Heavy metal contents as indicators of environmental pollution in the sediments of the Baltic Sea

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Abstract: This paper provides a short literature review on the use of heavy metal contents in sediments as indicators of environmental pollution. Special emphasis is placed on the sediments of the Baltic Sea. Major objectives of this study are to summarize the available literature with a view to determining and to identifying the most appropriate method for measuring and interpreting heavy metal contents. This makes it possible to compare heavy metal contents in sediments from different regions of the Baltic Sea, to find a natural background and an anthropogenic input. The conclusions presented in this paper are applicable more widely to lake and river sediments outside the study area.

Key words: Heavy metals, environmental pollution, Baltic Sea, sediments

Zusammenfassung: Im vorliegenden Artikel werden Schwermetallgehalte in Sedimenten als Indikatoren von Umweltverschmutzung genutzt. Untersuchungsgegenstand sind die Sedimente der Ostsee. Ein Hauptziel dieser Studie ist die Zusammenfassung der verfügbaren Literatur mit dem Schwerpunkt, eine Auswahl der günstigsten Methoden für die Messung und Interpretation von Schwermetallgehalten zu treffen. Diese Methoden sollen einen Vergleich von Schwermetallgehalten in Sedimenten aus unterschiedlichen Gebieten der Ostsee ermöglichen. Außerdem sollen die natürlichen Schwermetallgehalte von möglichen anthropogenen Einträgen abgegrenzt werden. Die Schlußfolgerungen dieser Arbeit haben eine breite Anwendbarkeit und können allgemein auf See- und Flußsedimente übertragen werden.

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Introduction

Heavy metal analyses in sediments of the Baltic Sea have been carried out and discussed by many authors (NIEMISTÖ, VOIPIO 1981; BRÜGMANN, LANGE 1990; PERTTILÄ, BRÜGMANN 1991; NEUMANN et al. 1997, 1998; LEIVUORI 1997; MÜLLER 1999). When investigating marine sediments in different parts of the Baltic Sea, one is often faced with the task of how to interpret measured heavy metal contents, how to compare them with other areas, and how to define natural background levels and anthropogenic inputs. This paper reviews the literature on the use of heavy metal contents in sediments as indicators of environmental pollution with special emphasis on the sediments of the Baltic Sea. Major objectives of this study are to summarize the available literature with a view to determining and to identifying the most appropriate method for measuring and interpreting heavy metal contents. This makes it possible to compare heavy metal contents in sediments from different regions of the Baltic Sea, to find a natural background and an anthropogenic input.

Binding forms of heavy metals in the sediments of the Baltic Sea

The binding forms of heavy metals differ according to the mechanisms of their formation (cf FÖRSTNER 1976; NIEMISTÖ, VOIPIO 1981; BRÜGMANN, LANGE 1990; PERTTILÄ, BRÜGMANN 1991; NEUMANN et al. 1996, 1997). Metals can be bound to different carrier substances. According to FÖRSTNER (1976), heavy metals can be bound in the minerals of the lithogenous components. In addition, they can be precipitated as hydroxides, carbonates, and sulfides, and can be fixed by sorption processes on hu--

mus substances, hydroxides, Fe/Mn oxides, or calcium carbonate. Chelates can be formed by humic substances. Metals can be coprecipitated by hydroxides/oxides and carbonates. These different binding forms of heavy metals mostly occur in transition in the natural environment. In addition, there are other mechanisms: Clay minerals can adsorb organic substances and Mn/Fe hydroxides. Humic acids can also be bound to $Fe(OH)_3$ and MnO_2. There are two mechanisms of sorption: cation exchange (chemisorption) or adsorption (physical sorption) with the latter having relatively minor importance (FÖRSTNER, PATCHINEELAM 1976).

With increasing depth, the fraction of metals, which are available for biotic and other remobilization processes in the sediments, decreases. In the Baltic Sea, this fraction is lowest for iron and aluminum, which mainly are derived from terrigenous mineral detritus. Large proportions of lead, zinc and manganese can be remobilized; copper, nickel, and cadmium are less readily mobilized. This is explained by differences in stability of bonds, and by an increase of the relatively mobile, anthropogenic fraction towards the sediment surface (BRÜGMANN, LANGE 1990).

