HOAc buffer, pH 5.0	Tessier et al., 1979
HOAc	Chester, Hughes, 1967
<u>Reducible phases (in appr. order of Fe release)</u>	
Acidified hydroxylamine-hydrochloride	Chao, 1972,
EDTA, pH 8.0	Chao and Zhon, 1983
Ammonium oxalate buffer (Tamm's reagent)	Borraard, 1976
Hydroxylamine/acetic acid	Schwertmann, 1973
Dithionite-citrate buffer	Chester, Hughes, 1967
	Holmgren, 1967
<u>Oxidizable phases (incl. sulphides and org. matter)</u>	
Acidified H ₂ O ₂ , extracted with NH ₄ OAc/6 % HNO ₃	Gupta, Chen, 1975
NaOH, extracted with H ₂ SO ₄	Volkov, Fomina, 1974
Organic solvents	Cooper, Harris, 1974
NaOCl	Gibbs, 1973
Alkali pyrophosphate	Eaton, 1979
0.1 HCl, bubbled with air (sulphides)	Kitano, Fujiyoshi, 1980

Taking into consideration the above-mentioned problems with extraction procedures (practicability, blanks, etc.), the following sequence has proved successful (Förstner and Calmano, 1982; Tessier et al., 1979):

- a) Exchangeable cations: 1 M NH_4OAc , pH 7; solid: solution = 1:20
- b) Carbonate phases: 1 M NaOAc/HOAc buffer, pH 5; 5 hours/20 °C; 1:20,
- c) Slightly reducible phases (e.g., manganese oxides/hydroxides):
0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.01 N HNO_3 , pH 2; 12 hours shaking; 1:100,
- d) Moderately reducible phases (e.g., amorphous iron oxides/hydroxides: 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3; 24 hours shaking; 1:100,
- e) Organic forms and sulphides: 30 % H_2O_2 + HNO_3 , pH 2, at 85 °C, extracted 24 hours with 1 M NH_4OAc ; 1:100,
- f) Residual fraction (e.g., silicates): "total" digestion using $\text{HNO}_3/\text{HCl}/\text{HF}$ (see above).

Between the different steps of the sequential extraction procedure, the solid residues are washed and separated by centrifuging. It may be advantageous for the subsequent AAS analyses to evaporate the diluted extraction solutions to dryness and take them up again using always a defined matrix solution.

For the determination of mercury in sediments most laboratories use separate digestion procedures. It has been shown that for the quantitative release of Hg from sediments, an oxidation step with strong acids is sufficient; the silicate lattice must not be dissolved by use of HF. All relevant procedures include digestion with HNO_3 which can be obtained in high quality, i.e., low Hg blanks, by sub-boiling distillation in a silica quartz apparatus. The digestion may be carried out in teflon bombs (e.g., about 2 hours at 130 °C) or several hours at 60 to 80 °C under ambient pressure. The oxidation of sediments only with HNO_3 is not sufficient to decompose the organic matter entirely to CO_2 and other oxides. Therefore, an additional oxidation of the HNO_3 extract, e.g., with some milliliters of saturated KMnO_4 solution, is necessary. If from the beginning a mixture of HNO_3 and H_2SO_4 is used for digestion, the treatment with permanganate may be omitted. The use of HNO_3/HCl mixtures may result in lower concentrations (Loring, 1987). However, in the presence of cinnabar (HgS), HCl should be added for quantitative recovery of Hg.

Most laboratories use the AAS reduction/aeration "cold-vapour" method for the instrumental determination of Hg. The majority of them use Sn(II) solution as a reducing agent. Before, an excess of KMnO_4 must be destroyed by adding $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution. The absorption of the Hg^0 vapour is measured at 253.7 nm using relatively inexpensive equipment. Preferably, an instrument with dual beam long quartz absorption cells should be used, thereby providing the opportunity for background correction (volatile matrix components which may absorb in the UV-range). The application of mercury traps (e.g., mercury-coated silica wool or glass beads etc.) from which the Hg^0 can simply be released again (e.g., by electrical heating) will reduce the risk of interferences by matrix components and will lower the detection limit by at least one order of magnitude.

Instrumental analytical techniques

In an ideal, general sense, a routine analytical technique for geochemical analysis should (Willis, 1986):

- have a wide coverage of elements,
- have a wide concentration range,
- be accurate and precise,
- have high sensitivity,
- be capable of analysing a range of sample sizes, from single grains to grams,
- be capable of analysing at least 4 to 6 samples per day for up to 40 elements,
- be simultaneous or near-simultaneous, if the technique is destructive,
- have trace element capabilities in the ng g^{-1} range,
- be cost effective,
- be safe and easy to use by relatively unskilled personnel,
- be as free as possible from matrix effects, and
- preferably be capable of analysing solid samples.

One day we may be fortunate enough to have such a technique at our disposal, but meanwhile, with all their limitations, we must use those techniques presently available.

The six most important instrumental methods employed by geochemists today working in the field of trace elements are Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-ray Fluorescence Spectrometry (XRFS), Instrumental Neutron Activation Analysis (INAA), thermal source Mass Spectrometric Isotope Dilution analysis (MSID), and Electron Microprobe Analysis (EMPA). In the following table (Table 4.3.3) these six techniques have been compared with respect to different criteria. Taking all these criteria together, AAS is an excellent choice when determining very low concentrations of elements such as As, Hg and Cd in sediment digests with high precision. For the analysis of samples for which only very small volumes are available, such as interstitial waters, AAS with electrothermal atomization is almost unbeatable.

Comparison of instrumental analytical techniques

Table 4.3.3 Comparison of instrumental analytical techniques.

	AAS	ICP-OES		XRFS		INAA	MSID	EMPA
		sequ.	sim.	sequ.	sim.			
qual. anal. - range - speed - sensitivity - selectivity	wide v. poor v. high moder.	wide high v. high moder.	lim. v. high v. high moder.	wide moder. high high	lim. high high high	wide high high high	wide moder. v. high v. high	wide high moder. high
quant. anal. - dyn. range - few samples - many samples - precision	poor fast slow high	good fast moder. moder.	good fast fast moder.	good moder. moder. high	good fast fast high	good moder. slow v. high	good moder. slow v. high	moder. moder. moder. high
sample type - liquid - solid	yes no	yes no	yes no	yes yes	yes? yes	yes yes	yes yes	no yes
destructive method setup matrix effect spectr. interf. cost (1000 \$)	yes moder. moder. low 15-65	yes diffic. low high 60-90	yes diffic. low high 80-250	no moder. high low 100-150	no moder. high low 200-350	no? moder. none high 2000	yes moder. low low 500	no moder. high low 300

Despite some disadvantages (poor dynamic range, poor speed) AAS continues to hold the first place in most laboratories working in the field of environmental geochemistry. In the near future, ICP-OES will certainly not replace AAS, however, both techniques will complement each other because many refractory elements which are measured only with poor sensitivity by AAS are analysed without problems by ICP-OES. The other methods mentioned above are mostly used either

- for a quick semi-quantitative screening covering major and minor elements in adequately prepared solid samples (XRFS),
- for highly precise and accurate analyses on selected samples, e.g., exotic samples (material from the moon, meteorites etc.) or those from intercomparison exercises (INAA, MSID), or
- for mineralogical investigations on selected particles as a supplement to bulk AAS and/or ICP-OES analyses (EMPA).

The relatively new method of inductively coupled plasma mass spectrometry (ICP-MS) has got a number of good references (McLaren et al., 1987). However, it is not expected that this technique will make the AAS or the conventional ICP-OES in environmental (geochemical) analysis needless.

Finally, some trends recognizable when applying AAS for trace metal analyses in sediment digests should be listed:

- For calibration, standard addition methods are mandatory.

- All flameless (GFAAS) and most flame AAS (FAAS) analyses should be performed in the background correction mode, preferably with a Zeeman device.
- For many elements, the STPF (stabilized temperature platform furnace) concept has proved successful (Rantala and Loring, 1987).

(This includes the use of a platform, preferably of glassy carbon, in a pyrolytic coated graphite tube, fast jumps from ashing to atomization temperatures, a cooling step after atomization and application of matrix modifiers in combination with high performance instrumentation. This is particularly important for highly volatile elements with very low contents in the digests (Cd) or which show relatively low analytical-spectroscopic sensitivity (Pb).)

- FAAS should be used when the elemental concentration levels in solution are adequate for precise determinations. FAAS is also faster and less prone to interferences for most elements than GFAAS (Loring, 1987).
- Air-acetylene flame should not be used for Cr due to numerous inter-element and oxidation state effects. These problems are not evident in an N₂O flame which is recommended for this element.
- FAAS is not recommended for Cd. This is due to potential spectral interferences and unsatisfactory background corrections by the mostly used deuterium background correctors that can result in serious over-compensation and apparent negative values.
- Precision in GFAAS determinations will be improved considerably by automatic sample injection rather than manual pipetting of the sample into the furnace tube.
- The determination of Cr by GFAAS requires relatively diluted solutions, otherwise results will be low.

4.4 ORGANIC CONTAMINANTS IN SEDIMENTS

4.4.1 Organochlorine compounds (OCs)

Lutz Brüggemann and Matti Perttilä

UNEP (1982) has proposed a reference method which can be used for the quantification of pp'DDT, pp'DDD, pp'DDE, PCBs and PCCs (toxaphene) by gas chromatography (GC) with electron capture detector (ECD) after solvent extraction and suitable clean-up. The freeze-dried sediments are Soxhlet extracted with hexane (20 g/250 ml, 8 hours). The extract is concentrated with a rotary evaporator to about 10 ml (water bath temperature not exceeding 30 °C), transferred to a Kuderna-Danish concentrator and brought to about 1 ml. Clean-up is performed by treating the extract on the top of a column with partially de-activated Florisil (4-3) and eluting with 60 ml hexane (=fraction 1) and 50 ml hexane/diethylether (9:1) followed by 20 ml of hexane/diethylether (8:2) (=fraction 2). The two fractions are concentrated to the appropriate volume (0.5 to 1 ml) for injection into the GC. Fraction 1 is then treated with pre-cleaned mercury to bind sulphur compounds often present in sediments and interfering in the GC analysis (1 drop Hg⁰, 1 min. shaking, centrifuging). Fraction 1 contains the DDT metabolites and the PCBs, in fraction 2 the PCCs are present.

An alternative extraction method has also been suggested (Perttilä and Haahti, 1984). About 1 g of freeze-dried sediment is extracted with 1:1 hexane-acetone solution for one hour in an ultrasonic bath. The agitation caused by the ultrasonic vibration is enough to effectively extract organic components from the sediment material. Several samples can be treated quickly.

Elemental sulphur, which is also extracted, must consequently be removed. This can be done either by column chromatography using 2-3 cm long, 4 mm wide glass columns filled with copper powder. The copper powder (50-200 mesh) must first be treated with dilute nitric acid to remove contamination. A faster treatment is offered by an acid-cleaned copper wire spiral. Sulphur is reduced on the copper surface as sulphide. The procedure is repeated until the wire stays clear in the solution. The remaining liquid is then free of sulphur and can be fractionated and analysed.

Analysis is done using capillary columns. The use of internal standards, which should be added to the samples prior to extraction, is urged. Dehydrochlorination of pp'DDT to pp'DDE and pp'DDD to pp'DDMU with KOH in methanolic solution provides confirmation of these compounds. Whenever possible, confirmation should be carried out using GC with mass-spectrometric (MS) detection. For the PCBs, selected single compounds should be quantified by using a standard addition of mixtures with known mass ratios of the congeners most relevant in relation to toxicity, persistence, environmental impacts but also analytical detectability.

Standards should be injected at least every fifth sample in auto-mode or, alternatively, at the beginning and end of the working day in the case of manual injection.

The apparent state-of-the-art for analysis of PCB congeners is an interlaboratory variability of about 80 % and an intralaboratory variability of about 40 % at the tens of ng g^{-1} dry weight concentrations in sediments (Calder et al., 1988). Improvements may be made by HPLC approaches for clean-up which offer better separation of interfering compounds in relation to gravity flow clean-up columns.

4.4.2 Petroleum hydrocarbons (PHs)

Robin Law

Introduction

The analysis of sediments for hydrocarbons is a component of many investigations and monitoring programmes as concentrations are generally higher and thus easier to measure than in water, and also less variable in the short term (less patchy). Around point sources, such as offshore oil production platforms or refinery outfalls, gradients of concentration may be established which help to determine the maximum area of effect. Hydrocarbons deposited in sediments may persist for a long period of time, particularly under anoxic conditions. The hydrocarbon composition within the sediments can be altered both by degradation, which leads to the loss of some components, and by early diagenetic reactions in shallow sediments, which lead to the *in-situ* production of particular compounds, such as perylene.

The range of hydrocarbon concentrations found in sediments is very wide, total hydrocarbon concentrations varying from about $1 \mu\text{g g}^{-1}$ dry weight in clean offshore sand deposits to $> 10 \%$ in areas impacted by oil spills or close to platforms discharging cuttings resulting from the use of oil-based drill muds. In addition, different particle sizes and types within a given sediment may have different hydrocarbon compositions (Thompson and Eglinton, 1978). The wide range of boiling points and polarities of hydrocarbon compounds found in sediments also complicates the analysis as no single method can extract and concentrate all hydrocarbons present. To some extent, therefore, the analytical method chosen will determine the types of hydrocarbons found.

Extraction and clean-up

Hydrocarbons in the range $C_1 - C_{10}$ are not amenable to routine solvent extraction techniques because of their high volatility. Methods for their isolation and analysis are mainly limited to sea water, although dynamic headspace techniques using inert gas purge and trap systems have also been used in sediments (Bernard et al., 1978).

A number of different solvent extraction methods are commonly used for the extraction of hydrocarbons ($> C_{10}$) from sediments. No standard method exists, but most methods involve the combined use of polar and non-polar solvents to obtain an efficient extraction (IOC, 1982). Fine sediments (mud, silt, clay) are much more difficult for solvents to penetrate so as to release the hydrocarbons bound to sediment particles, and may require a more careful choice of method and solvents to extract effectively than coarser and relatively open sediments (sand, gravel). Very high concentrations of hydrocarbons, e.g., $50\,000\ \mu\text{g g}^{-1}$ dry weight, may also require smaller sample sizes than normal if the capacity of the solvent to dissolve a mass of hydrocarbons is not to be exceeded. Solvent extractions may be carried out at ambient temperature with mixing of the sediment and solvent phase by shaking, ball-mill tumbling, or the use of ultrasonic probes. Refluxing with solvent, or with methanolic KOH to perform an alkaline digestion prior to solvent extraction, and the use of Soxhlet extraction with either methanol alone or a mixed solvent, such as dichloromethane/methanol, complete the suite of most commonly used extraction techniques. Although historically benzene was very commonly used as an extraction solvent or as one component of a solvent mixture, it has now been generally discarded on health grounds and replaced by toluene or dichloromethane. The use of carbon tetrachloride as a solvent in studies using infra-red spectrophotometry has also now begun to decline for similar reasons, 1, 1, 2-trichlorotrifluoroethane being a suitable alternative.

Comparisons of the performance of a number of these extraction methods have been reported. Farrington and Tripp (1975) compared by gas chromatography:

1. Soxhlet extraction (benzene/methanol),
2. Alkaline hydrolysis (methanolic KOH; benzene), and
3. Soxhlet extraction (acid wash, benzene/methanol).

The sediment used was a wet sandy silt containing about $250\ \mu\text{g g}^{-1}$ dry weight of hydrocarbons. No significant differences were found in the efficiency of the three techniques.

Awad compared 7 different methods for the extraction of a sediment from the Loire estuary, with analysis by UV fluorescence (Awad, 1977) and gas chromatography (Awad, 1981). The methods used were:

1. Soxhlet extraction (methanol/benzene),
2. Soxhlet extraction (methanol/pentane),
3. Waring blender (chloroform/methanol),
4. column elution (dried, petroleum ether),
5. shaker (pentane),
6. cold solvent in mortar (hexane), and
7. Soxhlet extraction (methanol/hexane).

When extracts were analysed by UV fluorescence, considerable differences were found in the maximum fluorescence intensities obtained, up to a factor of 13. The positions of the fluores-

cence maxima and the shapes of the emission spectra were also very variable. Awad (1977) concluded that the major influence on the extraction efficiency was the solvent mixture used for extraction rather than the method employed. The most efficient method was the method 3, which utilised chloroform/methanol and was a variant of a total lipid extraction method intended for tissues (Bligh and Dyer, 1959).

The results of the gas chromatographic analyses (Awad, 1981) showed the most efficient method to be the method 1. Yields again varied widely, the least efficient method giving only 1.4 % of the total hydrocarbon (THC) from method 1. Chromatograms showed little agreement on the number and distribution of peaks, or of the relative size of the UCM. Awad's conclusion was that neither a quantitative nor a qualitative comparison of levels of petroleum hydrocarbon contamination in different areas of the ocean would be possible without standardisation of analytical methodology.

Hilpert et al. (1978) carried out an intercomparison exercise among eight laboratories using two intertidal sediment samples of fine to medium grain sand. Analysis was by gas chromatography for both aliphatic and aromatic hydrocarbons, and the methods used by the laboratories were:

1. Soxhlet extraction and headspace (dichloromethane/diethyl ether),
2. ball-mill tumbler (diethyl ether),
3. reflux (benzene/methanol),
4. cold solvent extraction (benzene/methanol),
5. ball-mill tumbler (heptane),
6. reflux (toluene/methanol),
7. alkaline digestion (methanolic KOH), and
8. reflux (toluene/methanol).

Concentrations of total extractable hydrocarbons were from 9 to 500 ng g⁻¹ and 49 to 6625 ng g⁻¹ dry weight for the two sediments, respectively, with results for aliphatic and aromatic hydrocarbons showing a similar variation. Pristane/phytane ratios were more consistent, but there was little agreement over which was the most abundant n-alkane or aromatic hydrocarbon. Little interpretation could be made of the results obtained against the extraction method employed.

Wong and Williams (1980) compared three extraction methods:

1. alkaline digestion (methanolic KOH),
2. Soxhlet extraction (chloroform), and
3. Soxhlet extraction (carbon tetrachloride)

by analysis of a heavily polluted estuarine sediment of fine particle size. With wet sediment, method 1 gave results which both indicated greater extraction efficiency and more reproducibility than methods 2 and 3, and method 2 was somewhat more efficient than method 3. When dried sediments were used, all three methods yielded broadly comparable results, although about 16 % of the hydrocarbons determined by the wet extraction procedures were lost as a consequence of the drying process.

Lake et al. (1980) compared the analysis of polycyclic aromatic hydrocarbons (PAH) in sediments by GC-MS, using three extraction techniques:

1. Soxhlet extraction (benzene/methanol),
2. ball-mill tumbler (methanol/dichloromethane), and
3. reflux (dichloromethane).

Methods 1 and 3 were found to be equally efficient, but method 2 was only about 72 % as efficient as the other two methods. The relative proportions of different compounds and compound types was, however, very similar for all three methods.

Brown et al. (1980) also compared a ball-mill tumbler method with other methods for an intertidal sediment (fine to medium sand), using gas chromatography. The methods used were:

1. ball-mill tumbler (dichloromethane/methanol),
2. alkaline digestion (methanolic KOH),
3. Soxhlet extraction (benzene/methanol), and
4. Soxhlet extraction (dichloromethane/methanol).

In this study, method 1 was found to be as efficient as the other three methods for the extraction of aliphatic hydrocarbons in the range C₁₃ - C₂₆, although Soxhlet extraction was more efficient in the range C₂₇ - C₃₁. Method 2 was generally the least efficient but the most reproducible for both aliphatic and aromatic hydrocarbons, and method 4 was the least reproducible in both cases. The better performance of the ball-mill tumbler method in this study may be due to particle size variations between this sediment and that used by Lake et al. (1980), but unfortunately their paper gives little detail of the sediment used.

MacLeod et al. (1982) compared the results of 13 laboratories, each using its own methodology in the first phase of an intercomparison exercise, using an intertidal harbour sediment and gas chromatography. Concentrations of 18 alkanes in the range 5-300 ng g⁻¹ dry weight generally agreed within a factor of 3. Less precise results were obtained for 10 aromatic compounds present at concentrations up to 10 times greater. The second phase of the exercise involved eight laboratories in the analysis of a subtidal river sediment. Two methods were used:

- | | |
|-----------------------|----------------------------|
| 1. Soxhlet extraction | } (solvent systems varied) |
| 2. Ball-mill tumbler | |

followed by capillary gas chromatography. Results from two laboratories were significantly different from those of the other six, whose results (within the range 10-2000 ng g⁻¹ dry weight) generally agreed within a factor of 2. Again the choice of solvents seemed more important than the choice of extraction method. Recommendations made for further improvement of comparability were:

1. to rechromatograph the aromatic hydrocarbon fraction from silica gel on Sephadex LH-20,
2. to specify the capillary GC column and mode of integration, and
3. the use of internal standards.

The first ICES intercomparison exercise on petroleum hydrocarbon analysis (Law and Portmann, 1982) used a fine sandy intertidal sediment from an industrial estuary, oven-dried, with a total hydrocarbon concentration of about 35 mg g⁻¹ dry weight. No methods were specified

and various cold solvent, alkaline digestion, and Soxhlet extraction techniques were employed. The largest set of data reported was for THC by UV fluorescence using excitation and emission wavelengths of 310 and 360 nm, respectively (IOC/WMO, 1976). The mean value obtained (30 laboratories) was 33.2 mg g^{-1} Ekofisk oil equivalents with an intra-laboratory RSD of 1.9 to 3.0 %. The means obtained by infra-red spectrophotometry and gas chromatography were 28.1 mg g^{-1} (RSD 79.4 %, 15 laboratories) and 26.2 mg g^{-1} (RSD 27.5 %, 9 laboratories), respectively. Results for specific aliphatic and aromatic hydrocarbons were fewer and much more variable. For total hydrocarbon analyses, at least, most extraction techniques seemed to be capable of yielding good results, although alkaline digestion methods seem to be the most reproducible.

Clean-up techniques seem to be fairly standard. Thin layer chromatography (TLC) methods have now been largely replaced by column chromatography on alumina and silica gel, and treatment with activated copper is commonly used to remove elemental sulphur. The aromatic fraction obtained from chromatography on silica gel will also contain olefins, which can be removed by chromatography using Sephadex LH-20. Preparative high performance liquid chromatography (HPLC) is also now beginning to be used as a routine clean-up technique for hydrocarbon extracts, particularly as it can easily be automated.

Analytical techniques

A number of methods are in routine use for hydrocarbon analysis, and a brief summary of their advantages and disadvantages is included in the following list:

1) Gravimetry

This is a relatively cheap and simple method with a sensitivity in the low mg g^{-1} range for total hydrocarbons, although errors are much greater at low concentrations. It cannot be used for volatile oils as evaporation to dryness entails heavy losses of low-boiling materials. No discrimination can be made between hydrocarbon and non-hydrocarbon material.

2) Infra-red spectrophotometry

This technique is largely unaffected by calibration errors for different oils, but is very insensitive to aromatics. Lipid-type materials will also be detected, so quantitative measurements are badly affected by inefficient clean-up. It has been commonly used for fingerprinting, either in the absence of or in addition to chromatographic techniques.

3) Ultra-violet fluorescence spectroscopy

This technique is very sensitive to aromatic hydrocarbons, but aliphatic hydrocarbons and lipids are not detected. Calibration of the technique is affected by the choice of oil, to a small extent for different crude oils for example, but to a large degree for the new low aromatic base oils used in drilling fluids in which the aromatic content may be 1 %. Synchronous spectra provide some qualitative information on the range of aromatics present, and contour diagrams may be used for fingerprinting. Care must be taken to make measurements and run spectra only in a dilution range where quenching and self-absorption effects are absent. Simple ways to check

this are:

- 1) monitor the size of the Raman absorption peak for both pure solvent and samples,
- 2) dilute the extract by a known amount and remeasure the fluorescence. The fluorescence signal should decrease by the same factor. If the fluorescence yield decreases by a lesser amount, then quenching or internal reabsorption of emitted light were occurring (and may still be doing so!).

4) *Capillary gas chromatography*

This technique is useful both quantitatively and qualitatively. Chromatograms of aromatic hydrocarbon fractions may be very complex if large quantities of alkylated PAH are present, but are much simpler when combustion PAH are the major source. It is excellent for fingerprinting. New column materials and more thermostable stationary phases may extend the useful analytical range for n-alkanes above n-C₅₀, possibly up to n-C₁₀₀ (Lipsky and Duffy, 1986).

5) *High pressure liquid chromatography*

A useful technique for the analysis of aromatics when coupled with UV absorption or (particularly) fluorescence detectors. Lacks resolution compared to capillary GC unless microbore systems are used, in which case the pumping system must be superior because of the very low flow rates required, and analysis times are very long (1-2 days). Resolution very similar to that of capillary GC may then be obtained, but it is of little use as a routine tool.

6) *Computerised gas chromatography-mass spectrometry*

Currently this is the most powerful technique available for the analysis of specific aromatic and aliphatic hydrocarbons. Mass spectra provide confirmation of compound identity and the ability to identify unknowns. The use of multiple internal standards allows correction for extraction efficiencies to be made at various points in the boiling range and for different compound types. The use of multiple ion detection (mass fragmentography) gives maximum sensitivity for pre-determined compounds with a high degree of specificity.

Fingerprinting techniques possible using GC-MS include:

- 1) sterane distribution patterns, and
- 2) alkylated aromatic isomer distributions.

In addition combustion PAH, geochemically produced PAH, biogenic and petroleum inputs can all be recognised from GC-MS information, although unequivocal estimates of the relative contribution from each source may be difficult as the same compounds may be derived from one or more sources.

Comparison of some techniques

A recent comparison (Howells, 1986) has investigated the effect of applying different analytical methods (gravimetry, infrared spectrophotometry, ultra-violet fluorescence, gas chromatography) to a range of sediment samples. These were obtained along known concentration gradients at several North Sea oilfields with contrasting contaminant types (i.e., at which

different types of oil-based drilling fluids have been used), in order to compare the absolute concentrations, concentration trends, and interpretation produced by each. A total of 31 sediment samples was analysed in all, and concentrations of total hydrocarbons were in the range 4 - 100 000 mg g⁻¹ dry weight. Results obtained by gravimetry, IR and UVF generally showed good agreement, providing that the correct choice of calibrant oil had been made for UVF. A specified extraction method (alkaline digestion) and clean-up was used. This had previously been shown to give good precision when applied to a variety of sediments and relatively good accuracy as determined from spiked samples, and this contributed greatly to the good agreement found between analytical techniques. It is still necessary, however, to exercise extreme caution when comparing results from different laboratories who may be utilising different methods and solvent systems.

4.5 REPORTING FORMAT FOR CONTAMINANTS IN SEDIMENTS

Lutz Brüggemann

The ICES reporting format for contaminants in sediments should be used in all data exchange, in order to ensure that all relevant supporting and background data are included.

4.6 GOOD LABORATORY PRACTICE

Lutz Brüggemann

Most of the environmental studies in the Baltic Sea based on sediment studies are aimed

- to detect signs of anthropogenic impacts and to quantify them,
- to identify the geo-chronology of those impacts, and
- to provide necessary information for contaminant mass balances.

In each case, accurate and precise data on the concentrations of contaminants in the total sediment samples or in selected fractions are needed. (No data are always better than data of poor quality!) Data of the necessary quality can only be produced when in each single step of the whole analytical procedure, from the planning/sampling step until the data processing/reporting, the general principles of "Good Laboratory Practice" (GLP) are taken into consideration. A short guidance shall be given for GLP below (see IOC, 1985):

- a) Each study should be conducted in response to clearly stated aims.
- b) Sampling strategy/programmes should be given careful consideration, since unrepresentative samples will lead to poor data. Matters to be considered include sample location, sampling frequency, sample type, number of samples, statistical requirements for replication and collection procedures. This should ensure representative samples from a geographical and temporal viewpoint.
- c) During sample pre-treatment, care should be taken in the handling of samples to ensure that contamination is avoided and that losses of analyte are kept to a minimum. Procedural blanks should be processed in the same way as samples.

- d) The laboratory facilities should be planned to meet the needs of the particular analysis being conducted so that the contamination of samples during the processing and analytical stage is minimized. The analytical instrumentation should be well maintained and serviced to ensure optimum performance. Staff should have appropriate experience and training in the analysis in question. Participation in workshops should be encouraged and, where appropriate, visits to expert's laboratories should be arranged in order to gain additional experience and expertise. (The preparation and exchange of videos showing analytical procedures in the laboratory, sampling, sample dissection etc., should be encouraged, too.) Finally, and most important, analysts should be encouraged to be involved in all aspects of the work, including the assessment and interpretation of field data, thereby ensuring a commitment to the production of reliable data.
- e) For the storage of samples, suitable containers should be used which do not permit contamination or allow losses of the analyte under examination. If samples are to be stored for long periods prior to analysis, the storage procedure should be checked to ensure that the sample does not change during storage.
- f) The analytical procedure chosen must have the required sensitivity and level of detection to meet the needs of the analytical programmes. As a general rule, the limit of detection should not be more than 1/10 th of the lowest contaminant concentration that is considered might be present in field samples. The estimation of the accuracy and precision of the analytical method should be done on a standard or certified reference material of appropriate matrix and analyte concentration, i.e., the reference material should be made from the sort of material which the laboratory is going to investigate, and it must have analyte concentrations which are similar to those occurring in these natural samples.
- g) Throughout the period of analytical work (which may last months or years) for quality control, regular checks of accuracy and precision should be made to ensure that the quality of analysis remains reasonably constant. As an additional check on analytical performance, the analysts should be encouraged to participate in interlaboratory comparisons with other laboratories in their region/country, or as part of a national or international exercise.
- h) For quality assessment, checks should be made on the analytical performance and, when performance is found to deteriorate, an investigation should be made to identify where errors are occurring. During this check, no analysis of real samples should be made, and this analytical work should not be recommended until the errors have been identified and corrected. (Often "odd" results can be spotted during the interpretation and evaluation of geochemical data. It is important, therefore, to record and keep all details of analyses and the calculation of analytical work so that a systematic check can be made to locate the source of the errors. On some occasions, these errors can arise through mistakes in arithmetic work or transcriptional errors, e.g., writing down numbers or inputting them incorrectly into a computer.)
- i) For the proper storage, processing, reporting and dissemination of data it is important to record all analytical results and other relevant field data in a proper manner, i.e., to transfer data from rough laboratory and field books to the agreed record books once these data have been collected. This fair record should be maintained in a secure place. Besides reporting the sediment contaminant data to the HELCOM they should whenever possible, be published in the open literature. This ensures as wide a distribution of the results as possible and their critical scientific assessment.

4.7 REFERENCE MATERIALS

Lutz Brüggemann

As one necessary prerequisite for obtaining precise and accurate analytical data on contaminant levels in Baltic sediments, the availability and permanent use of suitable reference materials by any programme has been identified. There are several agencies, organizations and institutions on an international or national level which distribute such material, mostly on a commercial basis (Russell, 1984; Berkovits and Lukashin, 1984; NRCC, 1988; Muntau, 1986; IAEA, 1988; ICES, 1987a).

A short description of reference samples presently available is as follows:

- 1) National Institute of Standards and Technology (NIST) (formerly National Bureau of Standards (NBS)), Washington, DC, USA
 - "SRM 1646"/Estuarine sediment (for trace metals)
 - Dredged material from Chesapeake Bay, certified for 15 elements including As, Cd, Co, Cu, Pb, Mn, Hg, Ni, V, Zn, Al, Ca; information on 19 other elements.
 - (Under preparation, reference materials on "PCBs in freshwater sediments" (2), "PCBs (ppm level) and pesticides (ppb) in marine sediment", "Trace metals in freshwater sediment".
- 2) National Research Council of Canada (NRCC), Ottawa
 - "BCSS-1"/Estuarine marine sediment (for trace metals)
 - Gulf of St. Lawrence/Baie des Chaleurs
 - "MESS-1"/Estuarine marine sediment (for trace metals)
 - Gulf of St. Lawrence/Mirachimi River estuary
 - "PACS-1"/Harbour sediment (for trace metals)
 - Esquimalt harbour/British Columbia
 - "SES-1"/Estuarine sediment (for PAHs)
 - Spiked natural sediment from a Nova Scotian river estuary (15 PAHs certified)
 - "HS-3", "HS-4", "HS-5", "HS-6"/Harbour sediment (for PAHs)
 - Unspiked sediment samples from four harbours in Nova Scotia with varying degrees of commercial and industrial activity (16 PAHs certified)
 - "CS-1", "HS-1", "HS-2"/Coastal and harbour sediment (for PCBs)
 - Unspiked coastal sediment sample taken from the Laurentian Channel midway between Nova Scotia and Newfoundland ("CS-1") and two samples collected from Nova Scotian harbours (10 PCB congeners, i.e., IUPAC Nos. 101, 138, 151, 153, 170, 180, 194, 196, 201 and 209, certified).
- 3) Commission of the European Communities, Community Bureau of Reference (Joint Research Centre, Ispra/Italy)
 - 28 reference materials listed in a group including samples of soil, 3 sewage sludges (BCR CRM 144, 145 and 146), estuarine, lake and river sediments, and waste material which are currently produced in Ispra. (In addition, analytical work is underway to prepare a harbour sediment certified on organochlorine pesticides, PAHs and PCBs.)
- 4) US Geological Survey, Reston, VA, USA
 - "MAG 1"/marine mud (for trace metals)

Collected by the WHOI in 1967 from the Wilkinson Basin in the Gulf of Maine at a depth of 282 m. Holocene red-brown mud. 29 trace elements and the major/matrix constituents certified.

- 5) National Institute for Environmental Studies, Tokyo, Japan
 - "NIES No. 2"/Pond sediment (for trace metals)
 Material collected from the Sanahiro-ike pond, Tokyo, consists of Kanto loma, an ancient volcanic ash (13 trace elements certified).
 - 6) International Atomic Energy Agency (IAEA), Vienna, Austria
 - "Soil-7"/soil (for trace metals)
 27 elements certified
 - "SL-1"/lake sediment (for trace metals)
 28 elements certified
 - "SL-3"/lake sediment (for trace metals)
 26 elements certified
 - "SD-N-1/2"/marine sediment (for trace metals)
 27 elements (As, Ba, Br, Cd, Ce, Co, Cr, Cs, Cu, Eu, La, Lu, Mn, Nd, Ni, Pb, Rb, Sb, Sc, Sm, Sr, Tb, V, Zn) and 7 radionuclides (^{40}K , ^{210}Pb , ^{226}Ra , $^{230,232}\text{Th}$, $^{234,238}\text{U}$) certified
 - "SD-M-1/OC"/marine sediment (for organochlorines)
 9 organochlorines certified, including two Arochlors, dieldrin, HCB, DDT metabolites and HCHs
- Intercomparisons have been run in 1988 to certify another set of reference materials including
- "SD-M-2/OC"/Marine sediment (for PHs)
 - "SD-M-2/TM"/Lyophilized marine sediment (for major, minor and trace elements)
 - "IAEA-306"/Baltic Sea sediment (for radionuclides)
- 7) Institut für Meereskunde, Rostock-Warnemünde, Germany
 - "MBSS-2"/Baltic Sea sediment (for trace metals, minor and major elements, carbonate, C-org, P, N and other parameters)
 Mud sample, collected in 1982 from the Mecklenburg Bight
 - "ABSS-1"/Baltic Sea sediment (for the same determinands as "MBSS-2")
 Mud sample, collected in 1982 from the Arkona Basin
 Both materials were certified by an intercomparison run with 42 laboratories from 18 countries participating.
 - 8) Institute of Geophysical and Geochemical Exploration (IGGE), Beijing, China
 - "GSD-1" to "GSD-8"/8 stream sediments (for trace metals)
 Data for 38 elements available (intercomparison between 30 Chinese labs).
 - 9) National Water Research Institute/Canada Centre for Inland Waters, Burlington, Ontario
 - "WQB-1"/Lake Ontario sediment (for Hg, As, Se)
 - "WQB-2"/Lake Ontario sediment (for Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn)
 - "EC-2"/Lake Ontario sediment (for Hg, As, Se, total PCBs, chlorobenzenes, PAHs)
 - 10) Zentrales Geologisches Institut, Berlin, Germany
 - "Tonschiefer TB" (for trace metals)
 Clayey slate taken from ancient deposits

32 trace elements and 13 major/minor constituents certified

- "Schwarzschiefer TS" (for trace metals)

Black slate, taken from ancient deposits

17 trace elements and 15 major/minor constituents certified

- 11) Research Institute of Applied Physics/University Irkutsk and "Shirshov" Institute of Oceanology, Moscow, USSR (Berkovits and Lukashin, 1984)

- "SDO-1"/Bottom sediment standard (for trace elements)

Terrigenous clay, collected in the eastern Pacific, at a depth of 2962 m

14 trace elements and 12 major/minor constituents certified

- "SDO-2"/Bottom sediment standard (for trace elements)

Volcano-terrigenous silt, collected from the central Pacific in the vicinity of Hawaii, at a depth of 4680 m

14 trace elements and 11 major/minor constituents certified

- "SDO-3"/Bottom sediment standard (for trace elements)

Calcareous ooze, collected in the Red Sea, at a depth of 1350 m

10 trace elements and 13 major/minor constituents certified.

CHAPTER 5 - REVIEW OF TRACE ELEMENT STUDIES IN THE SEDIMENTS OF THE BALTIC SEA

Lutz Brüggemann

Introduction

Already in the previous assessments of the state of the Baltic Sea environment, special chapters have dealt with heavy metals in sediments (see Melvasalo et al., 1981, para. 6.1.3 "Sediments", pp. 206-208; and HELCOM, 1987, para. 3.1.3 "Metals in Sediments", pp. 106-111). Relevant publications which appeared up to about 1984 were reviewed there in summarized form. In this chapter a kind of "progress report" is given, which refers mainly to recently published data under the assumption that the reliability of contaminant measurements in sediments has further increased.

The outcome of a Baltic Sediment Intercalibration Exercise (ICES, 1987_b) was that most of the data available on trace metal contents in sediments delivered by laboratories from the Baltic Sea countries are not comparable. This is mainly due to pre-instrumental steps of the analytical determination, i.e., differences in techniques used for sampling, sample pre-treatment and digestion/extraction. Therefore, an overall discussion of combined trace metal data from all available sources seems not advisable. Consequently, the different papers had to be reviewed more or less separately. Finally, some more general conclusions will be drawn.

Preliminary mass-balance estimates (Brüggemann, 1986) yielded relatively short residence times for some of the environmentally relevant metals in the water body, in the order of 0.1 (Fe), 0.3 (Pb, Co), 2 (Zn), 3 (Hg), 4 (Cu, Ni) and 5 years (Cd). This results in comparatively low dissolved trace metal concentrations which do not deviate very much from those of adjacent seas (North Sea) or other marginal zones of the eastern Atlantic Ocean (Kremling et al., 1986). This occurs despite the high metal load from the bordering countries (HELCOM, 1987). For instance, a compilation of 1986 data for the total municipal, riverine, industrial and atmospheric inputs shows, in addition to nitrogen (940 000 t), phosphorus (55 000 t) and BOD (1 700 000 t), that about 12 100 t Zn (26 % from the atmosphere), 4600 t Cu (8 % from the atmosphere) and 140 t Cd (58 % from the atmosphere) reach the Baltic Sea. Most of these inputs will probably be deposited in the sediments, taking into account the above proposed short residence times in water of the contaminants mentioned and the time necessary before the water of the Baltic Sea itself will be exchanged with North Sea water (about 25 to 40 years).

One of the features of the Baltic Sea is the strong thermohaline stratification and reduced water exchange that result in oxygen depletion and episodic or, recently, quasi-permanent anoxic water areas 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 those anoxic water bodies. Concentrations of trace metals such as Cu and Cd and to a lesser degree also Zn and Pb decrease, probably due to (co-)precipitation as sulphides and carbonates. 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. During some periods, a layer of a jelly-like

Mn/Fe-hydroxide with a thickness of up to 1 cm can accumulate on the bottom and adsorb/co-precipitate trace elements (Emelyanov, 1986a). The resulting deposits are subjected to intensive diagenetic transformation. Very high bacterial activity causes the reduction of Fe(III) and Mn(IV) compounds and of sulphate together with the decomposition of organic matter. Fe-sulphides and Mn-carbonates of rather complex composition (rhodochrosite) are formed which bind an appreciable trace metal fraction (Moenke-Blankenburg et al., 1989).

On the following pages several papers by different authors are reviewed. Although it was attempted to sort these papers according to the sub-areas of the Baltic Sea treated, some regional overlapping could not be avoided.

Kattegat/Belt Sea/Western Baltic

The concentrations and distribution of some heavy metals (Hg, Pb, Cu, Ni, Zn, Cd, Co) in coastal sediment cores (about 0.5 m length) of the eastern parts of the Kattegat and Skagerrak between Idefjord in the north and Askimsviken Bay in the south, including also the Gullmarsfjord, Byfjord, fjords of Orust-Tjörn, the Göteborg Archipelago and Välen, have been reviewed (Cato, 1984). The data (see Table 5.1) show the anthropogenic contamination of these inner and outer Swedish coastal sediments by heavy metals (Hg, Pb, Cu, Zn, Cd) due mainly to direct municipal and industrial discharges. In the more offshore areas of the Skagerrak and Kattegat and in the Brofjord, a more diffuse contamination pattern was identified.

Generally, Hg and Pb are the two most enriched metals in the sediments. Gradients of decreasing metal concentrations with increasing core depths and from the land-based sources in an offshore direction were revealed. The Idefjord and (prior to 1974) the Välen were identified as the most contaminated areas. With respect to Hg, the Göteborg Archipelago also belongs to this group. Whereas Byfjord and Askimsviken Bay have to be considered 'contaminated', the other remaining areas showed only minor contamination; in some cases, the observed concentrations were close to natural background levels. In most of the areas mentioned the contamination situation did not change until 1980. Only the Välen estuary recovered after abatement of the sewage and waste water discharges in 1974 and subsequent restoration.

Table 5.1 Mean values of organic carbon and heavy metals in surface sediments of some areas along the Swedish west coast (in brackets: enrichment factors; background concentrations used are means from samples taken in the Brofjord at 50 cm depth).

Area	Corg %	Cd $\mu\text{g g}^{-1}$	Hg ng g^{-1}	Co $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Ni $\mu\text{g g}^{-1}$	Cu $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	References
Askimsviken Bay (1973; n=20)	1.3	-	270 (10)	-	9 (2.5)	3 (0.4)	7 (2.1)	42 (1.6)	Cato et al. 1978
Upper Välen (1973; n=6)	9.4	-	1350 (50)	-	190 (53)	14 (1.8)	97 (27)	529 (20)	Cato, 1977
Göteborg Archipel. (1982; n=32)	2.2	0.6	770 (28)	-	10 (2.8)	8 (1.1)	5 (1.4)	-	Cato, unpubl.
Orust-Tjörn (1970; n=29)	3.1	-	250 (9)	5	15 (4.2)	9 (1.2)	14 (3.9)	81 (3.1)	Olausson, 1975b
Byfjord (1970-74; n=9)	3.4	-	180 (6.5)	5	23 (6.4)	6 (0.8)	21 (5.8)	110 (4.1)	Olausson, 1975c
Gullmarsfjord (1981; n=12)	3.1	< 0.5	130 (4.5)	-	39	34	22	134	Joslin, 1982
Brofjord (1972; n=67)	3.3	-	160 (4.5)	-	16 (4.8)	10 (1.4)	8 (2.5)	62 (2.4)	Cato, 1977
Idefjord (1975; n=11)	8.1	5.8	1420 (52)	-	115 (32)	8 (1.0)	94 (26)	535 (20)	Olausson & Engvall, unpubl.
Kattegat (1979; n=66)	1.1	-	120 (4.5)	3	12 (3.2)	6 (0.8)	5 (1.3)	36 (1.4)	Olausson, 1975b
Skagerrak (1970; n=49)	1.7	-	80 (2.9)	3	11 (2.9)	8 (1.0)	5 (1.4)	34 (1.3)	Olausson, 1975b

In the Danish marine area, extended investigations of mud accumulation rates and trace metal concentrations in sediments have been carried out in recent years (Pheiffer-Madsen and Larsen, 1986). During the period 1979-1985, about 100 mud or muddy sediment cores were taken with a HAPS box corer from the Kattegat, Belt Sea and western Baltic Sea. Many of them were ^{210}Pb dated. (Additional surface samples were taken with a Van Veen grab.) Only 25 % of the cores showed a mixing depth of less than 2.5 cm and a mixing coefficient of less than $0.5 \text{ cm}^2 \text{ yr}^{-1}$. This means that most cores are rather heavily disturbed in the surface layers. Due to mixing, only 20 of the investigated cores included samples containing of pure pre-1850 material. From those 20 cores enrichment factors were calculated as the ratio of surface values to those in pre-1850 samples (see Tables 5.2 and 5.3).

Table 5.2 Enrichment of trace metal concentrations in the Belt Sea surface sediments compared to the pre-1850 level.

Metal	Kattegat	Belt Sea	Western Baltic
Pb	3.2	1.3 - 5.1	1.3 - 4.1
Cd	-	1.1 - 3.7	2.0 - 6.9
Cr	-	0.4 - 1.6	-
Cu	1.3	0.7 - 1.6	1.1 - 1.9
Ni	0.8	0.6 - 1.3	1.1 - 1.9
Zn	1.4	0.8 - 2.9	1.5 - 7.0
Hg	4.5	3.4 - 12.8	3.2

The magnitudes of the enrichment factors for the different areas are comparable. Variations are probably due to differences in local sources and influences by mixing.

The data were used, inter alia, to establish heavy metal budgets for selected areas (Larsen and Pheiffer-Madsen, 1986) taking into consideration as source functions estimates on inputs of metals via sewage, by shipping, from rivers and from the atmosphere. The only significant sink was considered to be the accumulation of metals in the sediments.

In Fig. 5.1 the investigated areas of the Kattegat, Belt Sea and western Baltic Sea are shown. The area has been divided into 45 sub-areas. The prevailing sediment types are indicated by double hatching ("mud"), vertical lines("sandy mud"), horizontal lines("muddy sand") and by dots ("sand, stones and/or gravel - lag deposits").

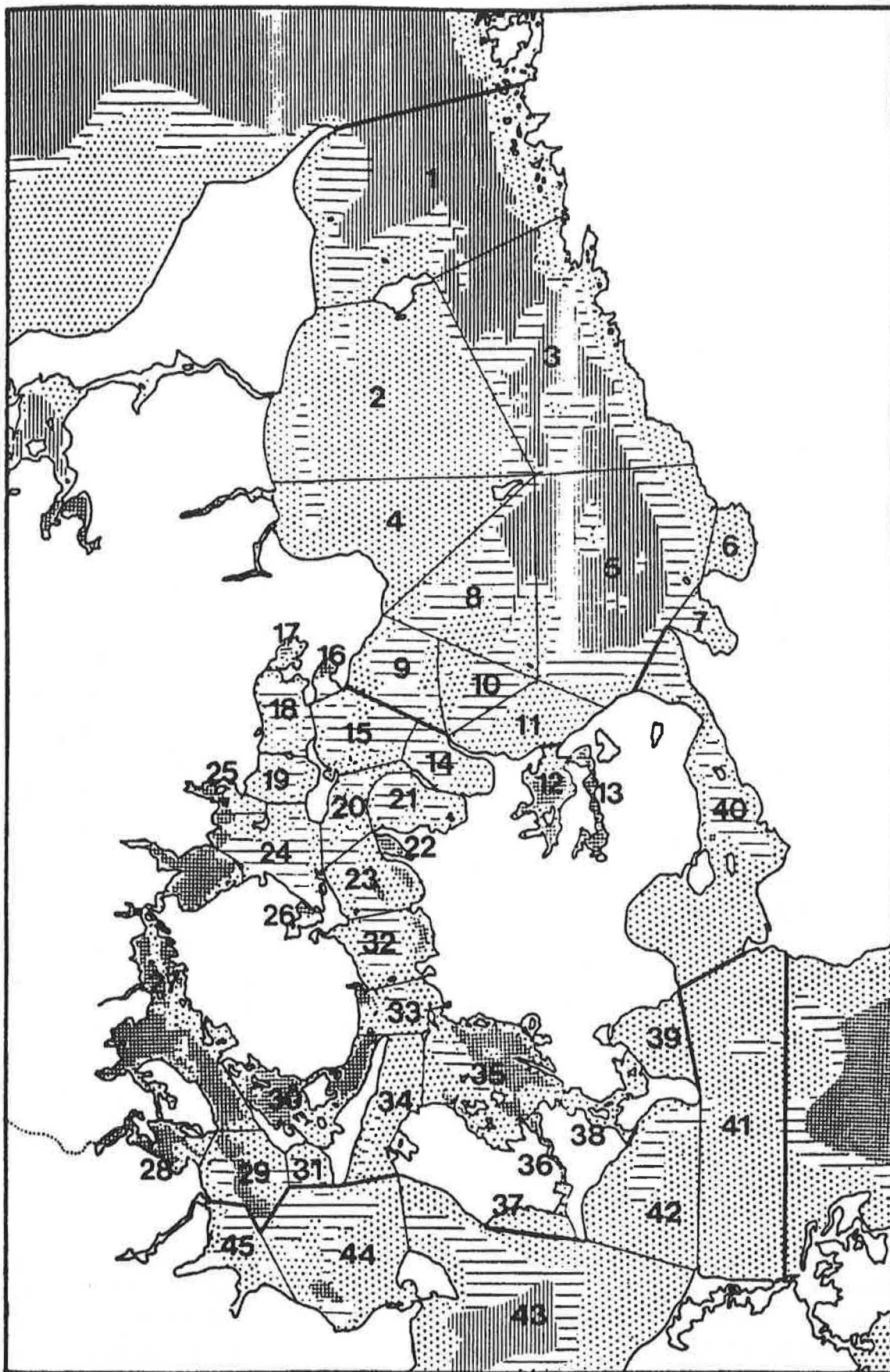


Fig. 5.1 Sediment map of the Belt Sea and Kattegat areas.

Table 5.3 Metal contents in muddy surface sediments (0-1 cm) from the Kattegat, Belt Sea and western Baltic Sea. (Data in Pfeiffer Madsen and Larsen, 1986)

Area No. (*)	Total Area km ²	Mud Area km ²	Accu- mul. Rate g m ⁻² y ⁻¹	Ignit. Loss of Mud (%)	Pb µg g ⁻¹	Cd µg g ⁻¹	Cr µg g ⁻¹	Cu µg g ⁻¹	Zn µg g ⁻¹	Hg µg g ⁻¹
1 (4)	4577	2673	2000	6.4	20	0.17	25	15	92	0.13
2	4154	11	825	6.4	20	0.17	25	15	92	0.13
3 (1)	3852	2268	825	6.4	20	0.17	25	15	92	0.13
4	1902	0	0							
5 (2)	3500	2394	825	6.4	20	0.17	25	15	92	0.13
6	390	138	385	6.4	20	0.17	25	15	92	0.13
7	277	94	385	6.4	20	0.17	25	15	92	0.13
8 (1)	1523	897	400	6.4	20	0.17	25	15	92	0.13
9	580	342	385	6.4	20	0.17	25	15	92	0.13
10	560	124	385	6.4	20	0.17	25	15	92	0.13
11	887	0	0							
12 (1)	218	94	560	11.1	37	1.50	13	21	95	0.32
13 (6)	100	34	340	16.7	25	2.80	150	29	180	0.53
14	422	243	385	5.1	22	0.15	25	12	55	0.15
15	649	396	385	5.1	22	0.20	25	12	55	0.15
16	68	39	385	12.0	22	0.20	25	20	85	0.15
17 (1)	79	45	1140	16.7	24	1.40	33	20	85	0.28
18 (3)	450	241	40	11.2	24	1.40	33	20	85	0.28
19	328	91	385	11.0	24	0.40	33	20	85	0.28
20	431	144	385	6.0	24	0.40	25	15	60	0.20
21	388	178	385	5.0	24	0.40	25	15	55	0.20
22 (3)	54	36	600	8.5	53	0.58	15	46	101	0.42
23 (4)	573	260	450	6.6	40	0.28	14	20	65	0.20
24 (4)	758	311	525	13.1	56	0.43	42	26	135	0.23
25	141	15	385	12.1	40	2.01	42	42	220	0.28
26										
27 (22)	1762	928	355	14.7	91	1.40	41	31	248	0.28
28 (3)	319	137	500	14.1	62	1.30	23	46	190	0.55
29 (2)	683	338	280	14.6	83	1.01	42	34	215	0.25
30 (14)	704	214	370	16.6	51	1.70	51	33	158	0.22
31 (1)	168	23	330	9.9	52	0.54	25	25	126	0.14
32 (2)	479	210	170	8.3	45	0.55	25	21	100	0.12
33	408	146	385	8.0	41	0.60	25	21	85	0.12
34	580	8	385	8.0	41	0.60	25	18	85	0.12
35 (1)	1291	463	250	8.0	26	0.64	25	19	81	0.10
36	54	18	385	8.0	26	0.64	25	19	81	0.10
37	197	0	0							
38	225	120	385	10.0	51	3.10	33	23	81	0.11
39	502	0	0							
40 (8)	2320	609	749	6.7	44	0.66	31	31	112	0.66
41	3267	0	0							
42	1337	91	385	2.0	45	0.60	25	15	100	0.10
43 (1)	4784	1609	540	8.7	90	0.60	25	27	165	0.15
44	1590	199	385	5.5	45	0.55	25	16	100	0.10
45 (1)	576	205	1030	11.0	70	1.30	35	39	188	0.31
(85)	48107	16386 (34 %)	447 +/-348 (0-2000)	9.1 +/-3.7 (2.0-16.7)	38 +/-20 (20-91)	0.75 +/-0.72 (0.15-2.80)	31 +/-21 (13-150)	22 +/-10 (15-46)	110 +/-48 (55-248)	0.21 +/-0.13 (0.10-0.66)

(*) number of Accumulation Rate determinations

From the DHI (1987) investigations in surface sediment and in one core taken in the Lübeck Bight, locally very high concentrations of heavy metals (Cd, Pb, Zn, Cu) were observed by AAS in the grain-size fraction < 20 µm after teflon bomb digestion with 1:1 HNO₃. Up to about 5 % Zn, 4 % Pb, 0.15 % Cu and 95 µg g⁻¹ Cd together with nearly 19 % Fe were observed as indications of dumping heavy-metal-rich wastes in the past.