NIEMISTÖ (1982) mentions that the character and the strength of chemical bonds depend on the amount and composition of the available organic matter. Humic acids have a great capacity for binding metal cations of which the greatest part forms chelate complexes. If the proportion of organic matter decay products increases within a water environment, e.g. because of eutrophication, then there is a tendency towards an increased binding of metal complexes with low solubility, which enrich heavy metals within the sediment (FÖRSTNER, PATCHINEELAM 1976).

A good oxygen supply supports the binding of the metal fraction to Fe/Mn-oxides and -hydroxides (FÖRSTNER, PATCHINEELAM 1976). An oxic sediment surface offers favourable conditions for the removal of phosphorus and iron from the water column and for the binding of a phosphate fraction with iron (or manganese) oxides and hydroxides. In the Bothnian Bay this process is supported by a relatively high natural supply of iron (NIEMISTÖ, VOIPIO 1981). When reducing conditions prevail within the sediment, organic matter decay is realized by sulfate reducing bacteria, resulting in the formation of hydrogen sulfide (H_2S). H_2S reacts with iron, leading to the precipitation of black FeS, which undergoes further reaction to form grey FeS_2, pyrite. Sulfur compounds with other metals can also occur; these compounds can be very stable (PERTTILÄ, BRÜGMANN 1991; FÖRSTNER, PATCHINEELAM 1976). Under reducing conditions, Fe(III) is reduced to Fe(II) and iron-phosphorus-compounds are destroyed. Both elements can migrate upwards in the pore waters towards the sediment surface. However, small amounts of phosphorus can be bound under reducing conditions (NIEMISTÖ 1982). Part of the iron fraction can be fixed in the reducing sediment in the form of iron sulfides. Thus the amount of phosphorus measured in the sediments below the transition zone from oxic to anoxic conditions reflects the phosphorus fraction that is bound in the sediments and permanently removed from the water column (NIEMISTÖ et al. 1978). This phosphorus fraction, which remains in the deeper sediment layers, is bound by organic material (NIEMISTÖ 1982). Phosphorus and iron migrating from the anoxic to the oxic zone of the sediment column can be reprecipitated at the sediment surface. When the sediments are suboxic, these elements and associated trace metals are released into the water (cf FÖRSTNER, PATCHINEELAM 1976; SUESS 1976; FROELICH et al. 1979).

Binding of nickel on iron hydroxides appears possible. The possibility of the binding of nickel with Fe/Mn-precipitates was also mentioned by PERTTILÄ, BRÜGMANN (1991) in connection with extended investigations of Baltic Sea sediments.

Copper contents are relatively high in the sediments of the Gulf of Bothnia. Because of the high contents of iron, manganese, and organic matter in this area, humus material and manganese/iron-oxides/hydroxides are the most important carrier substances for copper in oxic sediments. Under reducing conditions copper sulfides may be formed (BRÜGMANN, LANGE 1990).

PERTTILÄ, BRÜGMANN (1991) underscore the existence of a relatively high detrital fraction of lead for the Gulf of Bothnia. Lead, like zinc and cadmium, showed only a very small association with organic matter in the investigations of these authors. Cadmium is precipitated with sulfides under anoxic conditions (LAPP 1991). Cadmium has also been reported to be bound to Fe/Mn-oxides/hydroxides. Cadmium is dominantly bound with organic matter and has a considerable association with Mn/Fe-rich material, i.e. with oxides, hydroxides, and phosphates in the Gulf of Bothnia (BRÜGMANN, LANGE 1990).

The upper sediment layer is characterized by a direct interaction with the overlying water body (LAHDES 1982). Thus, binding forms - dependent on the oxygen saturation - have to be considered when discussing the fixing of metals in the sediments.

Migration processes within the pore waters can influence metal contents in the sediments. One must consider the release of metals from the sediments into the water column; this occurs in connection with migration processes, e.g. because of reducing conditions at the sediment surface, or because of redeposition of sediments (FÖRSTNER, PATCHINEELAM 1976).

According to FÖRSTNER (1976) the amount of metal which can be mobilized by increases in salinity are generally of minor importance. FÖRSTNER, PATCHINEELAM (1976) suggested that pH-values may effect the binding of metals with clay minerals, humus or oxides/hydroxides.