The maximum concentrations in the investigated core were found in the layer 6 to 8 cm. It is interesting to note that also in the uppermost layer of recent sediments (0 to 2 cm) most elements show strongly elevated concentrations in relation to neighbouring stations outside the probable dumping area (e.g., enrichment of Pb up to 4 times, Zn - 3 times, Cu - 2 times).

Indications of such anomalies came from a previous study on 11 stations in the Lübeck Bight in 1984 (DHI, 1986). In surface samples (0-2 cm, <20 μm) between 315 $\mu\text{g g}^{-1}$ and 4.2 % Zn, 107 $\mu\text{g g}^{-1}$ and 2.8 % Pb, 53 $\mu\text{g g}^{-1}$ and 0.17 % Cu, 1.7 and 77.4 $\mu\text{g g}^{-1}$ Cd, 0.2 and 27.3 $\mu\text{g g}^{-1}$ Hg, 13 and 940 $\mu\text{g g}^{-1}$ As, 2.7 and 11.7 % Fe, 250 and 2700 $\mu\text{g g}^{-1}$ Mn, 33 and 92 $\mu\text{g g}^{-1}$ Cr, and 29 and 870 $\mu\text{g g}^{-1}$ Ni were determined (see also Table 5.4).

Already Müller et al. (1980) in their study on contaminant profiles in three 1 cm-sliced dated cores (30 to 35 cm) from the Geltingen Bight (water depth 20 m), Eckernförde Bight (21 m) and Lübeck Bight (15 m) found, in the last-mentioned core, relatively high Zn and Pb concentrations for the section 5 to 6 cm (see Fig. 5.3). For both metals, more than 1100 $\mu\text{g g}^{-1}$ were registered at this layer whereas for both other cores, which also came from anthropogenically influenced areas, maximum levels of about 250 $\mu\text{g g}^{-1}$ (Zn) and 90 $\mu\text{g g}^{-1}$ (Pb) were not exceeded. Later on, in 1983, Irion (1984) took 25 surface (0 to 1 cm) samples with a Reineck box corer from the western part of the Lübeck/Mecklenburg Bight.

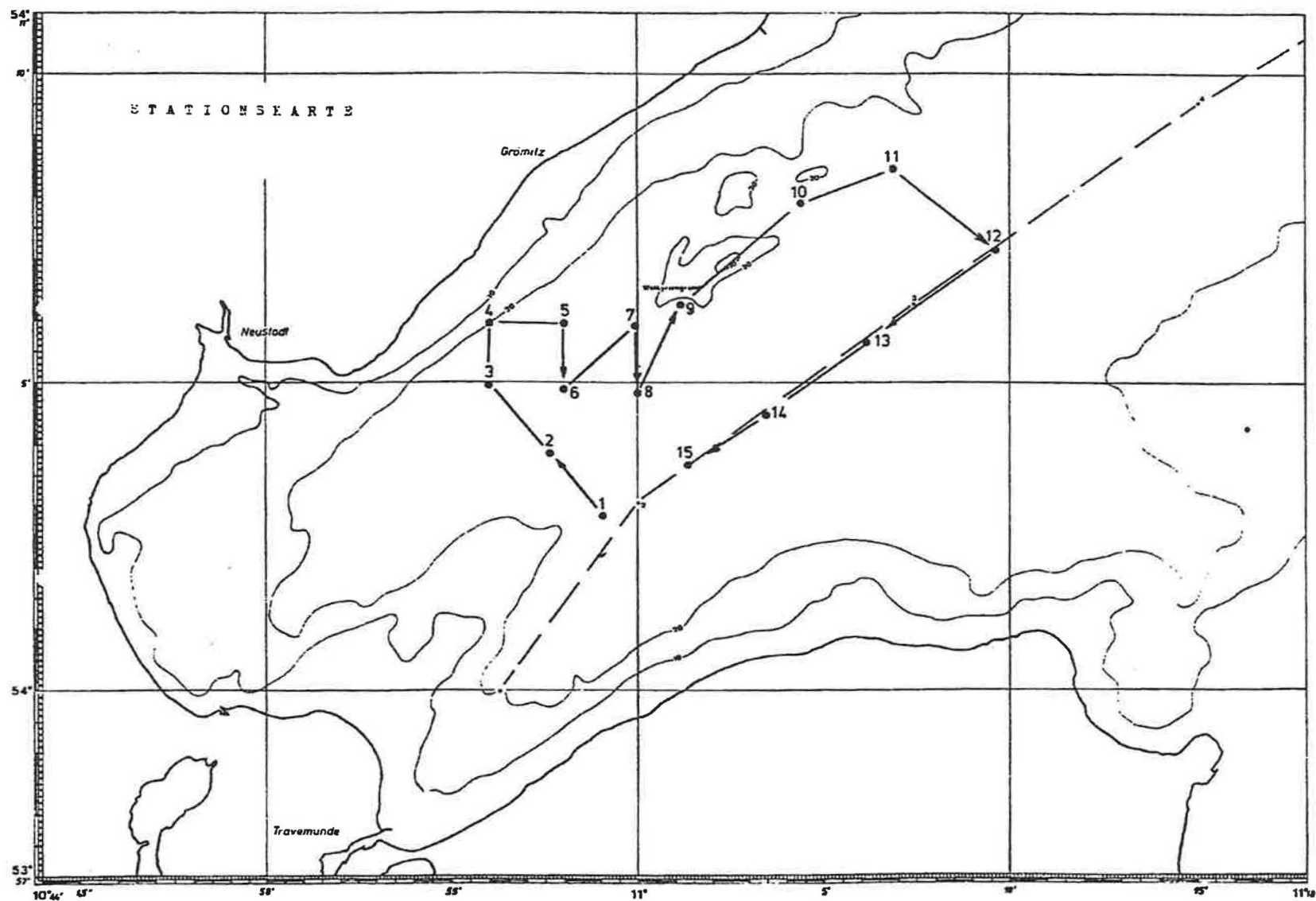


Fig. 5.2 Station network for Table 5.4.

Table 5.4 Heavy metal concentrations in sediments of the southern Lübeck bight (sampling: April 1985).

Station No.	Depth cm	Cd $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Cu $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	Fe %	Mn $\mu\text{g g}^{-1}$
1	0-2	2.1	181	65	365	3.46	353
	2-4	1.9	164	69	321	3.24	332
2	0-2	2.4	572	114	745	2.98	359
	2-4	4.7	1120	173	1750	3.70	327
3	0-2	2.0	87	64	286	3.25	546
	2-4	3.2	120	113	485	4.33	405
4	0-2	1.9	152	61	318	2.99	296
	2-4	1.7	187	64	386	3.16	299
5	0-2	1.4	214	66	316	2.95	304
	2-4	2.6	552	87	799	3.20	247
6	0-2	2.4	612	101	798	2.79	357
	2-4	3.9	1280	149	1911	3.27	287
7	0-2	1.8	421	80	575	2.97	267
	2-4	3.0	546	83	930	3.49	316
8	0-2	3.2	1700	174	1870	3.69	420
	2-4	22	9260	722	12000	7.22	453
	4-6	47	17400	927	29000	12.5	685
	6-8	95	38200	1260	50700	18.8	1540
	8-10	77	26200	1100	44600	17.9	1440
	10-12	58	19700	1090	33800	14.8	1400
	12-14	63	23800	1200	30600	10.1	1260
9	0-2	1.9	276	71	313	2.76	313
	2-4	2.6	411	83	324	2.86	291
10	0-2	1.1	159	58	231	2.61	267
	2-4	1.6	210	63	352	2.78	234
11	0-2	1.5	165	51	276	3.40	297
	2-4	1.3	169	51	281	3.29	287
12	0-2	3.4	539	66	1050	3.27	440
	2-4	3.5	613	71	1210	3.07	331
13	0-2	2.3	291	68	397	3.11	268
	2-4	2.1	334	63	464	2.94	264
14	0-2	2.1	308	65	373	3.26	417
	2-4	2.3	369	71	471	3.41	336
15	0-2	3.0	690	106	886	3.29	288
	2-4	3.4	975	119	1380	3.58	390

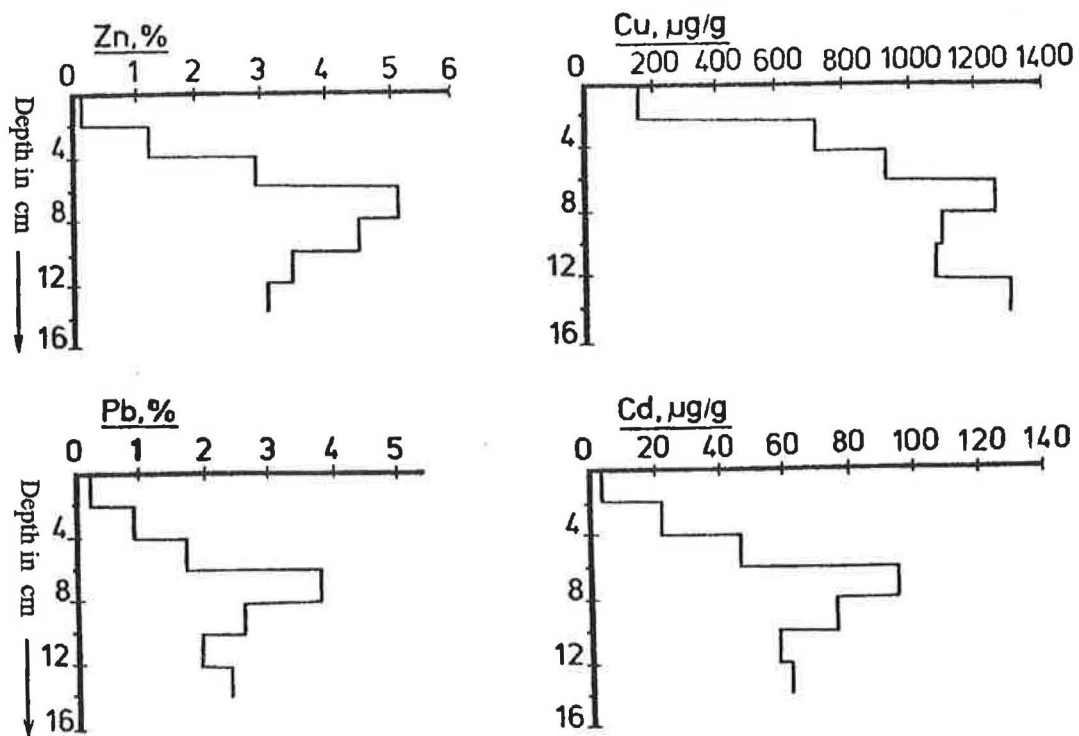


Fig. 5.3 Vertical profiles of heavy metal concentrations in sediment station No. 8 (see Fig. 5.2. and Table 5.4.).

In the $< 20 \mu\text{m}$ fraction, average concentrations of $558 \mu\text{g g}^{-1}$ (Zn), $377 \mu\text{g g}^{-1}$ (Pb) and $61 \mu\text{g g}^{-1}$ (Cu) were found. However, the maximum values were again high (Zn: 0.63 %; Pb: 0.51 %; Cu: $340 \mu\text{g g}^{-1}$; Cd: $33 \mu\text{g g}^{-1}$). As one possible explanation for this heavy metal contamination, metal wastes from the production of military equipment or ammunition was discussed. A causal connection with the contamination of sediments from the Trave River (maximum values of 0.40 % Zn, 0.13 % Pb, $270 \mu\text{g g}^{-1}$ Cu and $30 \mu\text{g g}^{-1}$ Cd; see: BFG, 1982) was deemed plausible.

Former GDR coastal waters

On 81 stations in the inner coastal waters of the former GDR between "Saaler Bodden" and "Oderhaff" sediment cores were taken between 1984 and 1987 and sectioned into 3 segments each (0-10 cm, 10-20 cm and 20-30 cm, respectively) (Table 5.5). The grain size fraction $< 63 \mu\text{m}$ was separated and analysed for some heavy metals (Fe, Mn, Pb, Zn, Cu, Ni) and organic carbon (Leipe et al., 1989). The total concentrations of metals were determined by AAS after teflon bomb digestion with HF. In addition, the 0.5 N HCl extractable metal fractions were determined. The results showed clearly:

- a general low level of heavy metal contamination with slightly elevated concentrations in the "Oderhaff",
- a decrease of total concentrations with core depth, particularly for Pb, Zn and Cu,
- relatively high (Pb, Zn, Cu), moderate (Cu, Mn, Ni) and low (Fe) fractions of leachable metals, and
- for some elements (Fe, Mn, Zn, Cu, Ni) a decrease of the 0.5 N HCl extractable fraction from the top section to the bottom.

Table 5.5 Concentrations of organic carbon and metals in 81 sediment cores from the former GDR inner coastal waters.

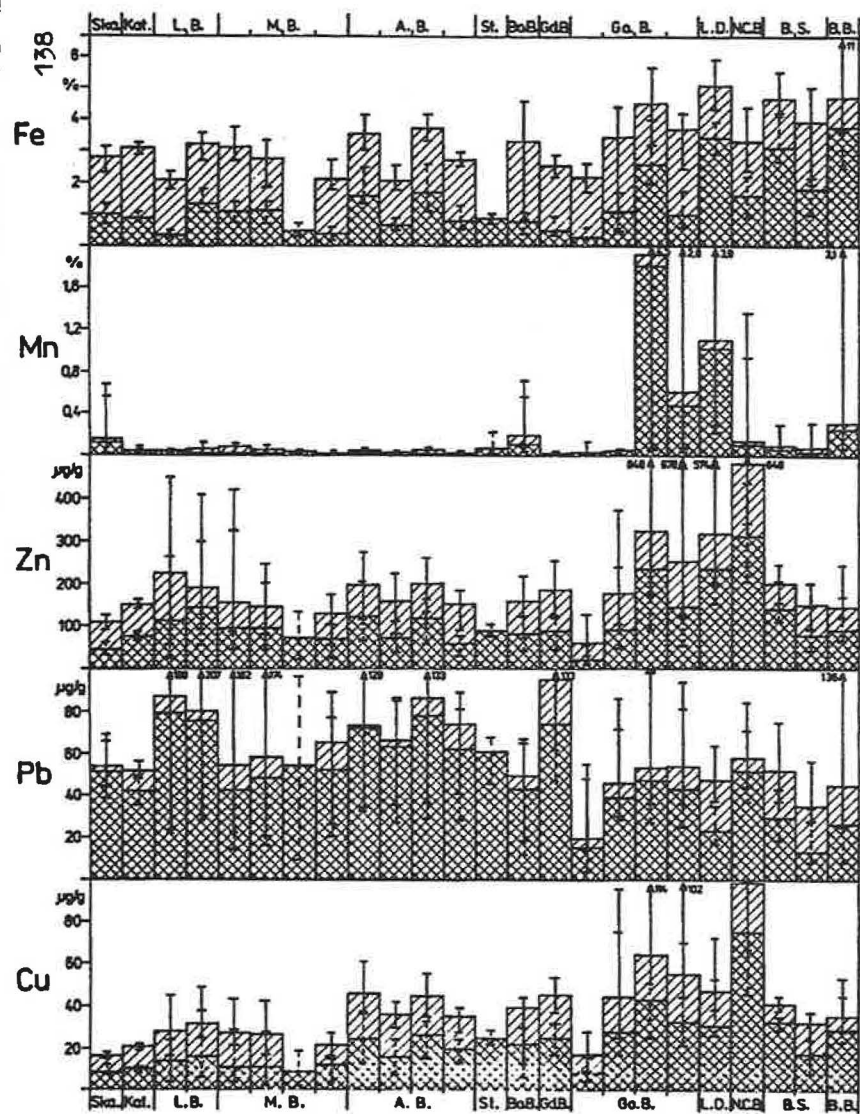
		0-10 cm Mean+/-s.d. (range)	10-20 cm Mean+/-s.d. (range)	20-30 cm Mean+/-s.d. (range)
Corg	- (%) - % HClex.	8.5+/-4.5 (2.2-17.9)	6.1+/-1.9 (4.1-10.6)	5.1+/-2.5 (1.0-9.2)
Fe	- (%) - % HClex.	2.1+/-0.6 (1.3-3.4) 29+/-9 (19-47)	2.8+/-1.1 (1.3-4.9) 21+/-10 (9-47)	3.3+/-1.4 (1.5-5.9) 18+/-9 (7-38)
Mn	- ($\mu\text{g g}^{-1}$) - % HClex.	670+/-600 (200-2230) 51+/-15 (30/84)	580+/-280 (230-1050) 39+/-20 (16-85)	600+/-200 (290-1020) 41+/-22 (17-84)
Pb	- ($\mu\text{g g}^{-1}$) - % HClex.	48+/-26 (21-110) 91+/-12 (55-98)	32+/-16 (11-60) 91+/-11 (56-98)	19+/-9 (5-33) 92+/-6 (86-98)
Zn	- ($\mu\text{g g}^{-1}$) - % HClex.	180+/-140 (64-580) 79+/-14 (50-96)	100+/-56 (46-240) 68+/-8 (58-86)	70+/-27 (36-120) 55+/-15 (36-81)
Cu	- ($\mu\text{g g}^{-1}$) - % HClex.	23+/-11 (9-46) 74+/-9 (58-85)	18+/-8 (9-34) 55+/-18 (18-80)	16+/-6 (6-28) 39+/-19 (9-67)
Ni	- ($\mu\text{g g}^{-1}$) - % HClex.	17+/-8 (6-33) 47+/-14 (18-65)	16+/-6 (9-25) 41+/-9 (19-54)	16+/-6 (6-27) 41+/-9 (23-51)

Baltic Proper

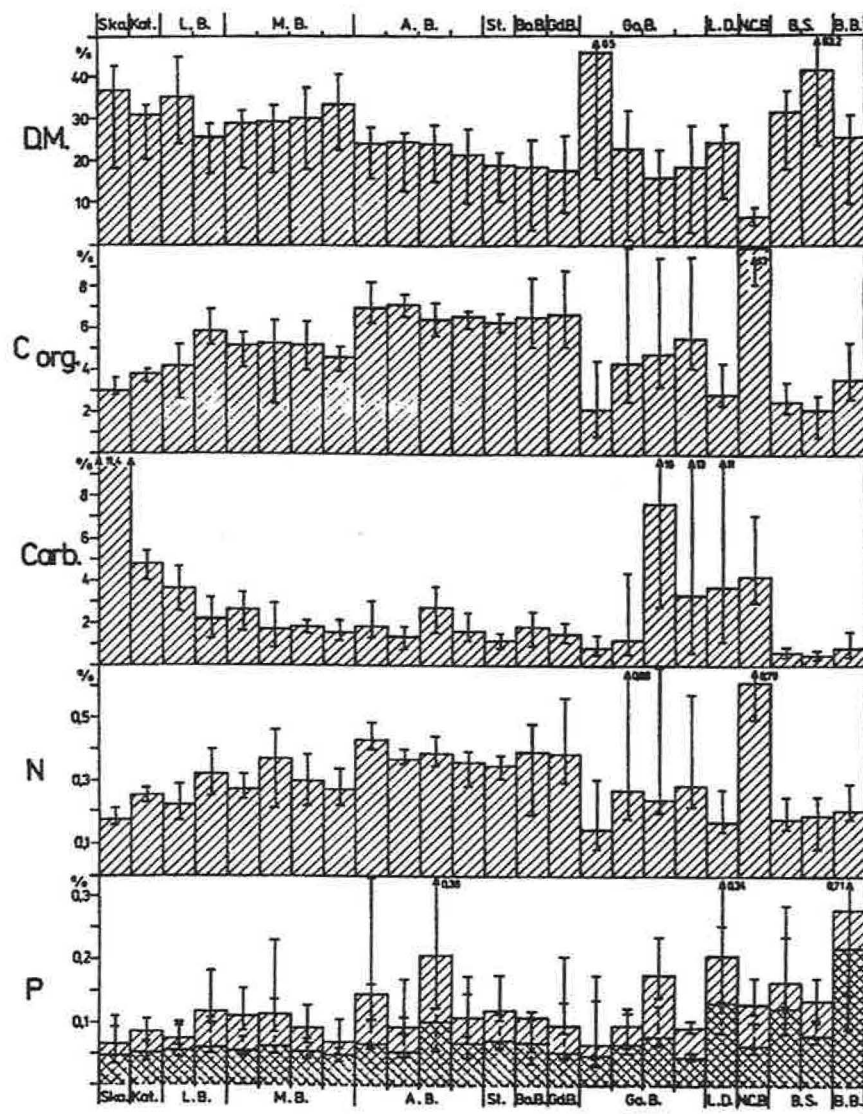
Between 1981 and 1983 Brüggmann and Lange took more than 20 cores of 20 to 25 cm length with a Niemistö sampler from representative net sedimentation areas between the Belt Sea and the Bothnian Bay (Brüggmann and Lange, 1989). The cores were sliced into 1 cm thick sub-samples and analysed for trace metals (Zn, Cr, Pb, Ni, Cu, Cd, Hg by AAS; partly also Ti, V, Be, Sc, Y, La, Sr, Li, Mo by ICP-OES), background parameters (grain-size spectrum, organic carbon, N, P, S, carbonate, Al, Fe, Mn) and partly radionuclides ($^{210}\text{Pb}/^{210}\text{Po}$) for dating. As a rule, the investigated samples consisted of 99 % of material in grain-size fractions below 63 μm and must be categorized as "silt" or "clayey silt". However, in the Gotland Basin the clay fraction dominated and the sediment type changed to "silty clay". For the trace metal determinations, the freeze-dried and sieved samples were subjected to a "total" digestion with $\text{HNO}_3/\text{HCl}/\text{HF}$ and an extraction with 0.5 N HCl. The results are presented in vertical contaminant profiles of selected cores from different basins and, using mean values over the core's length for the different parameters, in horizontal sections from the Belt Sea to the Bothnian Bay (Brüggmann and Lange, 1989) (Figs. 5.4a-d and 5.5).

Fig. 5.4

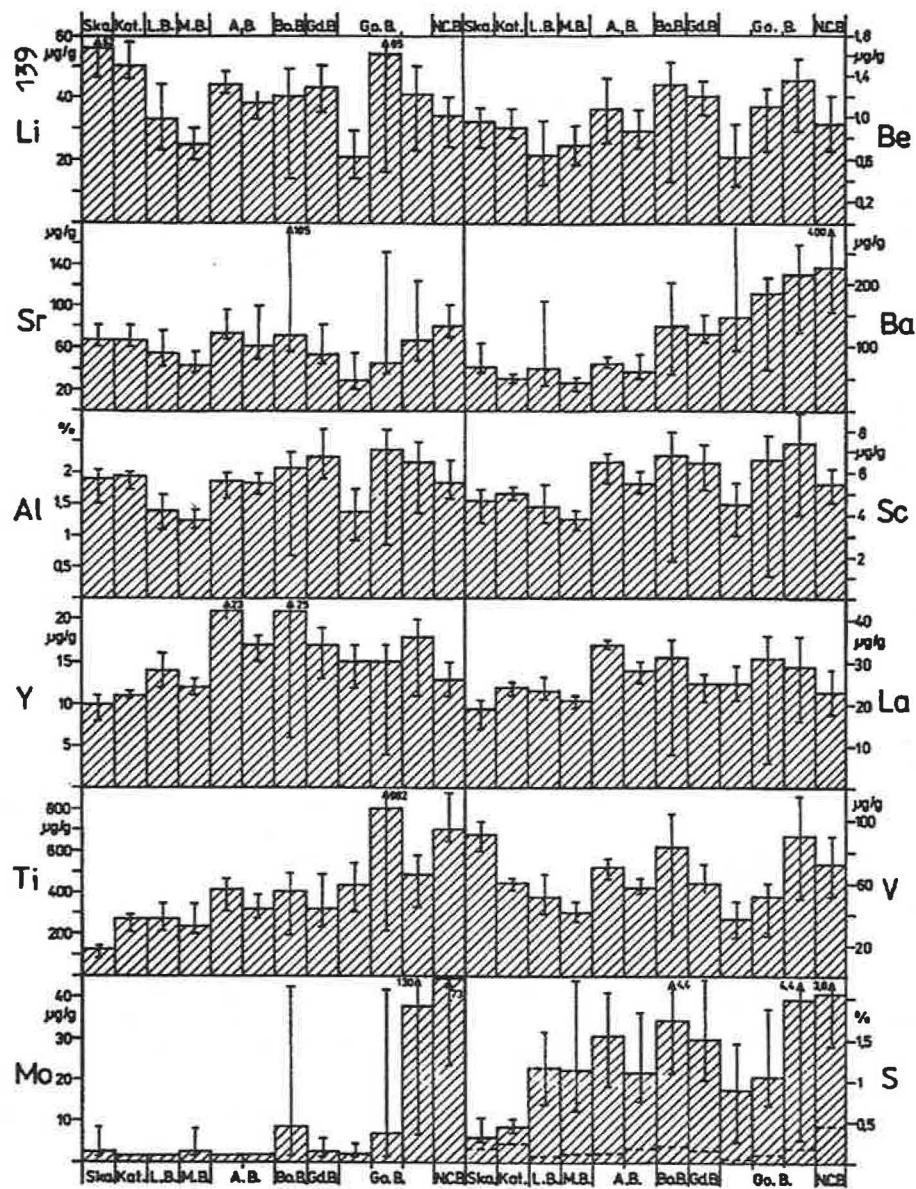
Sampling stations of Fig. 5.5a-d.



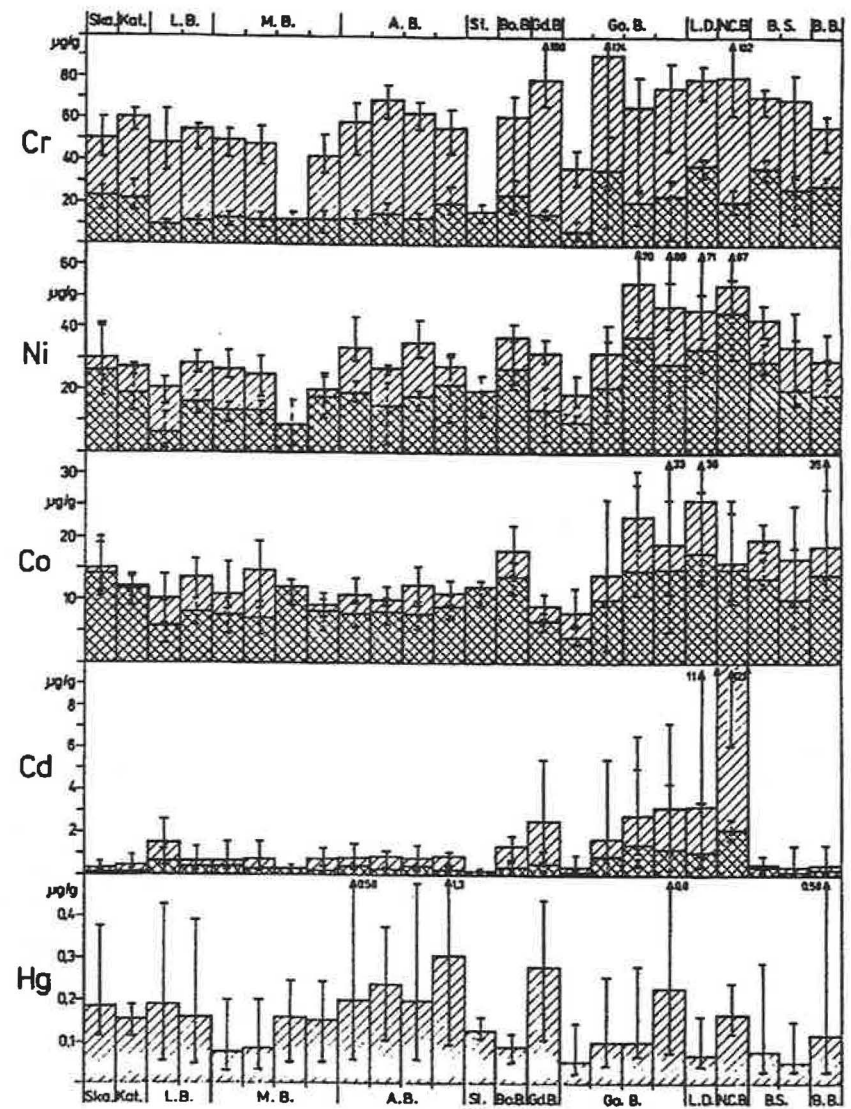
b)



a)



d)



c)

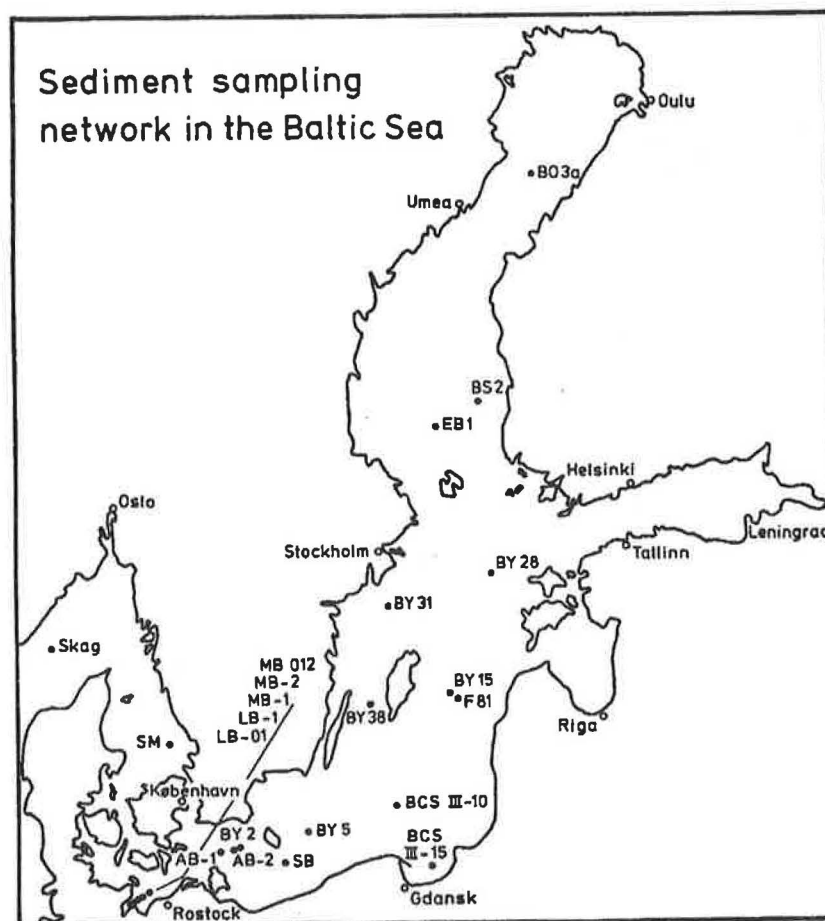


Fig. 5.5 Overview of the mean values and standard deviations of concentrations of trace metals and background parameters in sediment cores, arranged on a section through the Baltic Sea (see Fig. 5.4).

- a) dry matter, organic carbon, carbonate, nitrogen, phosphorus
- b) Fe, Mn, Zn, Pb, Cu
- c) Cr, Ni, Co, Cd, Hg
- d) Li, Sr, Al, Y, Ti, Mo, Be, Ba, Sc, La, V, S

The 0.5 N HCl extractable fraction of the "total content" was low (below 50 %) for elements existing mainly in detrital forms (Al, Cr, Fe). Other elements (Pb, Zn, Mn) are extracted by 0.5 N HCl often quantitatively, whereas Cu, Ni, Co and Cd show a behaviour between these extremes. For all mentioned elements, the extractable parts decrease with increasing sediment depth.

The vertical variability of the Fe concentrations is low. Higher concentrations were found in the Gotland Basin and in the Gulf of Bothnia. For Mn, extremely high concentrations - up to 4.5 % - were observed in the Gotland Basin and the Landsort Deep. Frequently, pronounced maxima appeared at the sediment/water interface or just below. This great Mn "excess" above a small detrital fraction was soluble in HCl.

Maximum Zn concentrations were found in the central Baltic Sea, i.e., at stations BY15, BY31 and BY28. Generally, to the north (Bothnian Bay) and south (Kattegat) the Zn concentrations decreased. Significant increases towards possible land-based sources could reflect anthropogenic influences. The speciation of Zn in sediments includes, similarly for Cd, organic associates, carbonates and sulphides (only at core BY15). Detrital forms are only indicated for the southern Gotland Basin and for the Arkona Basin.

For Pb, more anthropogenically governed distribution patterns were found, with maxima in the Lübeck Bight and in the Gdansk Deep. In most cases, for the first 10 or 15 cm sections the difference between the total concentrations and the 0.5 N HCl extractable fraction was minor. However, for the Landsort Deep and for the Gulf of Bothnia, a significant detrital fraction was noted. Probably due to diagenetic redistribution, the maximum Pb concentrations were often observed one or two cm below the water/sediment interface. In relation to Zn and Cd, correlation coefficients showed only a weak association of Pb with the organic matter. Sulphide forms cannot be excluded to occur at cores BY15 and BY28, in the latter case as co-precipitates with FeS_x . Significant detrital Pb fractions are indicated for stations in the Lübeck Bight, Kattegat and southern Gotland Basin.

For Cu, in all samples a detrital (non-HCl soluble) component of about 10 to 25 $\mu\text{g g}^{-1}$ was present. The Cu profiles are shaped similarly to those of Pb, whereas the pattern of regional maxima resembled those of Zn (i.e., maximum in the central basins, decrease to the north and south). According to correlation calculations, the organically associated forms of Cu seem to dominate. At core BY15, carbonate and sulphide fractions must be considered. Binding to detrital material seems to occur at those stations which have already been mentioned in connection with Pb.

For Cr, a relatively even distribution of the total concentrations and of the low HCl soluble fraction throughout the cores, together with an absence of higher concentrations at the sediment/water interface, seems to be typical. Again, maximum concentrations appear in the central basins. Only for a few cores a weak correlation of Cr with the organic carbon, or with S, Mn, P, N or carbonate, could be shown. Otherwise, a highly significant correlation with detrital indicators (Al, Sc, Fe) was always observed.

The distribution patterns of the Ni concentrations resemble those of copper, with a maximum in the Gotland Basin, without indication of nearshore "hot-spots" and even with an inert fraction, superimposed by more variable 0.5 N HCl extractable phases. At the expense of organic forms, for Ni the detrital binding became more important than for Cu. The probability of the occurrence of carbonate phases must be valued similarly as for Zn. An accumulation of Ni by Fe/Mn-precipitates seems to be documented, too. Sulphide forms are only minor, as indicated by correlation calculations.

For Cd, anthropogenic influences from land run-off or other anthropogenic activities seemed to be reflected by higher concentrations in cores from the Lübeck Bight and from the Gdansk Deep. Opposite to Pb, however, maximum concentrations were found in the central basins. Mean values up to 12 $\mu\text{g g}^{-1}$ are extraordinary (with the exception of strongly contaminated spots in the Lübeck Bight - see above) for the Baltic Sea because they would fall into the range of contaminated lakes and rivers. Minimum values were noted for the Gulf of Bothnia, which is sufficiently ventilated. Areas with increasing probability of the occurrence of anoxic conditions in bottom waters seem to act particularly as Cd traps. (The extreme enrichment of Cd in anoxic sediment, up to 50 times higher than the Clarke value, is not unique for the Baltic Sea. Brüggmann (1980) found more than 50 $\mu\text{g g}^{-1}$ in cores of diatomaceous oozes off Namibia/Walvis Bay. Holmes (1986) explained the extreme enrichment of Cd - up to 130 $\mu\text{g g}^{-1}$, Zn - up to 1.1 %, and Hg - up to 10 $\mu\text{g g}^{-1}$, in Texas marine sediments by (co-)precipitation of the corresponding metal sulphides.)

Correlation coefficients show prevailing organic binding forms for Cd. In the Gotland Basin and in the Gulf of Bothnia, an association with Mn/Fe-rich materials (oxides/hydroxides, phosphates) could be noted. (Co-)precipitation as carbonates must be considered for the Arkona and Gotland Basins. The occurrence of Cd sulphides is attributed to the cores BY38, BY28 and BY15.

The distribution patterns of the mercury concentrations are different from those of the other trace metals. A preferred place for the accumulation of this element seems to be the Arkona Basin. This is interpreted as follows:

The concentrations of colloidal and dissolved humic substances (HS) in Baltic waters decrease sharply in the western Baltic Sea due to flocculation of the organic macromolecules. Hg forms HS-complexes with formation constants up to the order of pK 20. Therefore, Hg could (co-)precipitate with the organic carrier. Likewise, this would explain the relatively low mercury concentrations in sediments from the Gulf of Bothnia. The low salinity and high humic concentrations of these waters could prevent the flocculation and enable the Hg transfer to other sub-areas of the Baltic Sea. Correlation calculations confirm that Hg seems to be combined predominantly with organic matter, especially with compounds rich in nitrogen. However, in cores taken between the Gotland Basin and the Bothnian Sea, (co-)precipitation with Mn-oxides seems to compete. In the anoxic mud deposits at stations BY28, BY15 and BY38 sulphide forms could play a significant role, too.

In Table 5.6, the total concentrations of trace metals and some background parameters - averaged over the entire lengths of 22 cores (20 cm, sectioned into 1 cm slices) - are listed together with the percentage of the 0.5 N HCl extractable fraction.

Table 5.6 Mean total concentrations and percentage of the 0.5 N HCl extractable fraction plus some background parameters in 22 cores (20 cm length, 1 cm dissected) taken in 1981 and 1983 in the Baltic Sea between the Kattegat and the Bothnian Bay.

		Mean	+/- s.d.	(Range)	% HCl extractable fraction	
Corg	(%)	5.0	+/- 2.0	(2.1-10.1)	-	(-)
Carb	(%)	2.9	+/- 2.5	(0.5-11.4)	-	(-)
N	(%)	0.30	+/- 0.11	(0.14-0.61)	-	(-)
P	(%)	0.13	+/- 0.05	(0.07-0.28)	61 +/- 9	(49-75)
Fe	(%)	3.3	+/- 0.9	(2.1-5.1)	39 +/- 17	(13-80)
Mn	(%)	0.23	+/- 0.45	(0.02-1.93)	55 +/- 21	(25-94)
Zn	($\mu\text{g g}^{-1}$)	195	+/- 89	(62-485)	55 +/- 11	(33-74)
Cr	($\mu\text{g g}^{-1}$)	62	+/- 14	(37-91)	32 +/- 11	(19-52)
Pb	($\mu\text{g g}^{-1}$)	61	+/- 19	(19-95)	77 +/- 16	(38-95)
Ni	($\mu\text{g g}^{-1}$)	33	+/- 10	(19-54)	64 +/- 14	(30-89)
Cu	($\mu\text{g g}^{-1}$)	39	+/- 18	(17-100)	56 +/- 12	(35-82)
Co	($\mu\text{g g}^{-1}$)	15	+/- 5	(8-26)	73 +/- 14	(50-98)
Cd	($\mu\text{g g}^{-1}$)	1.7	+/- 2.5	(0.3-12.1)	36 +/- 19	(6-83)
Hg	(ng g^{-1})	151	+/- 72	(53-303)	-	(-)
Ti	($\mu\text{g g}^{-1}$)	400	+/- 195	(124-806)	-	(-)
V	($\mu\text{g g}^{-1}$)	64	+/-	18(37-91)	-	(-)
Sr	($\mu\text{g g}^{-1}$)	60	+/- 15	(29-80)	-	(-)
Li	($\mu\text{g g}^{-1}$)	40	+/- 11	(21-56)	-	(-)
La	($\mu\text{g g}^{-1}$)	26	+/- 5	(19-34)	-	(-)
Y	($\mu\text{g g}^{-1}$)	15	+/- 4	(10-21)	-	(-)
Mo	($\mu\text{g g}^{-1}$)	9	+/- 15	(2-44)	-	(-)
Sc	($\mu\text{g g}^{-1}$)	5.6	+/- 1.1	(3.8-7.4)	-	(-)
Be	($\mu\text{g g}^{-1}$)	0.98	+/- 0.25	(0.64-1.36)	-	(-)

The profiles of metal concentrations in dated sediment cores were used for crude estimates of the metal masses accumulated from the year 1900 until sampling. Only "representative" cores without serious indication of disturbances were selected. The resulting data show that for areas with a high percentage of very fine-grained mud sediment in which heavy metals are accumulated, the metal masses deposited during the last 80 years do not deviate so much from those at areas with much lower metal concentrations in the sediments. This is shown in Table 5.7. (An exception is cadmium. This element is probably deposited as sulphide and shows for the central basins both types of maxima, for the metal concentrations and for their accumulated masses.)

Table 5.7 Masses of metals, organic carbon, nitrogen and phosphorus accumulated between 1900 and 1983 (1981) in different sub-areas of the Baltic Sea (Ehlin et al., 1974); one third of the sea bottom is considered as "net sedimentation area".

Net sedimentation area (km ²)	Corg	N	P	Zn	Cr	Pb	Ni	Cu	Cd	Hg
Mass/area	mg/cm ²			µg/cm ²						
Mass, absolute	10 ⁶ t			10 ³ t						
Bothnian Bay (12268)	46 5.6	2.5 0.31	3.3 0.41	192 24	56 6.9	94 11.5	34 4.2	44 5.4	0.8 0.10	0.33 0.041
Bothnian Sea (26358)	63 16.6	4.7 1.24	4.6 1.21	527 139	173 45.6	154 40.6	105 27.7	98 25.8	1.8 0.47	0.32 0.083
Northern Baltic Proper (15770)	98 15.5	6.0 0.95	1.3 0.21	440 69	74 11.7	52 8.2	50 7.9	89 14.0	10.3 1.62	0.14 0.023
Gotland Deep (14797)	91 13.5	4.6 0.68	1.5 0.22	455 67	123 18.2	100 14.8	80 11.8	92 13.6	5.5 0.81	0.35 0.052
Gdansk Basin (8533)	81 6.9	5.1 0.44	1.2 0.10	242 21	98 8.4	120 10.2	36 3.1	56 4.8	4.3 0.37	0.42 0.036
Landsort Deep (2382)	123 2.9	7.5 0.18	9.7 0.23	1495 36	352 8.4	217 5.2	208 5.0	216 5.1	16.7 0.40	0.34 0.008
Western Gotland Basin (9025)	65 5.9	4.2 0.38	1.5 0.14	280 25	121 10.9	73 6.6	50 4.5	72 6.5	2.8 0.25	0.18 0.016
Bornholm Basin (12997)	64 8.3	3.7 0.48	1.1 0.14	193 25	60 7.8	59 7.7	38 4.9	40 5.2	1.6 0.21	0.69 0.090
Arkona Basin (6224)	155 9.6	9.3 0.58	3.2 0.20	487 30	135 8.4	139 14.9	77 4.8	108 6.7	2.1 0.13	0.67 0.042
Sound/Belt Sea (6784)	157 10.7	9.5 0.64	3.1 0.21	589 40	133 9.0	266 18.0	70 4.7	88 6.0	3.6 0.24	0.48 0.033
Kattegat (7348)	52 3.8	3.4 0.25	1.3 0.10	197 15	77 15.7	70 5.1	35 2.6	27 2.0	0.7 0.05	0.23 0.017
Accumulation rate (weighted mean, mass/cm ² /yr)	0.99	0.061	0.031	4.9	1.4	1.4	0.81	0.95	0.046	0.0044
Sum of masses (122486 km ²)	99.3	6.13	3.16	491	141	143	81	95	4.7	0.44

Emelyanov (1988) reported that zinc and copper in the upper layers of bottom sediments of the Baltic Sea are distributed according to the occurrence of the pelitic ("fine") fraction. But in their distribution they show characteristic peculiarities: their maxima was confined not to the finest sediments - to clays, but to aleuritic-pelitic muds. Thus, in the distribution of Zn and Cu over the area, their clear confinement to the central parts of basins was not seen: their maxima were

often found in the outlying districts of basins in the shape of separate small areas (Fig. 5.6). Possibly this is due to the fact that Zn and Cu are associated more with sulphides than with clayey minerals. Statistically significant positive correlations of these two elements with C_{org} in muds were not found. In some regions Zn and Cu show nearshore elevated concentrations in sediments. Obviously, this is connected with anthropogenic contamination of sediments.

As seen from Table 5.8, the main part of Fe is present in fractions which are fixed in the crystalline lattice and so in the state of hydroxides. On the contrary, manganese is present, in general, in its reactive forms. The ratios of these forms (terrigenous clastic to the mobile reactive ones) are different for Zn and Cu in relation to Mn. In some samples of muds, the first two elements are associated with hydroxides and, apparently, with other authigenous minerals to 80-100 %.

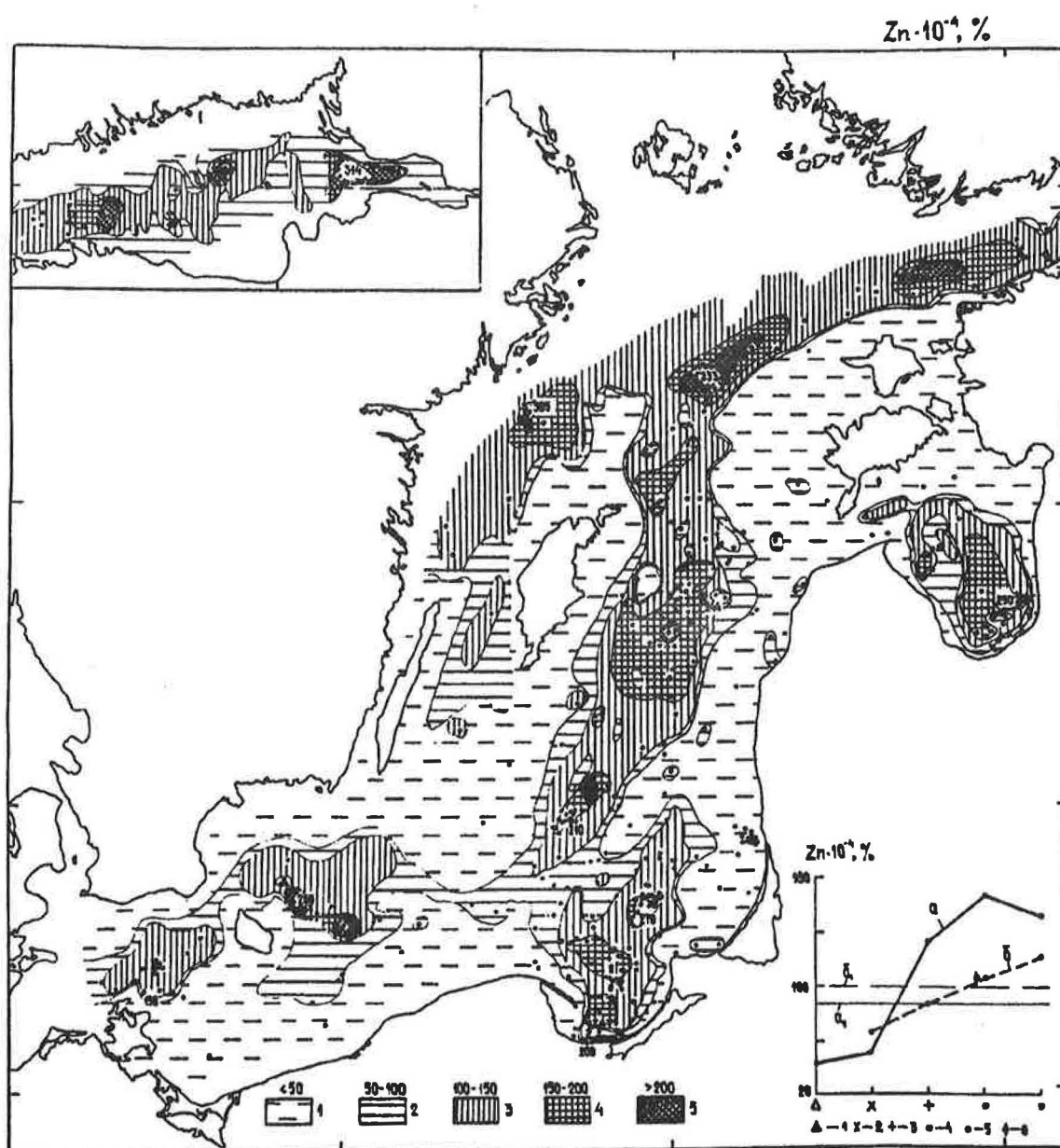


Fig. 5.6 The distribution of Zn in the upper layer (0-5 cm) of bottom sediments of the Baltic Sea.

On the diagram (Fig. 5.6) there is a curve of distribution of average concentrations of Zn according to granulometric types of sediments: 1 - sands; 2 - coarse aleurites; 3 - fine aleurite muds; 4 - aleurite-pelitic muds; 5 - pelitic muds; 6 - late-glacial clays (usually homogeneous); a - average for the upper layer (0-5 cm); b - average for the columns (Holocene muds and late glacial and varved clays and sand-aleuritic sediments). Horizontal lines mean the average for all types of sediments of the Gdansk Basin (a1 - for upper layer, b2 - for Holocene muds and clays of the sediments).

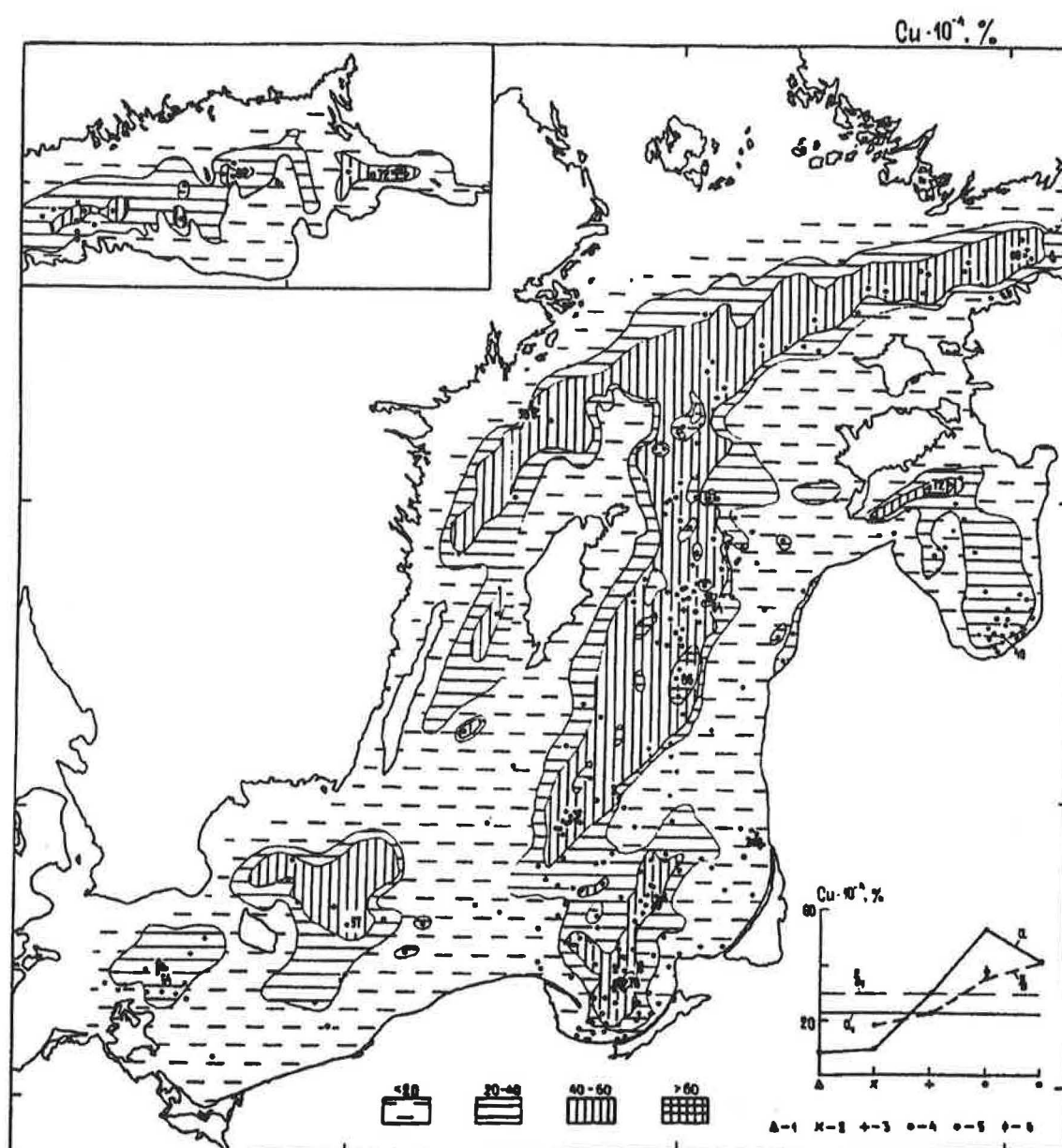


Fig. 5.7 The distribution of Cu in the upper layer (0-5 cm) of bottom sediments of the Baltic Sea.

On the diagram (Fig. 5.7) there is a curve of distribution of average concentrations of Cu according to granulometric types of sediments: 1 - sands; 2 - coarse aleurites; 3 - fine aleuritic muds; 4 - aleurite-pelitic muds; 5 - pelitic muds; 6 - late-glacial clays (usually homogeneous); a - average for the upper layer (0-5 cm); b - average for the column (Holocene muds and late glacial and varved clays and sand-aleuritic sediments).

Table 5.8 Fe, Mn, Zn and Cu forms in the muds of the deeps of the Baltic Proper (based on material supplied by Emelyanov).