The use of heavy metal contents as indicators of environmental pollution in the sediments of the Baltic Sea

Most interpretations given in the literature consider sources of heavy metal enrichment. Sometimes even anthropogenic inputs are quantified. Many case studies are based on total rather than on partial analyses of heavy metals. Important parameters which are used for qualitative and quantitative statements about possible enrichment of heavy metals, are contents of organic carbon, carbonate carbon, phosphorus, nitrogen, iron, manganese and aluminum. If enrichment patterns of organic matter, phosphorus and nitrogen are compared to the relevant patterns of heavy metal distribution, it may be possible to draw conclusions about the origin of inputs. For example, organic carbon is a proxy for fine grained organic matter and often acts as an accumulator of metals (PERTTILÄ, BRÜGMANN 1991).

Enrichment of heavy metals in a marine system can be of natural or anthropogenic origin. Depending on the character of the lithogenous components supplied, differences can occur in form and amount of heavy metal supply because of differences in mineralogical composition. Heavy minerals and clay minerals, for example, contribute to a higher supply of heavy metals than do other silica minerals (FÖRSTNER, PATCHINEELAM 1976).

The Gulf of Bothnia receives a relatively high natural supply of heavy metals when compared with other parts of the Baltic Sea (ENCKELL-SARKOLA et al. 1989). This is especially true for iron and zinc. Also BRÜGMANN, LANGE (1990) described for this part of the Baltic Sea a large proportion of mineral-detrital fractions of the metals which may be of anthropogenic origin in other areas.

NEUMANN et al. (1996) found heavy metal deposition in the Arkona Basin to be 2-3 times higher than in the Bornholm Basin. These differences in heavy metal deposition rates were believed to be linked to variations of the Oder River input as the preferred outflow direction is northwest towards the Arkona Basin during spring time when the river load is highest.

As a basis for identifying changes in metal contents towards the surface, analyzed heavy metal contents, as characterized by several authors, are given in Table 1. In order to identify the so called enrichment factor, consideration was given to the fraction of metals that exists within the sediments above natural background values. This enrichment factor is equivalent to the ratio of heavy metals in recent sediments to values of sediment records of deeper layers (especially from older periods of the history of the Baltic Sea) for which an anthropogenic influence could be excluded.

In order to obtain more reliable evidence about origin and character of enrichments of metals, it is necessary to consider the obtained values in relation to components which are not anthropogenically influenced. These latter components are used to determine a baseline; consequently, it is why they are called "conservative elements" by PERTTILÄ, BRÜGMANN (1991).

In this sense the content of aluminum is a tracer for aluminum silicates. This includes both the metal-rich fine silt and clay fractions. Aluminum is a good indicator of clay minerals. However, it can not be applied as a tracer in sediments which are derived from glacial erosion of igneous rocks. It is therefore not an applicable normalization parameter for sediments of the Baltic Sea (PERTTILÄ, BRÜGMANN 1991). NEUMANN et al. (1996), however, used the aluminum content as a normalization parameter for sediments of the Oder River estuary and its offshore basins, where riverine input is expected to be high.

The iron content reflects iron-bearing clay minerals of the fine silt and clay fractions, iron rich heavy minerals, and iron hydroxides. Often linear regressions between Fe- and/or Mn normalized ratios of heavy metal contents are used as indicators for contamination. However, there is also the possibility that iron and manganese can be enriched in the form of very small concretions at the sediment surface, and thus give an inaccurate picture of the accumulation of heavy metals in the surface sediments. A normalization could then be done with other non-anthropogenic elements like lanthanum, when it shows an enrichment pattern similar to zinc, nickel and copper under changing redox conditions and the presence of Fe/Mn-micronodules (PERTTILÄ, BRÜGMANN 1991).

Consequently, enrichments of up to 10% as compared to the deeper sediment layers (again for the application of values from the total extraction) are not necessarily due to anthropogenic influences but can rather be a possible effect of diagenetic processes (PERTTILÄ, BRÜGMANN 1991). For example, BRÜGMANN, LANGE (1990) explained observed lead enrichments in the upper centimeters of the sediments with a diagenetic redistribution of the metal. NIEMISTÖ (1982) mentions a possible enrichment of zinc in the surface sediments by diagenetic processes.

In order to make quantitative estimations of the enrichment of a component at the sediment surface, natural background values are often used. These are, for example, heavy metal contents of sediments from depth, for which anthropogenic influence and bioturbation effects are not to be expected.