Station	Depth m	Horizon cm	Sediment type	Contents			
				Total	1	2	3
Iron, % from dry sediment							
PD 3160	30	1-2	C. al.	1.02	0.20	0.35	0.42
PD 3162	200	0-2	P.m.	8.68	3.00	2.50	3.00
PD 3169	200	0-1	P.m.	5.12	0.62	2.26	2.26
		70-80	P.m.	5.60	0.36	1.33	3.91
PD 3172	205	15-20	P.m.	5.53	0.46	1.66	3.41
PD 3173	249	168-176	P.m.	5.78	0.70	1.93	3.15
Manganese, % from dry sediment							
PD 3160	30	1-2	C. al.	0.02	0.01	0.00	0.01
PD 3162	200	0-2	P.m.	0.13	0.06	0.01	0.04
PD 3169	200	0-1	P.m.	0.07	0.03	0.02	0.02
		70-80	P.m.	0.07	0.02	0.02	0.03
PD 3172	205	15-20	P.m.	0.08	0.04	0.02	0.02
PD 3173	249	168-176	P.m.	0.18	0.06	0.03	0.09
Zinc, 10 ⁻⁴ % from dry sediment							
PD 3160	30	1-2	C. al.	33	5	20	8
PD 3162	200	0-2	P.m.	333	150	180	40
PD 3169	200	0-1	P.m.	366	220	106	40
		70-80	P.m.	138	21	66	51
PD 3172	205	15-20	P.m.	145	29	66	50
PD 3173	249	168-176	P.m.	149	31	73	45
Copper, 10 ⁻⁴ % from dry sediment							
PD 3160	30	1-2	C. al.	14	3	3	8
PD 3162	200	0-2	P.m.	57	26	31	0
PD 3169	200	0-1	P.m.	77	10	36	31
		70-80	P.m.	87	2	17	68
PD 3172	205	15-20	P.m.	43	3	32	8
PD 3173	249	168-176	P.m.	50	7	25	18

Sediment types: coarse aleurites - C.al.; P.m. - pelitic mud.

Forms of elements: 1 - represented by hydroxides and sorbed by hydroxides of iron and manganese.
 2 - connected in species of crystalline hydroxides or connected with these hydroxides.
 3 - forms which are fixed in the crystalline lattice.

Hallberg (1989) investigated 10-cm long sediment cores taken with a Niemistö corer from 59 sites in the Baltic Sea (Fig. 5.8).

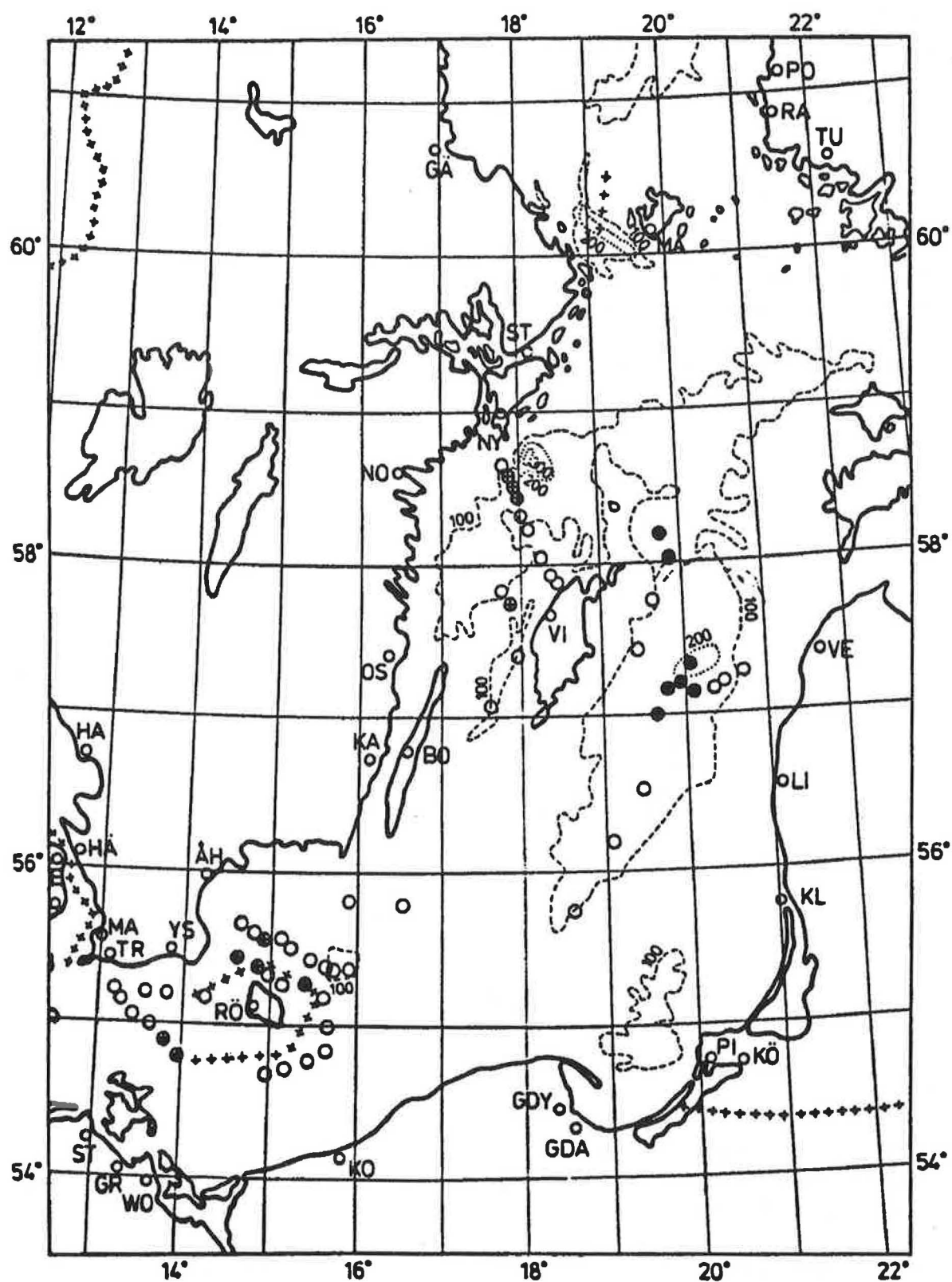


Fig. 5.8 Sampling stations for the Baltic Proper (Hallberg, 1989).

The cores were dissected into 1 cm slices. For trace metal analysis (Zn, Cu, Ni, Cd, Co, Fe, As, Mo, Mn, V, Pb, Hg), the dried samples were digested with 5 M HNO₃ in an autoclave at 100 °C for 1 h. Analyses were performed by AAS; for the determination of As and Hg the AAS was applied in the hydride and "cold-vapour" flameless modes, respectively. A few samples were analysed using neutron activation. In addition, measurements of the redox potential and of the organic carbon content (through ignition loss determination at 500 °C) were performed.

Applying cluster analysis on the analytical results, the 59 cores could be sorted according to the main geochemical facies types for the investigated area, namely:

- A) sites with a predominance of reduced bottom water,
- B) sites with a predominance of oxidized (well ventilated) bottom water, and
- C) sites which are a mixture of A) and B).

These facies types are described in Fig. 5.9.

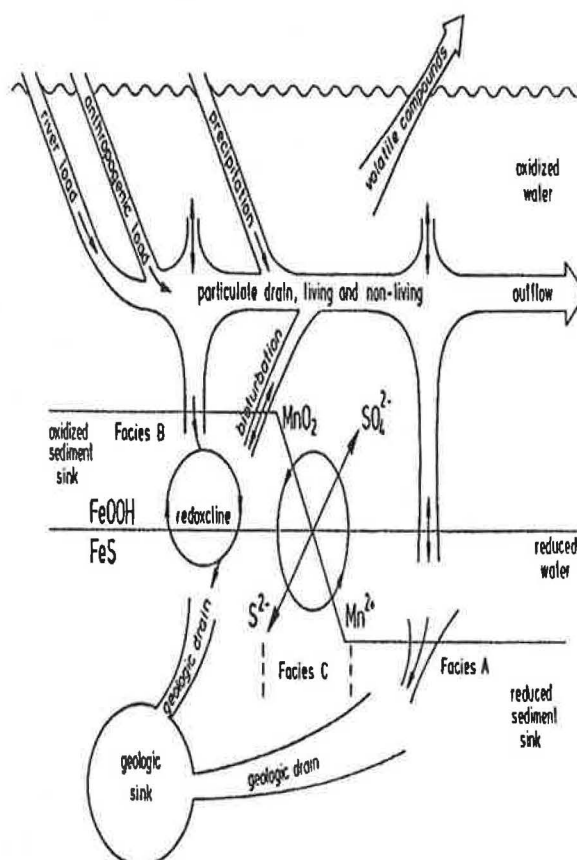


Fig. 5.9 Geochemical types of sediments of the Baltic Proper (Hallberg, 1989).

Facies A proved to contain all 7 cores from the deep basin to the east of Gotland. The sediments were black, entirely reduced and the topmost part showed redox values between 0 and -125 mV, with a mean value of -50 mV.

Facies B included 42 cores. The top sediment was brown or grey and the redox values varied between -190 mV and +410 mV (mean: +100 mV).

The remaining 10 cores belonged to facies C. They were taken in marginal areas of the basins where frequent redox variations of the bottom water occur. Their redox values varied between -340 mV and +290 mV (mean: +55 mV). The top sediment was black or grey.

Statistical methods were also used to correlate and identify factors influencing the variability of metal concentrations. All metals except Hg were positively correlated to each other on a significant level (0.001). The highest correlation factor ($r = 0.83$) was recorded between Zn and Cu. Also most of the other metals (Pb, Ni, Cd, Mo, V) had their highest correlation in sediments for the Baltic Proper with Zn. Therefore, their distribution can be illustrated likewise by the distribution of Zn, for which the author had the most data available from his sediment investigations in the Baltic Sea area. The distribution of Zn shown in Fig. 5.6 was based on mean values for the uppermost three 1 cm slices from this study and on values from the uppermost 5 cm from cores taken during other studies. The uppermost part of the sediment should reflect the depositional conditions better than the underlying sediments which have been affected more by diagenetic processes. The regional distribution of Zn (Fig. 5.10) was found to be very similar to the distribution patterns of soft sediments in the Baltic Proper (Fig. 2.5.1). However, data points outside the mud basins are missing in this investigation.

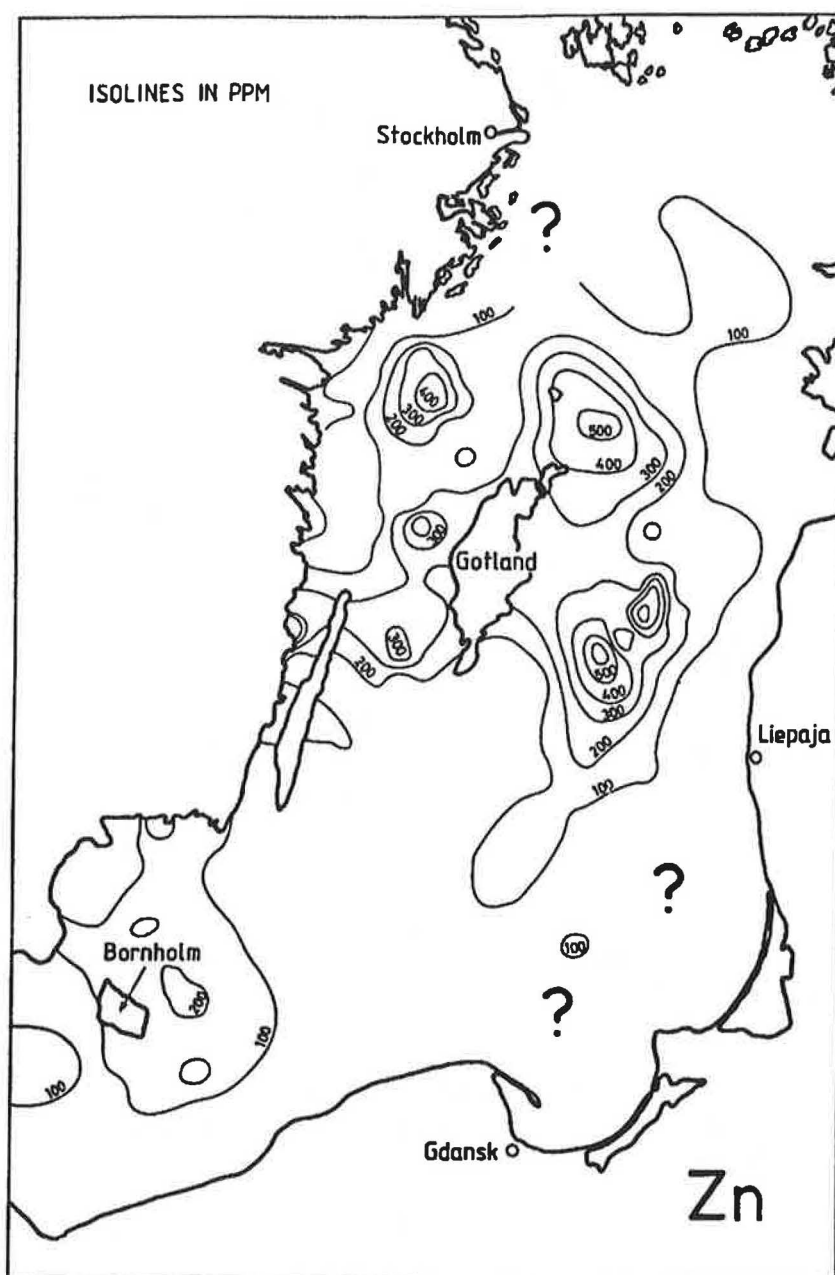


Fig. 5.10

Distribution pattern of zinc in soft sediment areas in the Baltic Proper (Hallberg, 1989).

For Hg, the author found relatively high values (Fig. 5.11) with 10 % of them greater than $2.5 \mu\text{g g}^{-1}$. Extremely high mercury concentrations, up to $86 \mu\text{g g}^{-1}$, were found in the sediments of the Arkona Basin and explained by the possible dumping of remains from WW II.

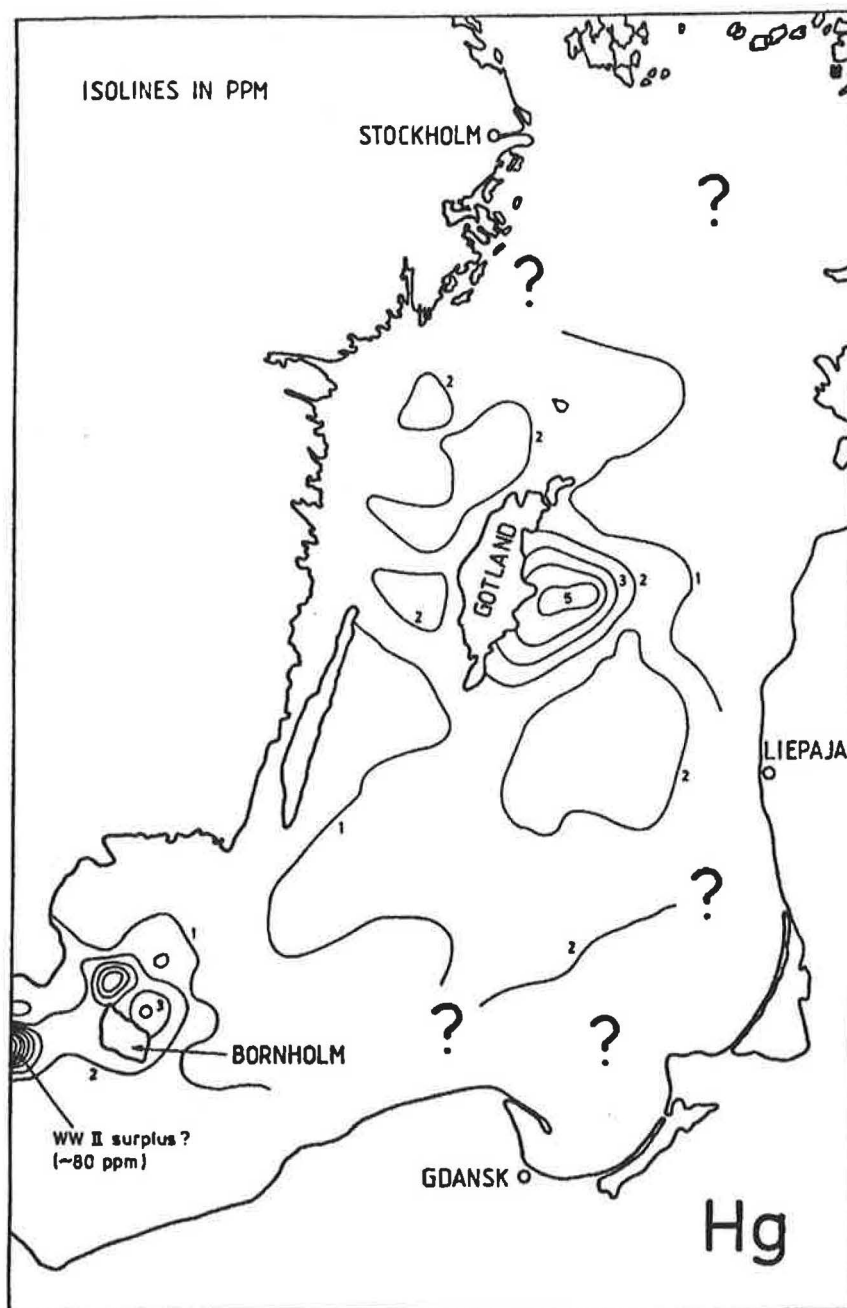


Fig. 5.11 Distribution pattern of Hg in soft sediment areas in the Baltic Proper (Hallberg, 1989). (Note: the values should be interpreted with care, as they are roughly two orders of magnitude higher than the values published elsewhere. The pattern, however, agrees with other results.)

For Mn, 97 % of the variance could be explained by the "strata effect" (core depth). This element reflected the redox conditions. 92 % of the data were below the mean (0.3 %), which was governed very much by some very high values.

Summarizing, it was shown that the lateral distribution of elements like Hg, Mn and Fe was governed by the redox conditions, whereas the patterns of most other elements could be

explained mainly by the organic carbon distribution. The atmospheric input was considered to be the predominant source for metals found in the sediments of the Baltic Proper.

Gdansk Basin/Eastern Gotland Basin

The concentrations and speciation of heavy metals (Fe, Mn, Zn, Cd, Pb, Co, Cr, Cu, Ni) were determined in 12 surface (grab) samples ($< 60 \mu\text{m}$) taken from the Gdansk Basin (Belzunce Segarra et al., 1987). Sampling extended from 7 to 125 km from the Vistula River mouth at depths between 40 and 110 m. Five mineralogical/geochemical fractions, i.e., (a) exchangeable, (b) carbonates, (c) Fe/Mn-oxides/hydroxides, (d) organic/sulphide and (e) residual binding forms were separated. For Cd, Cu, Mn, Pb and Zn, a high (re-)mobilization potential was observed. That means that a high percentage of those metals occur in the Gdansk Basin sediments in fractions (a), (b), (c) and/or (d), whereas other elements (Co, Cr, Fe, Ni) were found mainly in the residual fraction. A significant exchangeable part was only observed for Cd and Mn. Cu and Cd were found mainly in fraction (d), probably in the form of sulphides. In most cases, the total metal concentrations (Cd: $3\text{--}7 \mu\text{g g}^{-1}$; Cu: $32\text{--}161 \mu\text{g g}^{-1}$; Ni: $35\text{--}164 \mu\text{g g}^{-1}$; Co: $48\text{--}86 \mu\text{g g}^{-1}$; Pb: $70\text{--}155 \mu\text{g g}^{-1}$; Cr: $79\text{--}212 \mu\text{g g}^{-1}$; Zn: $121\text{--}1168 \mu\text{g g}^{-1}$; Mn: $307\text{--}535$ (one sample: 15270) $\mu\text{g g}^{-1}$; Fe: $3.1\text{--}5.0 \%$) decreased from the inner to the outer part of the Gdansk Basin. The studies showed further that the mode of heavy-metal fixation distinguishes sediments of riverine origin from the re-worked Pleistocene material.

Further investigations were carried out by these authors (Belzunce Segarra et al., 1989) on the $>2 \mu\text{m}$ fraction of a 0.5 m core from the southern Gotland Basin and an 11-m core from the Gdansk Basin. Both the mode of binding and the total concentrations of metals differed significantly between recent material and ancient material, whereby metals in recent material occurred exclusively in easily extractable forms rather than in the residual fraction. The increase in the Gdansk Basin core (Pb from 35 to $70 \mu\text{g g}^{-1}$; Cr from 25 to $75 \mu\text{g g}^{-1}$; Cu from 35 to $90 \mu\text{g g}^{-1}$; Zn from 40 to $165 \mu\text{g g}^{-1}$) was attributed first of all to human impacts on the clay fraction of soils and fluvial sediments supplied from the land. In the more offshore Gotland Basin core, Pb (from 100 to $250 \mu\text{g g}^{-1}$), Zn (from 20 to $70 \mu\text{g g}^{-1}$) and Ni (from 350 to $700 \mu\text{g g}^{-1}$) increased significantly, too, whereas Cr showed an opposite behaviour with lower concentrations at the surface in relation to the 50 cm sediment depth.

Widrowski and Pempkowiak (1987) investigated four 1 cm-sliced and ^{210}Pb dated cores taken with a Niemistö-corer from the Gdansk Basin, from the southern Gotland Basin and from the Stolpe Trench and analysed for metals (Hg, Cd, Cu, Ni, Co, Cr, Pb, Zn, Mn, Fe) by AAS following $\text{HNO}_3/\text{HClO}_4/\text{HF}$ digestion and the organic carbon, carbonate and clay mineral content. The average concentrations of the metals investigated in the first five slices (0 to 5 cm) were between 0.7 and 1.8 (Cd), 0.8 and 1.9 (Hg), 18 and 24 (Co), 19 and 34 (Cu), 29 and 49 (Cr), 48 and 52 (Ni), 88 and 132 (Pb) and 176 and 233 $\mu\text{g g}^{-1}$ (Zn). The ratio of these averaged surface values to the averaged concentrations in "background" layers of the same short cores resulted in "Enrichment Factors" (EF) of 4.8 (Hg), 1.6 to 2.4 (Pb), 1.3 to 2.5 (Zn), 1.3 to 2.4 (Cu), 0.9 to 2.1 (Cd), 1.0 to 1.2 (Ni) and 1.0 to 1.1 (Co, Cr).

Sediment cores taken from four stations in the southern Baltic Sea (1) and the Gdansk Bight (3) were investigated for the contents of Mn, Pb, Ni, Cu, Co, Zn, Cd, U, Th, Ca and Mg following $\text{HF}/\text{HClO}_4/\text{HNO}_3$ digestion (Szefer and Szefer, 1984). The mean metal concentrations in the investigated 4 cores which had lengths between 20 and 46 cm and were 5 cm - or 1 to 2 cm -

sliced (Cd: 0.6 to 5.1 $\mu\text{g g}^{-1}$; Cu: 3 to 12 $\mu\text{g g}^{-1}$; Co: 9 to 24 $\mu\text{g g}^{-1}$; Ni: 24 to 54 $\mu\text{g g}^{-1}$; Pb: 39 to 120 $\mu\text{g g}^{-1}$; Zn: 81 to 500 $\mu\text{g g}^{-1}$; Mn: 460 to 2300 $\mu\text{g g}^{-1}$; U: 1.6 to 5.2 $\mu\text{g g}^{-1}$) fall (except for Cu, owing possibly to losses during ion-exchange treatment of digested samples?) into the range of other data for this area. Enrichment factors of 2.1 (Zn), 1.7 (Cd), 1.4 (Pb), 1.6 (Cu), 0.9 (Co), 0.8 (Ni) and 1.0 (Mn) were found for one core taken in the Gdansk Deep area.

In the inner part of the Gdansk Bight, especially in the shallow Puck Bay, organic fine-grained mud with relatively high trace metal concentrations, up to 4300 (Zn), 3200 (Cu), 2900 (Pb), 980 (Ni), 450 (Cd), 240 (Co) and 45 $\mu\text{g g}^{-1}$ (Hg) were observed. Otherwise, in sandy mud from the Polish part of the "Szczecin Lagoon" (Oderhaff) much lower trace metal concentrations were present in material which contained about 20 % organic matter (Radziejewska and Drzycimski, 1987).

The Gdansk Basin was studied intensively also by Emelyanov (1986a) with regard to spatial distribution patterns of total trace metal concentrations. Some of the results are given below in two tables which again clearly demonstrate that the concentrations of most of the elements investigated are positively correlated with the water depth. In the central part of the Gdansk Basin, with a depth between 100 and 110 m, maximum concentrations occurred (Tables 5.9 and 5.10).

Table 5.9 Concentrations of Fe, Mn, Cu and Zn in surface (0-2 to 0-7 cm) sediment layers of cores taken from the Gdansk Basin (Emelyanov, 1986a).

Station	Depth (m)	Fe (%)	Mn ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)
301-1	85	3.42	300	35	121
301-3	85	4.55	300	46	142
302-1	89	4.20	300	44	150
303	108	4.85	500	48	165
306	88	4.08	200	34	118
304	63	3.40	200	32	125
307	42	1.80	200	24	64
308	50	2.03	200	15	95
309	20	1.25	300	7	31
311	110	4.88	500	44	159
313	100	-	300	42	157
324	63	3.72	200	26	66
329	46	1.86	200	18	80
330	77	3.00	600	19	58
331	81	4.69	500	27	88

Table 5.10 Metals in surface sediments of the Gdansk Basin (Emelyanov, 1986a).

Au	:	0.1-5.4 $\times 10^{-7}$ ng g^{-1}
U	:	1-20 $\mu\text{g g}^{-1}$
Ni	:	33 (-115) $\mu\text{g g}^{-1}$
B	:	26-180 $\mu\text{g g}^{-1}$
Cu	:	25 (3-65) $\mu\text{g g}^{-1}$
Mo	:	25 $\mu\text{g g}^{-1}$
Cr	:	68 (10-185) $\mu\text{g g}^{-1}$
Zn	:	97 (20-270) $\mu\text{g g}^{-1}$
V	:	190-200 $\mu\text{g g}^{-1}$
Ba	:	<200-810 (1690) $\mu\text{g g}^{-1}$

Blazhchishin et al. (1986) investigated sediment cores taken on a section with 7 stations through the central Gotland Basin (Deep) at depths between 90 and 240 m. The cores were sectioned into about 5 cm intervals and analysed for their trace metal concentrations. In addition, 3 grab samples were taken and sub-sampled into the 0-2 cm, 4-6 cm and 16-18 cm intervals. In the following table, the concentrations of trace metals (Cu, Zn, Ni, Co, Cr, Li) and of background parameters (Fe, Mn, C_{org}, CO₂) in those samples have been listed. Typically, with increasing water depths some metal concentrations (Zn, Ni) in the surface layer increase. Generally, the concentrations of other metals decrease from the western to the eastern part of the Gotland Basin (Cr, partly also Cu and Co).

Table 5.11 Concentrations of chemical elements and other components in sediments on a transect through the Gotland Basin (Blazhchishin et al., 1986).

Station (Depth in m)	Core depth (cm)	Fe (%)	Mn (%)	C _{org} (%)	CO ₂ (%)	Cu µg g ⁻¹	Zn µg g ⁻¹	Ni µg g ⁻¹	Co µg g ⁻¹	Cr µg g ⁻¹	Li µg g ⁻¹
2620 (170)	0-2	4.9	0.09	3.72	0.55	56	135	65	20	106	-
	4-6	4.6	0.06	4.35	0.0	56	124	68	17	100	-
2618 (225)	0-5	4.2	0.17	3.09	0.55	48	165	62	18	90	-
	10-15	4.6	0.05	2.94	0.55	49	158	40	18	110	-
	20-25	5.0	0.15	3.00	0.10	54	146	46	10	115	-
2621 (235)	0-2	5.5	0.45	2.91	0.33	47	167	50	17	98	-
	4-6	6.1	0.74	2.85	0.66	36	146	50	14	98	-
2622 (240)	0-2	6.4	3.50	3.06	3.75	55	205	68	18	91	44
	4-6	5.2	0.21	3.27	0.24	53	180	78	15	70	55
	16-18	5.7	0.32	3.29	0.26	51	165	75	18	65	55
2623 (220)	0-3	5.6	0.08	3.23	0.22	53	190	75	28	69	57
	10-15	6.3	0.25	3.15	0.30	52	163	80	22	65	58
	20-25	5.9	0.20	3.17	0.23	54	160	80	16	70	59
2624 (205)	0-8	5.5	0.05	3.51	0.25	53	173	60	18	60	56
	10-15	5.3	0.04	3.37	0.20	52	196	70	10	73	56
	20-25	5.8	0.04	3.56	0.28	50	146	68	13	67	58
2625 (170)	0-5	4.4	0.04	3.64	0.51	45	150	56	10	82	48
	10-15	5.0	0.05	3.51	0.35	45	173	50	10	71	53
	18-22	4.7	0.05	3.33	0.22	41	154	45	10	76	51
	20-25	4.5	0.04	-	-	40	115	45	4	74	50
	40-50	4.6	0.05	3.60	0.91	52	128	55	-	104	-
2626 (127)	0-7	4.3	0.02	-	0.43	37	182	50	17	67	43
	10-15	4.4	0.03	2.12	0.22	38	127	47	13	62	45
	18-23	4.6	0.02	-	0.16	37	127	77	12	49	39
2627 (120)	0-7	4.0	0.02	3.00	0.42	45	154	55	17	50	41
	10-15	4.8	0.03	3.06	0.41	36	140	62	10	49	47
	18-23	4.0	0.02	3.17	0.40	40	132	51	15	61	49
2628 (90)	0-7	3.8	0.02	3.59	0.91	37	160	45	10	56	35
	15-21	3.9	0.03	3.27	0.26	32	101	35	10	51	36

Gulf of Bothnia and Gulf of Finland

Ingri and Ponter (1986a) took about 120 box cores from the western half of the Gulf of Bothnia and analysed them after sectioning for major/minor (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and some trace elements (Ba, Cu, Ni, Sr, V, Zn). They always found sediment layering comprising oxygenated water-rich brown surface layers and/or other Fe-rich layers, underlain by a grey layer with or without interbedded black horizons. This stratification appears to be predominantly

the result of a solution-precipitation mechanism. Fe- and Mn-oxihydroxides tend to be solubilized under reducing conditions, thus creating concentration gradients observed in the pore waters, to migrate upwards and precipitate as oxihydroxides again along favourable horizons. However, the character of the oxidized zone is quite different in the two sub-basins of the Gulf of Bothnia. In the Bothnian Bay, Mn-rich sediment layers were found in 40 % of the cases, whereas none of the cores obtained in the Bothnian Sea showed any visible Mn-rich layer. This difference in Mn content could be explained if the sediments in the Bothnian Sea are somewhat less oxidizing. This is in fact due to the greater mean depth, larger organic production and a more developed halocline. Thereby, the precipitation of Mn relative to Fe is inhibited and hence Mn and related elements (Ni, Ba, Zn, Cu) would more easily leave the sediment and migrate into the bottom waters than iron and related elements (P, Ca, Sr).

Furthermore, the presence of Fe/Mn-micronodules in surface sediments of many basins of the Baltic Sea obscures the interpretation of heavy metal contamination. 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) which show, up to 2 mm, relatively high trace metal concentrations. It is possible that non-anthropogenic elements, such as La, Y or Yb, can be used for normalization as they appear to show enrichment patterns, due to changing redox conditions and under the presence of Fe/Mn-micronodules, similar to those of Zn, Ni and Cu (Ingri and Ponter, 1986b).

Tervo and Niemistö (1989) analyzed five cores of about 40 cm length each which were taken in 1987 from "representative stations" in the Gulfs of Finland and Bothnia and in the Northern Baltic Proper. The studies aimed to repeat investigations carried out by the authors 12 years earlier (Niemistö and Tervo, 1978) at the same stations and applying identical methods (Niemistö corer, 1 cm slicing, freeze-drying, dating with the ^{210}Pb technique, strong decomposition with nitric acid and AAS measurements for the elements Fe, Mn, Cu, Zn, Pb, Cd and Hg). For organic carbon, nitrogen, phosphorus, Fe, Cu, Pb and Cd, the mean values over all 181 core sub-samples were practically the same as from samples taken in 1975. However, for Zn, Hg and Mn lower means were observed. For Mn, this is reflected by a pronounced decrease from 9.4 % to 0.08 % in the 1 cm surface layer of station "F81" (Gotland Deep) due to remobilization under anoxic conditions which have occurred there continuously since 1977 (Table 5.12).

Table 5.12 Results of measurements on 5 cores of about 40 cm length, taken in 1987 from stations "C-VI", "EB-1", "TEIL11" and "F81" (dissection into 1 cm slices, n = 181 samples).

Element	Mean	Range
C (mg g ⁻¹)	31	11-107
N (mg g ⁻¹)	3.4	1.4-10
P (mg g ⁻¹)	1.3	0.9-3.9
Fe (mg g ⁻¹)	47	23-72
Mn (mg g ⁻¹)	9.7	0.3-84.7
Zn (µg g ⁻¹)	133	43-613
Cu (µg g ⁻¹)	38	15-97
Pb (µg g ⁻¹)	33	4-95
Cd (µg g ⁻¹)	0.67	0.02-5.21
Hg (µg g ⁻¹)	0.08	0.01-0.47

The vertical distributions of the investigated elements (Fig. 5.12) show quite similar features to those in the earlier studies. Maximum concentrations were found in surface or sub-surface layers.

There were indications that Hg has been deposited in those sediments in mainly immobile forms. The observed sub-surface maximum for Hg, which was most pronounced in the eastern Gulf of Finland, corresponded to the 1960s. On the other hand, the Zn was found to be relatively mobile in the sediments.

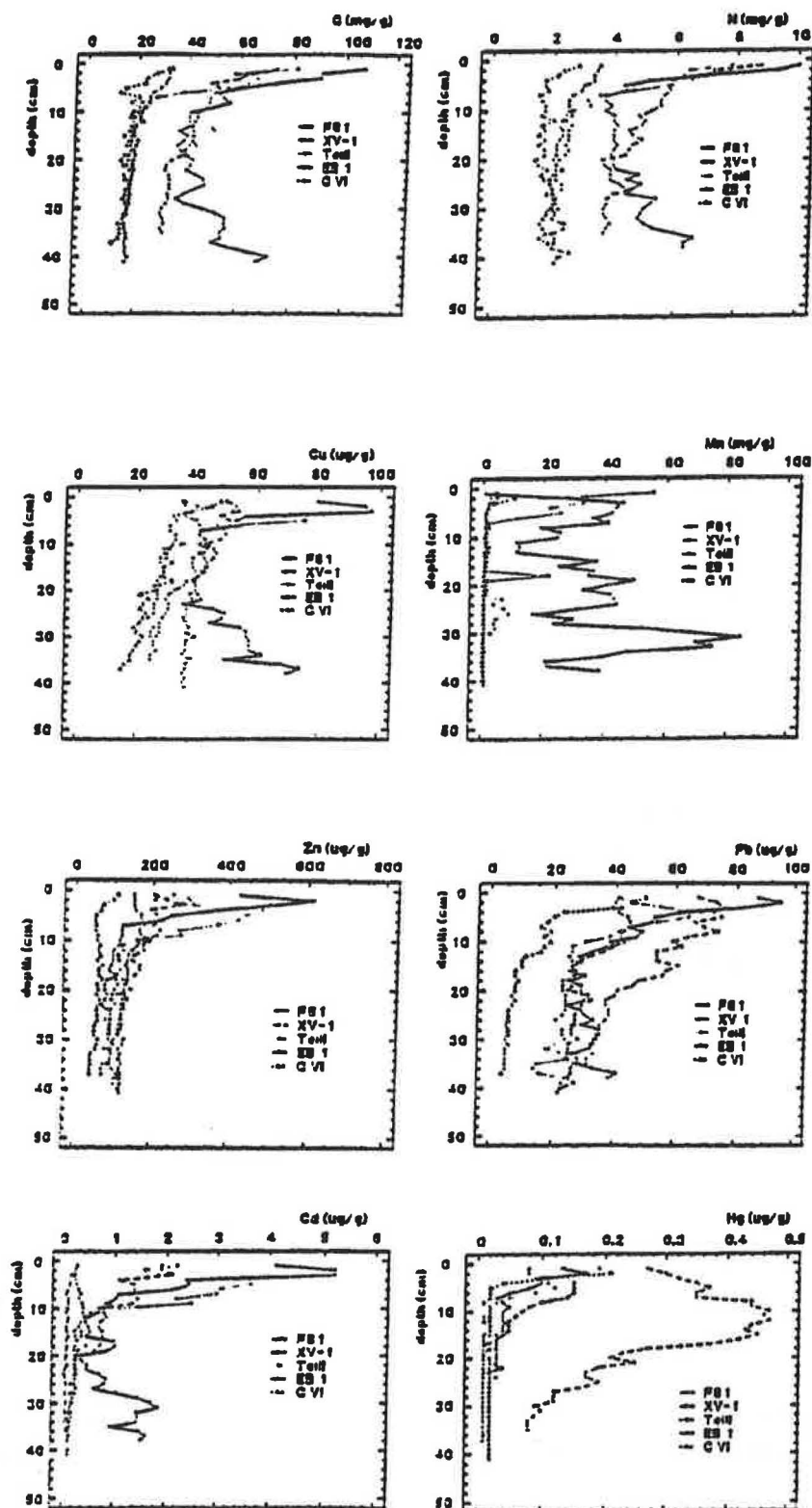


Fig. 5.12 Vertical distributions of trace elements in the core samples of the Gulf of Bothnia, Gulf of Finland, and the Northern Baltic Proper (Tervo and Niemistö, 1989).

Conclusions

- Further investigations of trace metal concentrations in Baltic Sea sediments using intercalibrated methods for sampling and analysis are urgently needed. As much background information as possible must be made available on sedimentological (e.g., mass accumulation rate, grain-size fractionation, representativeness of sampling area) and geochemical parameters (C_{org}, C_{inorg}, N, P, S, Fe, Mn, redox-potential) for a proper interpretation of the data. Mineralogical investigations should be included, too.

- Except for local areas where direct discharges of heavy metal wastes occur, the highest metal concentrations were found in the centre of basins with very fine-grained material. Obviously, it is not enough to "normalize" for the grain-size effect only by separating the < 63 µm fraction for analysis. With the increasing clay fraction in the central Gotland Basin (partly, more than 50 %), the concentrations of some elements increase appreciably in relation to material in which the silt fractions dominate.

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

Elderfield and Hepworth (1975) have shown that metal enrichment at the surface of sediment cores at least up to 10 % compared with deeper sections of the sediment cannot necessarily be interpreted as evidence of recent anthropogenic input and may be a consequence of diagenesis. Specifically, for anaerobic estuarine sediments it is now accepted that they may also act as a sink for elements like Cu and Cd in the common situation in which free sulphide concentrations are controlled by the co-existence of iron sulphide and iron oxide minerals. However, where free sulphides reach high concentrations of 1 µmol l⁻¹ or more, the concomitant increase in concentrations of bi-sulphide and poly-sulphide complexes may result in the sediments acting as a source of mobilized Cu and Cd (Davies-Colley et al., 1985). That the metal profiles (Cu, Pb, Zn) in sediments are mainly of diagenetic rather than anthropogenic nature was again shown by Ridgway and Price (1987). In addition, discrepancies observed between ²¹⁰Pb and ¹³⁷Cs dating chronologies were explained by diagenetic recycling of the ²¹⁰Pb, also. A study of metal contamination in the Baltic Sea by Suess and Erlenkeuser (1975) has also shown discrepancies in the timing of the onset of metal enrichment. These were interpreted as being due to a transport lag in the introduction of those contaminants but could now be re-interpreted in terms of variable diagenetic reactivity within the investigated sediments.

- Further results of field and laboratory (mesocosm) experiments are needed for getting reliable data on mass-fluxes at the water/sediment interface and in the sediments. Repeated monitoring activities with a frequency of about 5 years could be used to follow the trend in vertical and horizontal patterns of trace element concentrations.

- In some parts of the Baltic Sea, huge amounts of potentially toxic metals (Cd, Hg, Pb, Zn) 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., Cd) which could be quickly released due to oxidation following strong salt water (oxygen) inflows to the bottom water of the Gotland Basin.

CHAPTER 6 - ORGANIC CONTAMINANTS

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.

6.1 PETROLEUM HYDROCARBONS

Eugene Andrulewicz

The degradation of crude oil in sediments is a little-studied process and is understood only generally. In stagnant basins with low oxygen content, the degradation process is very slow, not only owing to the lack of oxygen but also because of the lack of photochemical oxidation. For example, crude oils have been shown to persist in sediments for several years without any sign of degradation. Rudling (1976) has shown that petroleum hydrocarbons are accumulating in the Baltic Sea sediments.

According to Rudling (1976) the content of paraffin-naphthalene hydrocarbons obtained by gas chromatography (GC) is dependent on the redox conditions of the sediment. Sediments from oxic clay-sand or silt-clay bottoms had low paraffin-naphthalene hydrocarbon concentrations, in the range of 8-16 mg g⁻¹ dry weight of the C₁₂-C₃₂ fraction, whereas sediments from stagnant anoxic basins or from heavily polluted urbanized areas contained concentrations higher than 160 mg g⁻¹ dry weight of the C₁₂-C₃₂ fraction.

Broman et al. (1988) studied the spatial and temporal distribution of 18 polynuclear aromatic hydrocarbon (PAH) compounds in the Stockholm archipelago by means of material which had been collected by sediment traps. PAH concentrations and fluxes exhibited a steep logarithmic decline with the distance from urban areas. These results confirm the heavy impact on the deposit bottoms in urban areas. PAH concentrations and fluxes were higher during the winter-spring period than during the summer due to increased emissions and more extensive wash-out during the melting of snow.

The concentrations of specific aliphatic hydrocarbons in sediments of the southern Baltic Sea obtained by GC-MS are given in Table 6.1.1 (Law and Andrulewicz, 1982).

Polynuclear aromatic hydrocarbons are very persistent in the aqueous phase and in sediments. The greater part of them probably reaches the marine environment from atmospheric fallout rather than by direct input. The unsubstituted PAHs are mainly derived from the combustion of fossil fuels and some of them are known to be carcinogenic (e.g., 3,5-benzopyrene and 1,2-benzanthracene).

Granby (1987) measured saturated hydrocarbons (paraffin-naphthalene hydrocarbons) in sediments sampled from 16 stations around Denmark. The highest pollution load (1342 mg kg^{-1} dry weight) was found at a station near Copenhagen. Elevated concentrations in samples from stations with no direct pollution sources could be explained by higher sedimentation rates and a higher content of organic material, including biogenic saturated hydrocarbons.

Mattsson and Lehtinen (1985) found "increased levels of petroleum hydrocarbons in the surface sediments of Swedish coastal waters". 61 of the sediment stations investigated by Rudling (1976) in 1974/1979 have been revisited in 1982. The levels of paraffin-naphthalene hydrocarbons showed a statistically significant increase from 199 to 252 mg g⁻¹ dry weight. The main increase could be found in coastal areas where the main pollution sources are situated. The authors calculated a yearly increase of paraffin-naphthalene hydrocarbons in surface sediments of a total of 8700 t in the area investigated. Thus, the first indication of an increase of PHC pollution in the Baltic Sea is given, which could be the result of the permanent deposition of PHC, mainly from urban run-off on the one hand, and low degradation rates due to low water temperatures and large areas of oxygen deficiency on the other hand.

Poutanen (1989) and Poutanen et al. (1982) investigated sediments in more open areas of the Baltic Sea. No clearly oil polluted bottom sediments could be found. The composition of the background content of PAH (0.5-7 mg g⁻¹ dry weight) indicated atmospheric input as the main source of contamination in these areas.

Table 6.1.1 Aliphatic hydrocarbon concentrations in sediments and mussels (ng g⁻¹ dry wt).

Station		Sediments								Mussels		
		1	2	3	4	5	6	7	8	9	10	11
n-C	13	5.5	34	36	190	94	60	1500	280	280	ND	360
	14	5.6	29	42	95	110	44	2000	370	390	3800	380
	15	5.0	19	62	61	170	41	2500	480	840	7400	1300
	16	14	51	55	61	290	50	2300	470	1400	1700	1500
	17	7.8	75	220	240	300	63	2200	610	1300	ND	450
Pristane		6.8	59	100	190	53	10	300	220	330	5000	1800
	18	14	21	57	50	83	40	1000	270	320	7200	350
Phytane		20	24	63	82	87	13	640	200	1100	ND	550
	19	11	31	160	87	43	26	700	230	740	7900	630
	20	17	44	160	51	37	27	480	230	350	2700	380
	21	5.6	14	360	170	45	27	970	220	610	2300	630
	22	11	23	210	110	39	25	360	220	450	1700	630
	23	9.3	34	400	230	61	24	500	230	520	1100	730
	24	14	35	240	150	53	24	200	220	710	760	950
	25	12	46	460	350	94	26	220	210	1100	1100	1200
	26	16	31	200	110	61	26	68	190	940	1300	1200
	27	10	49	650	250	190	20	55	130	940	1300	860
	28	7.4	29	92	120	69	14	73	120	440	1300	860
	29	6.2	42	ND	260	190	13	55	65	640	1400	1100
	30	5.0	15	ND	110	86	8.4	67	33	250	760	770
ND, not detected												

6.2 CHLORINATED HYDROCARBONS

Compiled by Matti Perttilä and Eugene Andruliewicz

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 (Andruliewicz et 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 and 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.

DDT, its metabolites and PCBs

The use of the "classical" organic biocide, DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) was started in large scale after the Second World War. During the following decades, DDT with its metabolites was spread all over the world. In the Baltic Sea area its use was banned in 1972 following a recommendation of the Baltic Marine Environment Protection Commission. As the DDT molecule slowly degrades in the environment into DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane) and finally into the more stable molecule DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethene), it gives a good opportunity to follow the recovery process of the marine environment through sedimentation. Especially in biota DDT has almost completely degraded into DDD and DDE. DDT and its metabolites are unquestionably always of anthropogenic origin, which makes their concentrations in sediments more easily comparable than those of the trace elements, whose distribution follows a more complex pattern depending on discharges, deposition, and natural sources. The half-life of DDT in the environment is several years (Jensen and Olsson, 1976). Thus the relation of the three molecules can be used to indicate the age of the DDT pollution.

The PCBs (polychlorinated biphenyls) have been in wide use in industry since their introduction in 1929. Together with the DDTs, they still form the two groups of organochlorines with the

highest overall concentration in nature. The discharges of PCBs have been strictly restricted, but because of their widespread use they are still a serious threat to the marine environment. PCBs are composed of 209 components, "congeners", which makes the comparison of "total PCBs" and main component concentrations difficult, if not impossible.

No complete study on the atmospheric transportation of chlorinated hydrocarbons to the Baltic Sea area has been carried out. In the early 1970s the overall DDT deposition in the coastal regions of southern Sweden was estimated to vary from 100 to 2075 ng m⁻²/month, with the PCB deposition being 550-10510 ng m⁻² yr⁻¹. Using these estimates, the total DDT burden in the Baltic Sea from the atmosphere is 500 - 10400 kg of DDT and 2700-53000 kg of PCB annually (Södergren, 1972; Kihlström and Berglund, 1978). Korolov (1985) gives the following estimates: DDT 11000 - 37000 kg yr⁻¹; DDE 3000 - 9000 kg yr⁻¹; DDD 4000 - 12000 kg yr⁻¹.

Discharges of both DDT and PCB components through rivers and wastewaters is probably of more local interest. The amount of DDT introduced by, e.g., the river Göta in Sweden into the Baltic Sea has been estimated at 10 - 15 kg per year (Ahnoff and Josefsson, 1975).

Hexachlorobenzene

Hexachlorobenzene (HCB) and other chlorinated benzenes are unintentionally formed in several industrial processes: e.g., magnesium production, chlorine gas production from sea water, production of chlorinated solvents. HCB is also formed in waste incineration. The use of HCB as a fungicide started during the 1940s and ceased in the western countries around 1975.

Due to its high volatility, the emitted product is to a great extent transported by air and thus globally distributed. The chemical properties of HCB result in a poor degradation in the environment. The accumulation of the chlorinated benzenes in biota and sediments increases with the increasing degree of chlorination.

The concentrations of HCB in sediments from the Elbe estuary were in the range 10-200 ng g⁻¹ dry weight (Sturm et al., 1986), while in heavily contaminated areas of the Frierfjord in Norway the corresponding values were 320-530 ng g⁻¹ (Bjerk and Brevik, 1980).

Dioxins

Dioxins, mainly particle bound, are transported by air and thus globally distributed. The emission and transport on a more narrow scale can be illustrated by a study of dioxins in settling particulate matter in the Stockholm archipelago and offshore in the Åland Sea (Broman et al., 1988). The flux of dioxins by this mechanism indicated a rapid decline with increasing distance from the city. The estimated flux at the offshore station was 0.7-1.0 mg TCDD-equivalents km⁻² month⁻¹. The contribution to this flux by air deposition as opposed to a resuspension mechanism could not be established in this study, but the major part was considered to be a result of fallout. Also, the congener profile changed with increasing distance from the emission sources.

Dioxins have been analysed and found present in recent as well as in old deep sediments with 20-50 times higher concentrations in the recent layers. The toxic isomers of dioxins are present only in the recent sediment (SNV, 1987).

Halogenated organic matter

A variety of halogenated substances are formed and released by human activities. The introduction of halogen into an organic molecule usually renders it a higher degree of stability and resistance to chemical and biological degradation. Halogenated man-made substances of various origins are today found widely distributed in the environment, thus giving rise to special concern.

Local and regional gradients in surficial sediment contamination by chlorine bleachery effluents have been established from extractable organic chlorine (EOCl) analyses of samples taken outside pulp mills. Very high concentrations of EOCl (generally above $1000 \text{ mg g}^{-1} \text{ IG}$) are found in sediments close to the mills. This is 50-250 times higher than in areas not exposed to local discharges (Håkansson et al., 1988).

The EOCl levels in Baltic Sea sediments in areas without point sources decrease from north to south (Södergren, 1989). The levels in remote lakes and in estuaries with only municipal discharges without any particular local source of pollution are about $10\text{-}30 \text{ mg g}^{-1} \text{ IG}$.

Specific chlorinated phenolic substances (e.g., guaiacols) and dibenzo-p-dioxins/dibenzofurans were found in sediment samples 150 km off the coast in the southern central Bothnian Sea and in the northwestern Baltic Proper (Rappe et al., 1987; Kirkegaard and Renberg, 1987). Dibenzo-p-dioxins/dibenzofurans may also emanate from other sources. Chlorinated guaiacols, however, have never been shown to be discharged from sources other than pulp bleacheries. These observations have been taken as evidence of a large-scale pollution of the Baltic Sea from pulp mills.

The other chlorinated hydrocarbons generally found in the marine environment include principally γ -hexachlorocyclohexane (HCH) with its isomers, hexachlorobenzene (HCB), the chlordane group and the toxaphene group (polychlorinated camphenes). They are still in production and, because of atmospheric transport, can be found all over the world.

The use of chlordane is common in central Europe. Toxaphene is used as an insecticide, especially in the eastern European countries (Wideqvist et al., 1985; Pyysalo et al., 1981).

Distribution of DDTs and PCBs in sediments

Niemistö and Voipio (1981) reported distinctive vertical gradients in the DDT and PCB concentrations in Baltic Sea sediments (Fig. 6.2.1). The age of the sediment samples was determined by the ^{210}Pb method. The figure shows clearly the rise of the concentrations which began at the end of the 1940s in all the areas. No measurements were made in the southern Baltic Sea. Concentrations in surface sediments of the Gotland Deep (F81) were significantly higher than in the Gulf of Bothnia. Surface sediments in 1972-1973 in the same area contained slightly higher amounts of DDT, but over ten-fold higher amounts of PCBs were reported (Oden and Ekstedt, 1976). Concentrations in the Gulf of Bothnia were slightly higher in Fig. 6.2.2 than in Fig. 6.2.1.

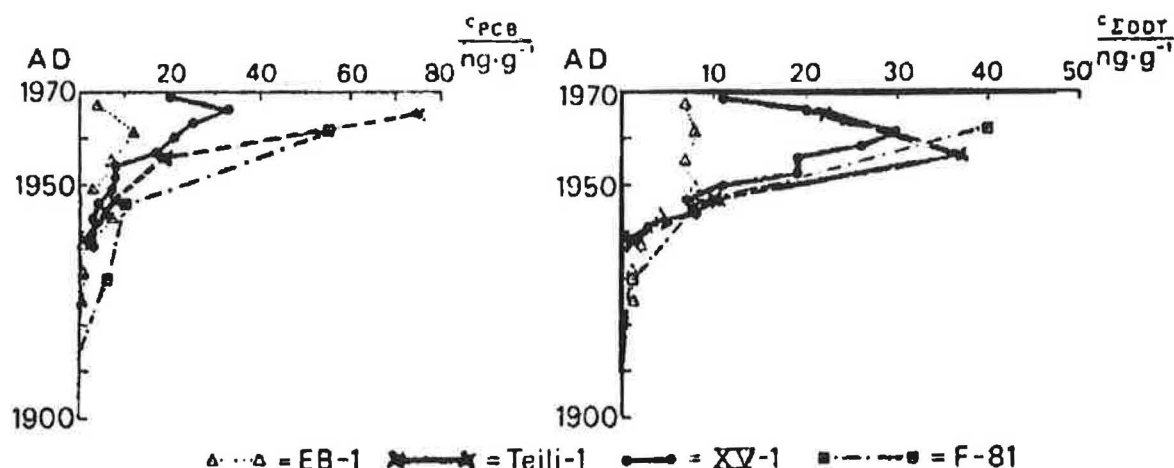


Fig. 6.2.1 Vertical distribution of PCBs and DDT and its metabolites in sediment cores from Baltic Sea stations (from: Niemistö and Voipio, 1981).

Perttilä and Haahti (1984) studied the relative concentrations of DDT and its metabolites in the sediments. In the earlier samples, DDT had metabolized only to a small extent; only 20 % of the total-DDT was in the form of DDD and DDE. However, in the continuously anoxic Gotland Deep region, up to 85-95 % of the total-DDT has been reported to be as DDD (Oden and Ekstedt, 1976). At the stations XV-1 (eastern Gulf of Finland) and Teili-1 (northern Baltic Proper), which are both relatively fast sedimentation areas, the amount of DDD is approximately 60 % of the total-DDT. In the slow sedimentation area of EB-1 in the southern Baltic Sea, the DDT metabolites are present in roughly equal amounts (Fig. 6.2.2). In XV-1 and Teili-1, the decrease in the DDTs, due to restrictions in use and discharges, can also be seen (Fig. 6.2.2). In the Gulf of Bothnia, with relatively slow net sedimentation ($1.2 - 2.4 \text{ mm yr}^{-1}$), such changes cannot yet be seen. Similar conclusions can be drawn for the PCBs (Fig. 6.2.3).

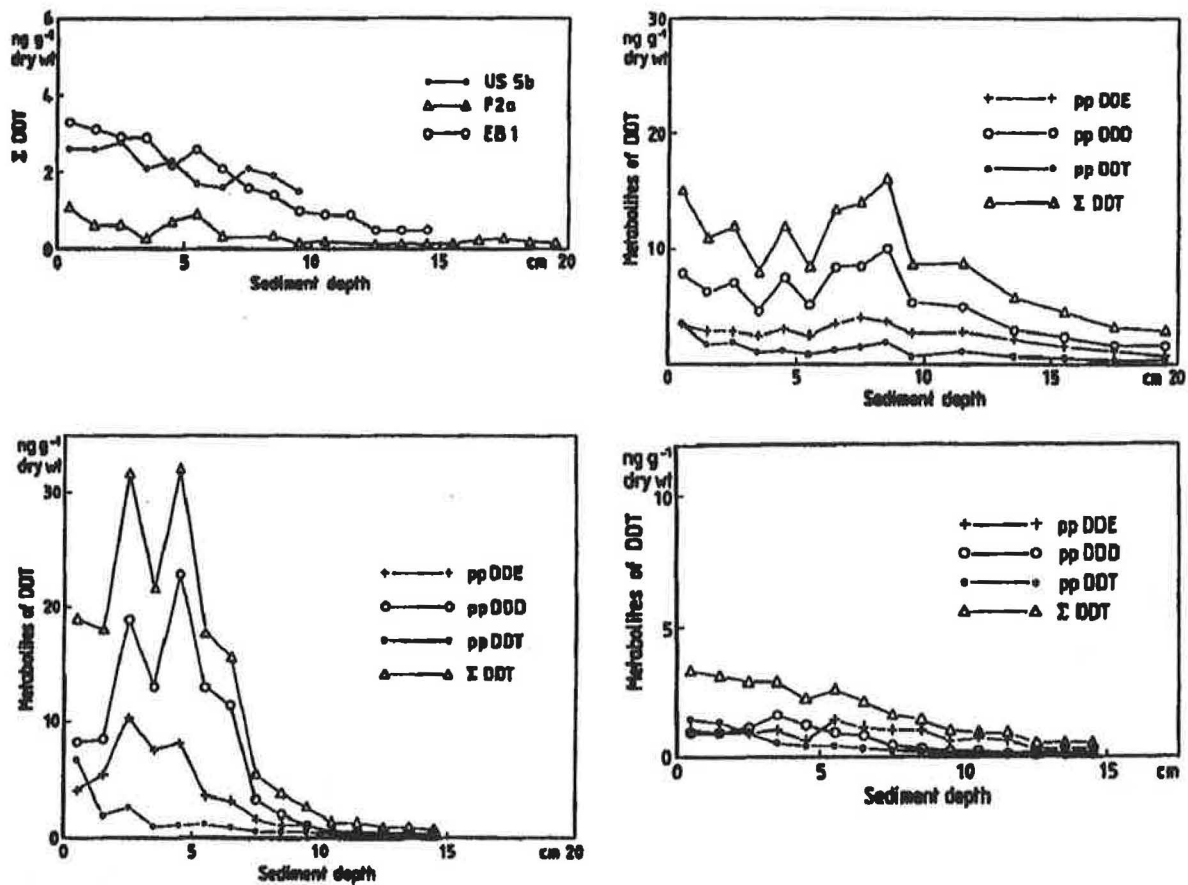


Fig. 6.2.2 Profiles for DDT, DDD, DDE and total DDT in sediments from the northern Baltic Proper (Teili-1), the Bothnian Sea (EB-1) and for the Gulf of Finland (XV-1) (from: Pertilä and Haahti, 1984).

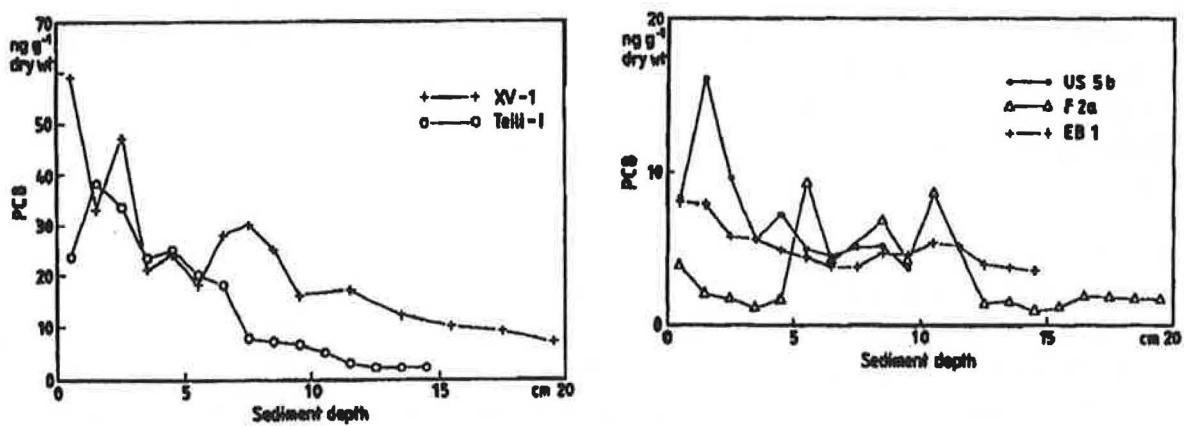


Fig. 6.2.3 Total PCB profiles in sediments from the Gulf of Finland (station XV-1), the northern Baltic Proper (Teili-1), southern Bothnian Sea (EB-1), northern Bothnian Sea (US-5b), and from the Bothnian Bay (F-2a) (from: Pertilä and Haahti, 1984).

In Table 6.2.1 surface sediment concentrations of total DDTs and total PCBs are shown from different parts of the Baltic Sea.

Table 6.2.1 Surface sediment concentrations of total DDT and total PCB in the Baltic Sea.

Area	Period of sampling	tDDT ng g ⁻¹	tPCB ng g ⁻¹	References
Gulf of Bothnia	1981-83	2-5	5-10	Perttilä, Haahti, 1984
Gulf of Bothnia	1972-73	10-41	9-30	Oden, Ekstedt, 1976
Archipelago Sea	1973		10	Linko et al., 1979
Gulf of Finland	1981-83		10-20	Perttilä, Haahti, 1984
Gotland Deep	1972-1973	8-50	950	Oden, Ekstedt, 1976
Gotland Deep	1977	22	31	Niemistö, Tervo, 1978
Bosex-77 area	1977	29	106	Niemistö, Tervo, 1978
Bosex-77 area	1972-73	1	175	Oden, Ekstedt, 1976
Southern Baltic Sea sand	1978	7	42	Andrulewicz et al. 1979
mud		17	203	ibid.
Kiel Bight	1978	2	10	Osterroth, Smetacek, 1980

Jonsson et al. (1986) have reported DDT and PCB values in surface sediments of the Swedish coastal area of the Bothnian Sea, close to the town of Norrsundet. DDT values varied from 118 ng g⁻¹ in the close-range (a few kilometres) recipient area down to 5.3 ng g⁻¹ further out. Correspondingly, total PCB values ranged from 1380 to 180 ng g⁻¹. The lower values relate to sediments at roughly 10-50 kilometres from the assumed outlet. It is interesting that they correspond to the concentrations in Table 6.2.1 for the open sea sediments, showing that the land-originating organochlorine molecules are effectively deposited in the close-range coastal areas.

Unfortunately, the DDT and PCB molecules form only a fraction of the total amount of chlorinated organic substances in the sediments (Jonsson et al., 1986). In the same regions, the total amount of extractable organic chlorine (EOCl) ranges from 1140 µg kg⁻¹ to 861 µg kg⁻¹, showing that, in contrast to the DDTs and PCBs, the total organic-bound chlorine is highly effectively carried out from the near-recipient area to the open sea. A transect study across the southern Bothnian Sea shows that the EOCl in the surface sediments is consistently diminished only after a distance of over 100 kilometers (Fig. 6.2.4). The persistent fraction (EPOCl) of EOCl, however, is more readily sedimented.

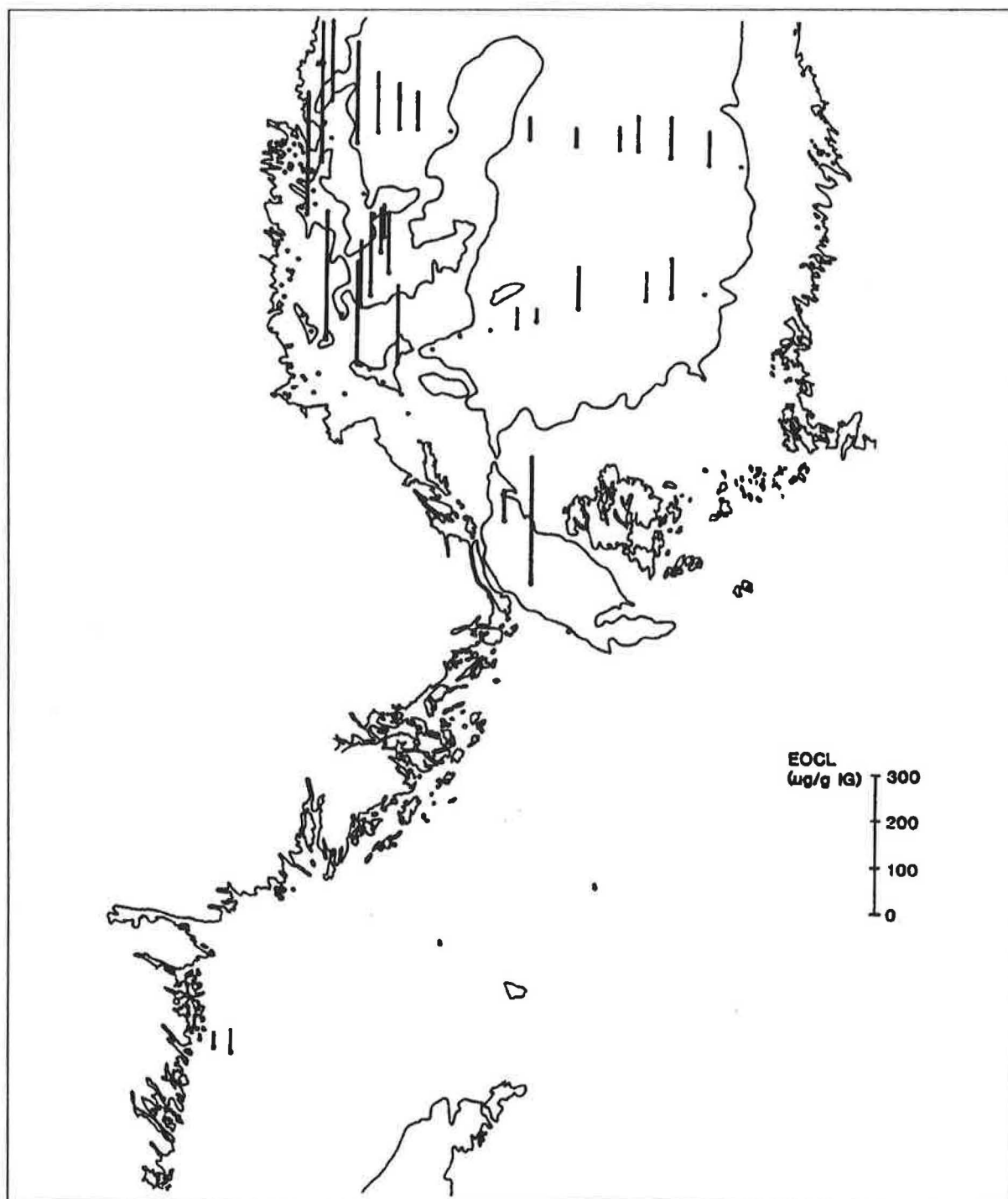


Fig. 6.2.4 Extractable organic chlorine (EOCl) in surface sediments of the Bothnian Sea (from: Jonsson et al., 1986).

Conclusions

The present state of knowledge on persistent organic contaminants in Baltic Sea sediments is far from ideal. Most of the available papers fail to give an adequate description of the analysed sediment, and very often they lack basic information on the sediment type (e.g., Corg content). Therefore, these results are only of limited value for comparative studies.

From the existing information it is not possible to assess the degree of contamination of Baltic Sea sediments by persistent organic compounds. However, there is enough evidence that they are contaminated by a number of anthropogenic substances.

Many different polynuclear aromatic hydrocarbons have been found in sediments. They seem mainly to originate from the combustion of fossil fuels. The degradation and transformation processes of these compounds in sediments are not fully understood.

There is no simple method that is specific and accurate enough for analysing individual organic contaminants in marine sediments. Each contaminant has to be determined separately out of a very complex and changing mixture of organic substances of anthropogenic, as well as biogenic, origin. This requires sophisticated instrumentation, time-consuming procedures of clean up, higher expenses and experienced analysts (Anon., 1977; Palmork, 1982).

The ultra-violet fluorescence (UV-F) technique is in general appropriate only as a screening method for the evaluation of PHCs in sediments. Sediments contain an undefined, but usually large, quantity of fluorescent material of biogenic origin. Therefore, UV-F values cannot reliably reflect pollution by petroleum hydrocarbons except some accidental cases of direct input.

It is proposed that the most appropriate compounds for monitoring petroleum pollution be chosen, e.g., unsubstituted aromatic hydrocarbons - fluoranthene, pyrene, benzopyrenes, etc., not generally included in biogenic organic material.

In general, the monitoring of organic contaminants in the sediments of the Baltic Sea is premature. Presently the analyses of only certain organic contaminants are at a more advanced state. Those contaminants could be included in a programme of repeated baseline studies. Examples are: DDT and its derivatives, γ -HCH, HCB and some of the PCB congeners.

CHAPTER 7 - PHOSPHORUS ACCUMULATION IN THE SEDIMENTS OF THE BALTIC SEA

Birger Larsen and Lutz Brüggemann

In recent decades, increasing nutrient concentrations have been observed in some Baltic Sea basins, in the Danish Straits and the Kattegat area. This eutrophication has contributed to more frequent occurrences of anoxic conditions in bottom water and sediments and to a spreading of affected areas. In order to counteract this development, a better understanding of turnover processes and fluxes of the nutrients nitrogen and phosphorus in the sea is needed.

In this chapter, the exchange of phosphorus between bottom waters and the sea floor is discussed, especially the net annual loss of P to the sediment. This loss is proved by the fact that all recent marine deposits in the Baltic Sea and the Kattegat contain significant amounts of P. That fraction of the total flux of P, which is deposited on the sea floor and incorporated into the sediment and not recirculated back into the water in a timescale of decades, is here called the Net Accumulated P (NAP).

The published phosphorus mass balances of the Baltic Sea are chiefly based on estimates of the contributions from rivers, atmospheric deposition, waste discharges, water exchange and mobilization from anoxic bottom areas (Fonselius, 1969, 1972; Sjöberg et al., 1972; Grasshoff, 1975; Holm, 1978). The NAP in the mass balance is determined by differences in the P fluxes in one or more compartments of the models. No independent check of the correctness of the items in the mass balance was thus possible. A direct determination of the NAP would be an important improvement of the mass balances and thus increase the reliability of the balances and, consequently, of the models of eutrophication. The NAP may be estimated by a determination of the annual accumulation of sediment dry matter and its P-concentration.

Based on geological mapping of the total mass of dry sediment, deposited in a basin since the establishment of the Baltic Sea 7000 years ago, and an estimate of its mean P-content, the mean annual NAP has been calculated for the Bothnian Sea (Niemistö et al., 1978), the western Bornholm Basin (Kögler and Larsen, 1979), the Bornholm Basin north of 54°50' (Larsen, 1979), the Baltic Proper (Voipio and Niemistö, 1979; Larsen, 1979), and the Little Belt (Isotopcentralen and Instituttet for Teknisk Geologi, 1983).

The results recalculated to mean NAP in $\text{g m}^{-2} \text{yr}^{-1}$ are shown in Table 7.1. Note that in Table 7.1 the figures under "A" apply to accumulation areas only and the figures under "B" to the total area.

This geological approach results in rough mean estimates over 7000 years and the whole basin. However, the thickness of the mud layer is not always an indication of the present-day sedimentation rate.

Dating of layers in the topmost 10-20 cm by ^{210}Pb offers a convenient measurement method for the determination of local accumulation rates within the last 10-100 years and possibly for the study of the recent development of the NAP. The aim of this chapter is to describe this method and report the first results.

Material and methods

Core samples of the upper 10-25 cm of the sea floor were collected, using a HAPS sampler (Kannevorff and Nicolaisen, 1973) or similar devices, and cut into 1 cm sub-samples. Only areas with reasonably steady accumulation of mud and partly of sandy mud were selected.

Table 7.1 Net mean annual P accumulation determined by mean sediment thickness, deposited in 7000 years, and estimated mean P concentration.

A. Accumulation areas only						
Accumulation area km ²		Sediment acc. g m ⁻² yr ⁻¹	Mean P mg g ⁻¹	Samples n	NAP mg m ⁻² yr ⁻¹	References
Bothnian Sea	32400	137	1.7	372	210	Niemistö et al., 1978
Bothnian Bay	14400	356	1.9		676	Tulkki, 1977
W. Bornholm Basin	256	400	1.2	52	500	Kögler and Larsen, 1979
Bornholm Basin	7060	372	1.2	52	450	Larsen, 1979
Little Belt N	211	405	1.19		480	Isotopcentralen og Inst. for Teknisk Geologi, 1983
Little Belt S	280	361	1.16		420	
B. Whole area						
Baltic Proper	374000	0.1 mm yr ⁻¹	0.2	52	60	Voipio and Niemistö, 1979
Baltic Proper	-	125 g m ⁻² yr ⁻¹	0.2	52	250	Larsen, 1979

During the period 1979-1985, cores from ca. 100 stations in the Belt Sea and Kattegat were ²¹⁰Pb dated by the Danish Isotope Center, chiefly as part of studies on trace metal pollution (Pheiffer-Madsen and Larsen, 1986). When sufficient P data were available for these stations, they were included in this study. In 1983, cores from the southern Baltic Sea were collected on a Soviet-Danish cruise. Some of them were dated, from which 15 datings were suitable. Additionally, information from the literature has been included (Niemistö and Voipio, 1981; Widrowski and Pempkowiak, 1987; Müller et al., 1980; Larsen and Somer, 1980).

The standard error on the individual determinations of accumulation rates is, in half of the cases, less than 10 % and only in few cases exceeded 20 %. However, the few examples of repeated coring and determination on the same stations seem to indicate differences of up to 50 % in areas with deep mixing (Pheiffer-Madsen, 1987; Widrowski and Pempkowiak, 1987).

Phosphorus analyses were carried out on sediment samples ignited at 550 °C in order to transfer all phosphorus to phosphate. The PO₄ is leached by boiling with hydrochloric acid and determined as the blue molybdatophosphoric complex, measured at 827 nm, using ascorbic acid as the reducing agent. Judged by comparison with ICES and Nordforsk standard sediments, the phosphorus determinations are reliable within ± 5 % (2 s).

Vertical distribution of phosphorus in the sediments

In order to select the P concentration for the calculation of NAP, it is necessary to study the vertical P distribution in the sediment cores. It is often observed that the concentration of P increases by a factor of 1.2-3 upwards in the topmost 10-50 mm of the sediment (Olausson et

al., 1979; Müller et al., 1980; own observations, Fig. 7.1). Below this enrichment zone, the P concentration is in many cases constant within 10 %, provided there is no change in the sediment type. This depth distribution is to some extent explained by the variation in organic content in the topmost layers. Müller et al. (1980) suggest that the increase in the sediment reflects the increase in input of P to the Baltic. Holm (1978) has, based on experiments, suggested that the enrichment above the background comprises the pool of mobile phosphorus. This may potentially be mobilized if a sufficiently long period with anoxic conditions is established.

An enrichment zone has not been observed in many cores from the deeper parts of the Bornholm and Gotland basins, where frequently anoxic conditions in the bottom waters occur. However, P enrichment was visible in several other cores in spite of a strong and deep mixing, as indicated by the ^{210}Pb profiles. This could indicate that the development of an enrichment zone has proceeded quickly in comparison with mixing processes.

Comparison of the background concentration of P closely beneath the enrichment zone with concentrations from deeper levels shows that the background concentrations represent the buried fraction of the P accumulation. In other words, they represent the net accumulated phosphorus "NAP". In cores with enrichment zones, the NAP concentration is accordingly defined below that zone, that is from sediment depths which are deposited at least 10-30 years before present.

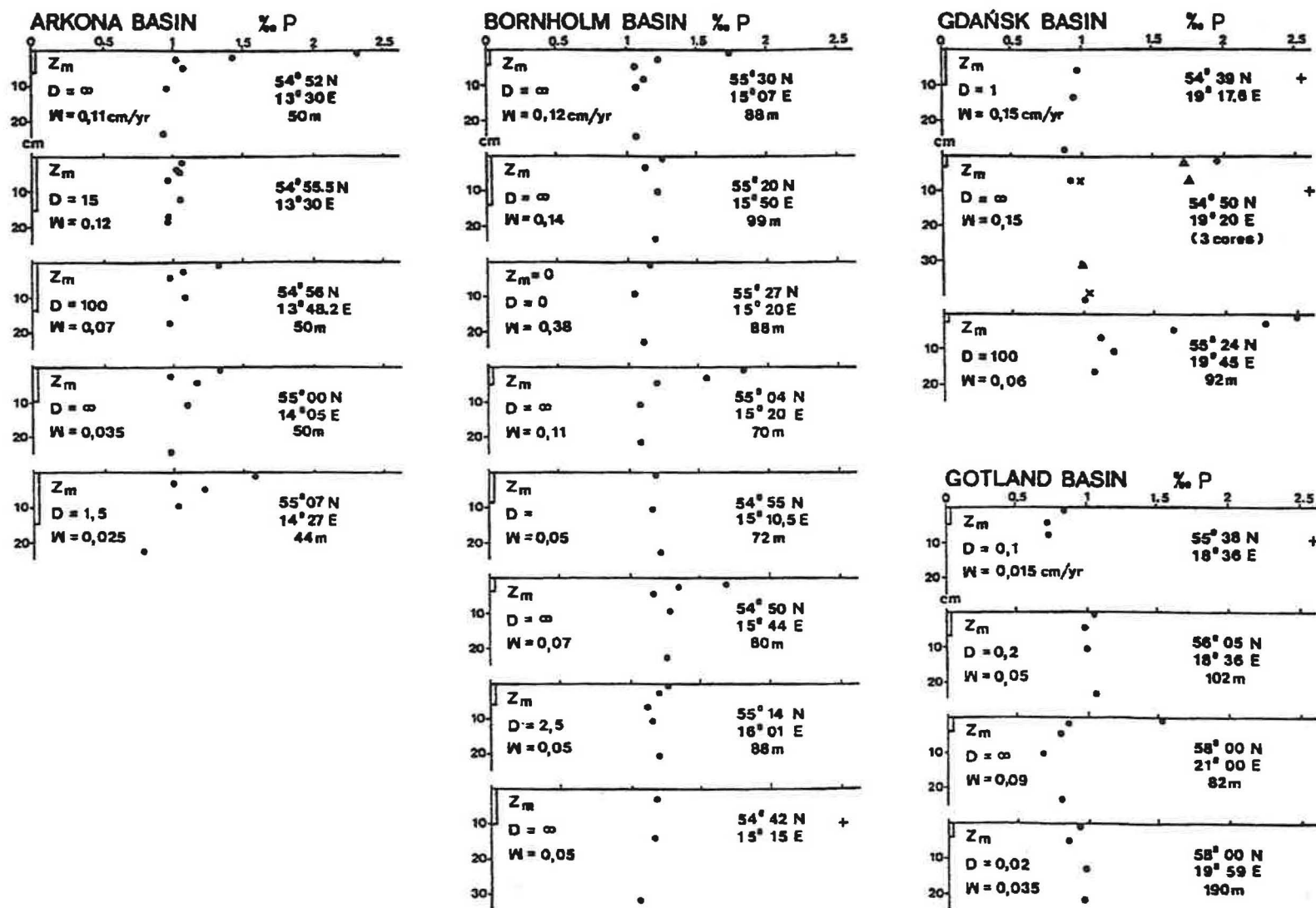


Fig. 7.1

P-content in $\text{mg g}^{-1} \text{ d.w.}$; profiles of the topmost 20-30 cm of the sea floor in the Baltic Sea. Z_m is the mixing depth, D the mixing rate in $\text{cm}^2 \text{ yr}^{-1}$ and w the accumulation in cm yr^{-1} as determined by ^{210}Pb . Mixing rates above two mean is almost total mixing.

Regional distribution of net accumulated phosphorus

Most of the available estimates on local P accumulation are shown in Figs. 7.2-7.4. These figures represent only mud accumulation areas. Furthermore, it should be noted that the near shore mud areas are not among that pool of data for the Baltic Sea. The number of determinations is small compared to the area of the Baltic Sea including the Danish Straits. With these limitations in mind, it appears that the rates of NAP in the mud bottoms vary, but chiefly are of the magnitude $100-500 \text{ mg P m}^{-2} \text{ yr}^{-1}$. This magnitude agrees with the regional rates estimated by mean sediment thicknesses deposited in 7000 years and estimated mean P content, as given in Table 7.1. The existence of several cores in proved accumulation areas in the Bornholm and Gotland basins (Fig. 7.1, and Olausson et al., 1979; Holm, 1978) with no enrichment zone suggests that the increase of P input to the Baltic Sea (Helsinki Commission, 1986; Gerlach, 1986) is still not significantly reflected in these sediments. Therefore, it seems reasonable to assume that the determined NAP rates may be applied to the present day also. It is uncertain whether this is the case in the Danish Straits (Larsen and Somer, 1980), but the figures may be regarded as minimum estimates.

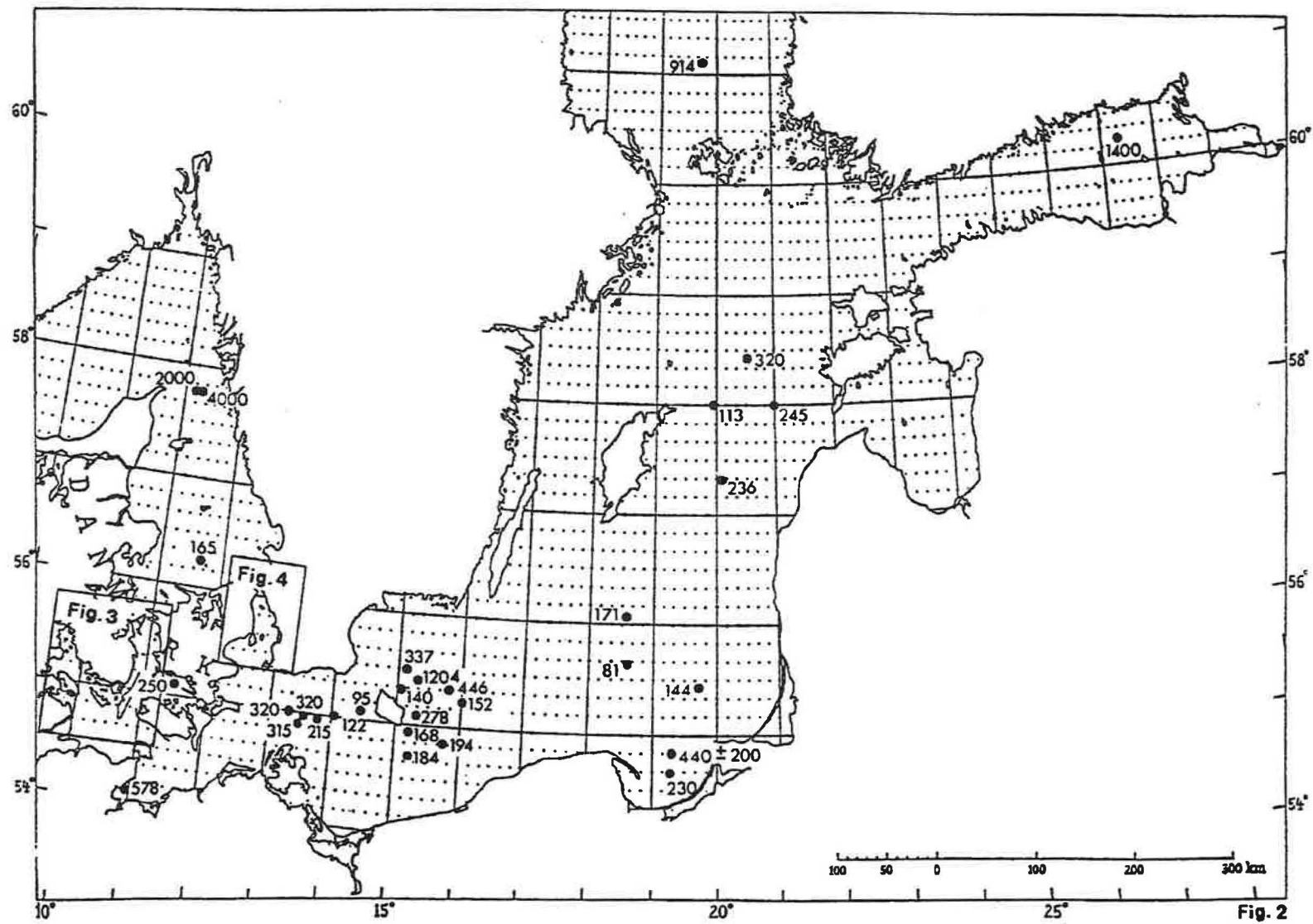
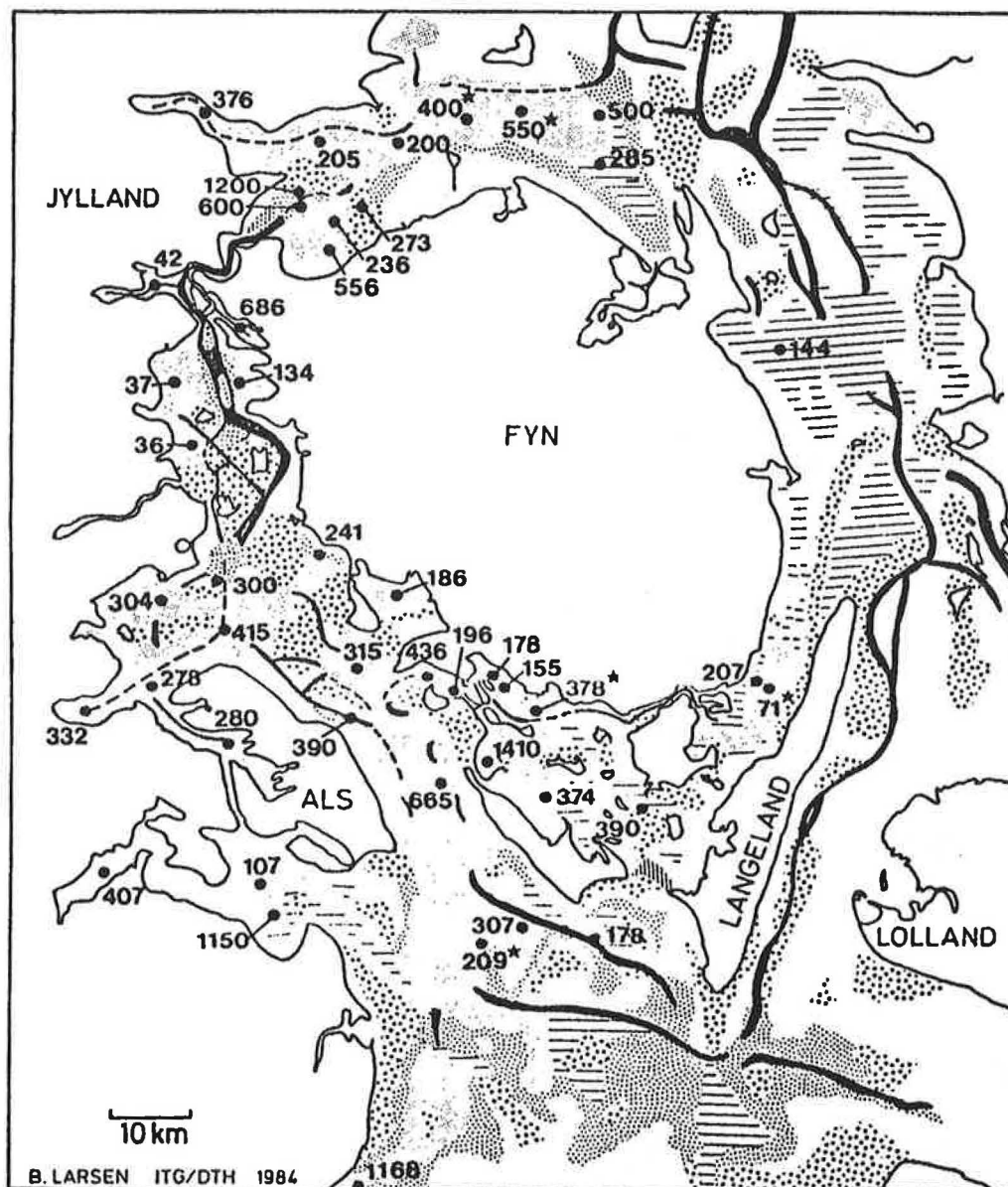


Fig. 7.2 Phosphorus background accumulation in $\text{mg m}^{-2} \text{yr}^{-1}$.



SURFACE SEDIMENTS

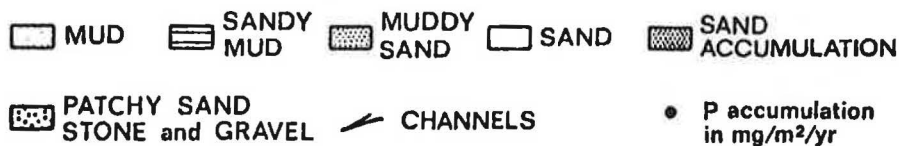


Fig. 7.3

Rates of "net accumulated P" in $\text{mg m}^{-2} \text{yr}^{-1}$. Including data from Müller et al. (1980). Rates marked with an asterisk are based on P concentration in 0-10 cm sediment, others are the background estimated from concentrations in the 10 cm level below the sea floor. Mud signatures are missing in Flensburg Fjord.

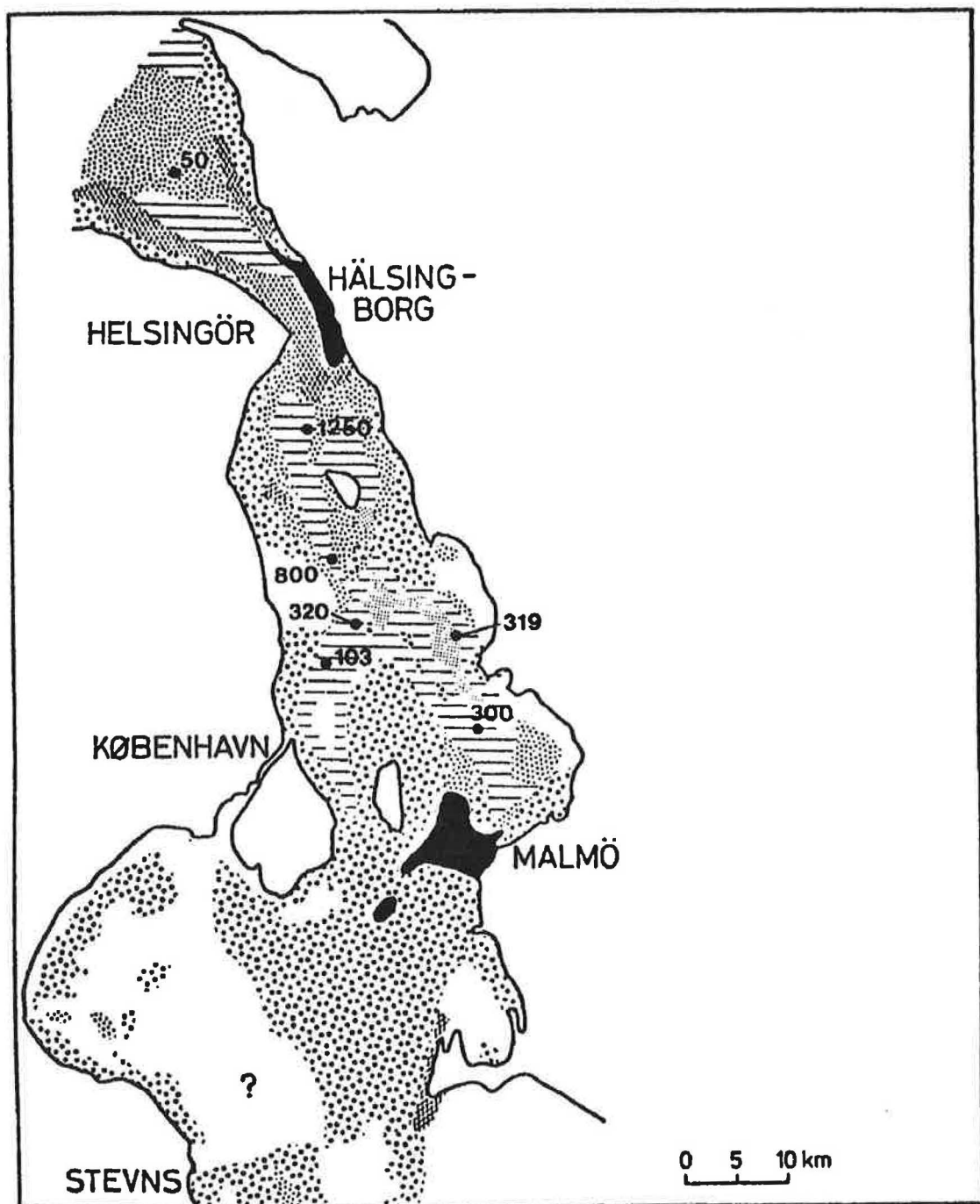


Fig. 7.4 Rates of "net accumulated P" in $\text{mg m}^{-2} \text{yr}^{-1}$. Sediment signatures are explained in Fig. 7.3. Solid black is rock bottom.

In Fig. 7.5 the NAP rates are plotted, versus the sediment accumulation rates. There seems to be a rather good positive correlation between them. This simply mirrors the fact that the P content in the investigated mud sediments varies but little, chiefly between $0.5\text{--}1.1 \text{ mg P g}^{-1} \text{ d.w.}$ The correlation implies that the rate of NAP accumulation to a great extent follows the other constituents of the sediments. In other words, the local rate of NAP is to some degree determined by the physical sedimentary environment, and to a lesser degree by the chemical-biological environment. An analysis of this aspect has not been finished.

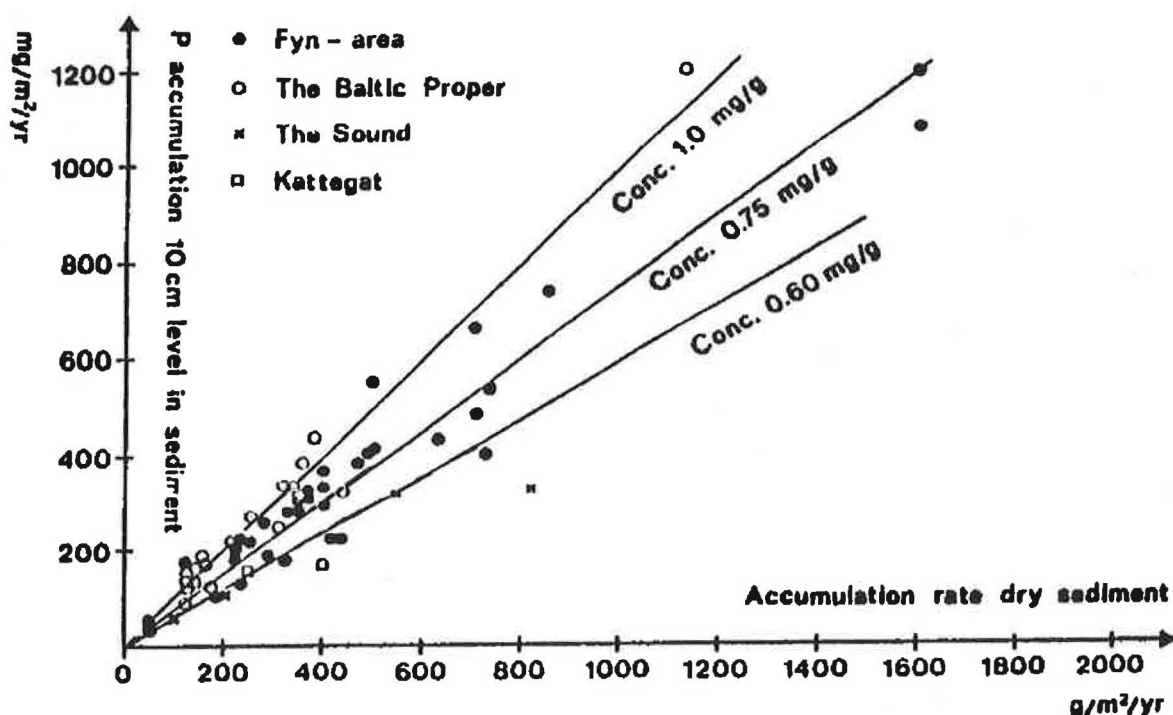


Fig 7.5 Accumulation rates of "NAP" in $\text{mg m}^{-2} \text{yr}^{-1}$ versus accumulation rates of clay sediment matter. P background defined as content in 10 cm depth in sea floor.

Holm (1978) has published a P budget for the Baltic. It is divided into 3 compartments: I-III. I is the water body and the sea floor above the halocline. II is the oxic water body and sea floor beneath the halocline, and III is the anoxic-sulphide areas. In this budget NAP is estimated as follows: I - $80 \text{ mg m}^{-2} \text{yr}^{-1}$, II - $50 \text{ mg m}^{-2} \text{yr}^{-1}$, and III - $140 \text{ mg m}^{-2} \text{yr}^{-1}$. In II and III the figures are calculated to balance the budget of the compartment. Box I is hardly represented in our data. Box II is represented by the Danish Straits (Figs. 7.3 and 7.4) and the measurements in the Arkona and Bornholm Basins, while Box III is represented by a few stations in the Gotland Basin. The few measured NAP rates from the sulphide environments seem to be of the same magnitude as estimated by Holm (1978), but the data material is too meagre for a discussion.

The measured rates of NAP in box II areas are 3-6 times higher than the estimate of Holm (1978). However, his estimate is an average for the whole area, whereas the measured rates only represent the mud basins. They are often surrounded by extensive areas of no deposition near the depth of the halocline (e.g., Kögler and Larsen, 1979, and map in Olausson et al., 1979). This may explain a factor of 1.2-1.5 of the increase of the NAP accumulation in the mud deposition areas. The remaining, which corresponds to an additional input of P in the order of $100 \text{ mg m}^{-2} \text{yr}^{-1}$ in the box II areas, needs to be explained. One possible explanation is that one or more of the P inputs to Holm's model is too low. Another possibility is that other sources are of importance. Fig. 7.2 suggests that the phosphorus to a great extent is sedimented together with the other constituents of the muddy sediments. It is not clear how much of the P is actually tightly incorporated in detritic particles, and how much is deposited in organic matter and coprecipitated with iron hydroxides.

The strong correlation between NAP rates and sediment accumulation rates suggests that budgets of sediment matter in the Baltic Sea may give a hint as to the origin of the additional P. Sediment budgets for the Baltic Sea have been published, among others, by Pustelnikov (1976), Larsen (1979), Boström et al. (1983), and for the Bothnian Sea by Winterhalter (1972), Niemistö et al.

(1978), for the Bothnian Bay by Tulkki (1977), and for the Danish Straits and Kattegat by Pheiffer-Madsen and Larsen (1986). These works clearly state that the recent mud sediment accumulation far exceeds the net river input of sediment matter. It is agreed that the main fraction (50-80 %) of the mud particles in the Baltic Sea have their source within the Baltic, and that this source is erosion of older glacial sediments (glacial clays and Ancyclus clays plus redeposited old marine *Litorina* clays). These old sediments are exposed extensively in rims surrounding the mud basins and in shallow waters. The erosion is facilitated by the postglacial uplift of much of the Baltic area. The internally eroded sediments contain P, according to Larsen (1987) ca. 0.9 mg g^{-1} in the southern Baltic and, according to Boström et al. (1983), 1.9 mg g^{-1} in the Bothnian Bay and Sea.

It is very likely that internal erosion of P-containing older sediments is a major source of P input to the Baltic Sea. Sediment transport from the North Sea is also of importance in the Kattegat area (Pheiffer-Madsen and Larsen, 1986). Gerlach (1986) and Balzer (1986) have discussed the influence of sediment erosion as a P source in the Kiel Bay, and concluded that this source is of minor importance there. It has to be investigated how much sediment P sources contribute to the P dissolved in the water, and how much is removed as inert sediment constituents.

Another approach was followed by Brüggmann and Lange (1989) to estimate the phosphorus accumulation in Baltic Sea sediments. However, the results are comparable to those of Larsen (above) and support most of his conclusions.

Sediment sampling was performed in several major basins and sub-regions of the Baltic Sea for which net accumulation is assumed. These included the Bay of Bothnia, the Bothnian Sea, the Northern Baltic Proper, the Landsort Deep, the Gotland, Gdansk, Bornholm and Arkona Basins, the Mecklenburg and Lübeck Bights, the Kattegat and the Skagerrak. Where possible, the central and deepest parts of those areas with high accumulation rates of fine-grained material were chosen. Often, this was identical to stations of the Baltic Monitoring Programme (BMP) of the Helsinki Commission. (Sampling network is shown in chapter "Trace elements" Fig. 5.5.)

In 1981, 10 sediment cores of 25 cm length were taken. In 1983, a further 14 cores of 20 cm length were sampled. The corer (diameter 2.5 inches) of the Niemistö type (Niemistö, 1974) was equipped inside with a pycnol tube. Immediately after sampling the cores were dissected into 1 cm slices. These slices were sealed in plastic petri dishes and stored deep-frozen until analysis.

The 1 cm thick sub-samples were freeze-dried, sieved (0.1 mm) and homogenized. The 'slightly extractable' P fractions were leached with 0.5 N HCl (25 ml/0.5 g dry sediment). For 'total' P analyses, two different digestion procedures were applied which used a mixture of HCl/HNO₃/HClO₄/HF in PTFE "pressure bombs" or a 1:3 mixture of HCl and HNO₃.

The dating of the sediment samples was performed with the ²¹⁰Pb technique (Häsänen, 1977; Pheiffer-Madsen and Sørensen, 1979). By the use of reference materials with certified metal concentrations and other known properties, the performance of the methods applied was ensured.

For details on the methods applied for the determination of background parameters, see Brüggmann and Lange (1983).

More than 99 % of the investigated material had grain sizes below 63 μm and must mainly be categorized as silt or muddy silt. At stations "F81" and "BY31" the clay fractions further increased and the sediment type changed to silty mud.

The difference between the 'total' concentrations and those leached by 0.5 N HCl seems to reflect the "detrital" part. In most cases, for P this detrital fraction was nearly constant throughout the whole core. It was obvious that the vertical gradients of the total P concentrations were mainly caused by the differences in the more mobile portion. Phosphorus showed a more or less constant "inert" fraction of around 400/500 $\mu\text{g g}^{-1}$. The fractions leached by HCl decreased together with the redox-potential, whereas the parallel concentrations in the pore water increased. The inert fraction seems not to be slightly available for a re-mobilization under anoxic conditions.

To get an impression of mass fluxes of phosphorus in and from Baltic Sea sediments, the gradients of phosphate concentrations in pore water were used supposing full control by diffusion. Preliminary estimates showed that the maximum fluxes in the sediments are in the same order of magnitude as the mean annual accumulation averaged over the last ten or more than 80 years. However, it is unknown how much of this potentially mobile phosphate will actually return to the bottom waters. Balzer (1984) found a molecular diffusive flux through the interface of about 13 $\text{mmol PO}_4^{3-} \text{ m}^{-2} \text{ d}^{-1}$ in the Kiel Bight (20 m water depth; muddy sediments). For a mass balance of the organic matter at this "Hausgarten" station, it was derived that from 31.4 $\text{mmol P m}^{-2} \text{ yr}^{-1}$ reaching the bottom 19.7 $\text{mmol P m}^{-2} \text{ yr}^{-1}$ were released again. From the difference (11.7 $\text{mmol P m}^{-2} \text{ yr}^{-1}$), 4.6 mmol were accumulated in organic forms and the other part probably in inorganic forms.

The profiles of P concentrations in dated sediment cores were used by Brüggmann and Lange (1989) for crude estimates of the P masses accumulated in the time period from 1900 until sampling. This was done as follows:

- a) Re-calculation of measured P concentrations (mg g^{-1}) into P masses for the different 1 cm segments (mg cm^{-3}) applying salinity-corrected dry masses.
- b) Retrospective summarizing of the P masses per segment until 1900 (mg cm^{-2}).
- c) Extrapolation of the accumulated P masses from the investigated cores to the corresponding net sedimentation areas.

Table 7.2 Mean accumulation rates and masses of phosphorus accumulated between 1900 and 1983 (1981) in different sub-areas of the Baltic Sea; one-third of the sea bottom considered as 'net sedimentation area'.

Net sedimentation area (km ²)	Total phosphorus	
	mg m ⁻² yr ⁻¹	10 ⁶ t
Bothnian Bay (12 268)	313	0.41
Bothnian Sea (26 358)	588	1.21
Northern Baltic Proper (15 770)	750	0.21
Gotland Deep (14 797)	575	0.22
Gdansk Basin (8 533)	638	0.10
Landsort Deep (2 382)	938	0.23
Western Gotland Basin (9 025)	525	0.14
Bornholm Basin (12 997)	463	0.14
Arkona Basin (6 224)	1163	0.20
Sound/Belt Sea (6 784)	1188	0.21
Kattegat (7 348)	425	0.10
Accumulation rate (weighted mean mg m ⁻² yr ⁻¹)	610	-
Sum of masses) (122 486 km ²)	-	3.16*

Only representative cores without serious indications of disturbances including erosion were selected. It was roughly estimated that, from the total area of the different basins (Ehlin et al., 1974), about one-third is characterized by net sedimentation (Brügmann, 1986; Larsen and Pheiffer-Madsen, 1986; Salo et al., 1986). It was decided to cover the time period back to the turn of the century. This was due to the fact that even in the case of high linear sedimentation rates with 20 or 25 cm core sections, the last 80 years were entirely enclosed. In this time period the most extensive/intensive industrial development took place in the countries bordering the Baltic Sea.

In evaluating the data given in Table 7.2 it should be kept in mind that (a) figures on accumulation rates and accumulated masses for phosphorus depend very much on the determination of the sediment accumulation rate itself, which is still under discussion among the specialists, and (b)

the figures on mean P accumulation given are related to a time span of more than 80 years. The annually deposited P masses could be higher in recent years. The same is true for the accumulation rate. It has not yet been tried to relate such figures to recent data on P accumulation at those cores which clearly showed a sharp increase of the P concentrations in the topmost layers. These kinds of profiles were found in areas with mainly oxic water layers above the sediment. The core regions with higher P concentrations extended over the first 3 cm (Arkona Basin) to about 4 cm (Bothnian Sea).

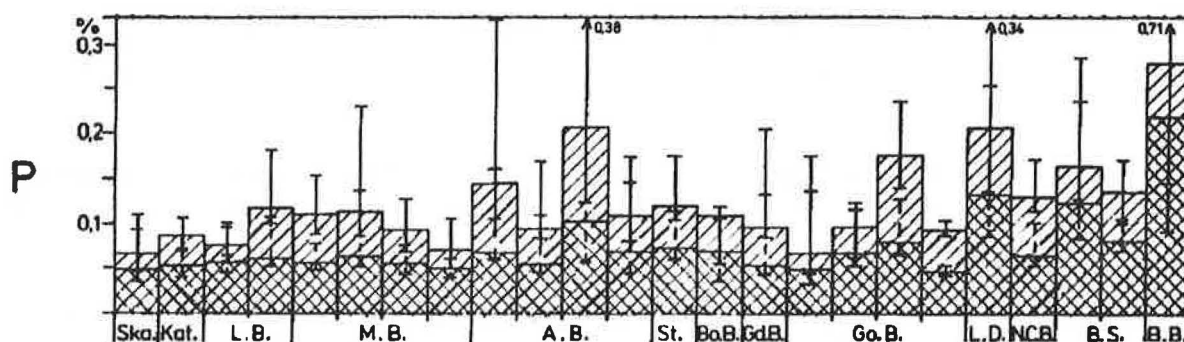


Fig. 7.6 Overview of the mean values and standard deviations of phosphorus in sediment cores arranged on a section through the Baltic Sea.

Remarks:

hatched columns/full lines - 'total' contents

double hatched columns/broken lines - 0.5 N HCl fraction

"Ska." - Skagerrak; "Kat." - Kattegat; "L.B." - Lübeck Bight; "M.B." - Mecklenburg Bight;

"A.B." - Arkona Basin; "St." - Stolp Trench; "Bo.B." - Bornholm Basin; "Gd.B." - Gdansk

Basin; "Go.B." - Gotland Basin; "L.D." - Landsort Deep; "N.C.B." - Northern Central Baltic;

"B.S." - Bothnian Sea; "B.B." - Bothnian Bay

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