NEUMANN et al. (1996) calculated the natural and anthropogenic contents of heavy metal accumulation since the beginning of industrialization. The anthropogenic amounts did not vary significantly between the Oder River lagoon, the Arkona Basin and the Bornholm Basin. The anthropogenic copper fraction was about 30% of the total copper accumulation, for zinc it was about 40% and for lead about 50%. Only the anthropogenic zinc content in

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necessary to consider the obtained values in relation to those which are not of anthropogenic origin. These background importances are used basically, consequently. It is why the content of elements mentioned by FREITAG & KRAWKZYK.

In this case the content/concentration is a basis for normalization of influences. This concerns both the material of silt and clay fractions. Aluminium is a good indicator of clay minerals. However, it cannot be appropriate as a tracer in sediments which are derived from glacial erosion of igneous rocks. It is therefore not an applicable normalization parameter. BRUMSACK (1989), however, used the iron content as a normalization parameter, where enrichment is expected to be high.

Iron is a structural relevant element in bearing clay minerals of the silt and clay fractions, too, such as heavy minerals, and iron increases. Often linear regressions between Fe and/or Mn normalized ratios of heavy metal contents are used as indicators for contamination. However, there is also the possibility that iron and manganese can be enriched in the small concentrations of the sediment where there is an inorganic pattern of the content of heavy metals in the surface sediment. The normalization could then be done with other enriched elements like aluminium, where iron shows an enriched pattern similar to zinc, and iron occur under changing redox conditions the presence of Fe/Mn oxyhydroxides (PETTERSSON et al. 1991).

Occasionally, enrichments of up to 10% as compared to the deeper sediment layers account for the application of values from the total extraction of heavy metals. For example HALLBERG (1974) explained the observed lead enrichment within the upper centimetres of the sediments with a diagenetic redistribution of the metal. NIEMISTÖ (1985) mentions a possible enrichment of surface sediments by diagenetic processes.

In order to make quantitative estimates of the enrichment of a component at the sediment surface, vertical background values are often used. These are, for example, heavy metal contents of sections at depths which anthropogenic influences are not to be expected.

NEUMANN et al. (1996) calculated the natural and anthropogenic contents of heavy metal accumulation at the beginning of industrialisation. The anthropogenic amounts did not very significantly between the Oder River lagoon, the Arkona Basin and Bornholm basin. The anthropogenic copper fraction was about 30% of the total copper accumulation, for zinc it was about 40% and for lead about 50%. Only the anthropogenic manganese in...

Table 1: Comparison of detrital mineral fractions and enrichment factors respectively in sediments of the Lower Rhine River and in sediments of the Baltic Sea. The sediments of the Lower Rhine River reflect a large drainage area and it is assumed that all important sources of pollution are represented (FÖRSTNER 1976).

FÖRSTNER (1976) Lower Rhine River	NIEMISTÖ, VOIPIO (1981) Baltic Sea	BRÜGMANN & LANGE (1990) Baltic Sea	NEUMANN ET AL. (1996) Oderhaff / Arkona Basin
Fe	Fe	Fe, Cr	Co
Detrital mineral proportions 100%	Detrital mineral proportions approxim. 50-60% = 1.5 to 2	Metals with constant vertical distribution	Enrichment factor towards surface = 1.4/1.5
Cr	Ni, Cr	Ni, Co	Fe, Cr
Detrital mineral proportions approxim. 40%	Enrichment factor towards surface = 3	Enrichment factor towards surface is weaker	Enrichment factor towards surface = 2.0/2.1
Ni, Co, Cu	Co, Cu	Cu, Zn, Pb, Cd	Co/Ni
Detrital mineral proportions less than 1%	Enrichment factor towards surface clearly recognizable	Enrichment factor towards surface clearly recognizable	Enrichment factor towards surface = 4.5/5.7
Pb, Zn, Cd	Zn, Pb		Cu/Pb
Detrital mineral proportions greater than 10			Ni/Cu
Cd	Cd		Zn, Pb
	Zn		Enrichment factor = 2.4
	Enrichment factor = 15		Ni, Co

the Oder River lagoon was very high (76%) and, according to these authors, probably due to a local zinc source in this lagoon.

Another way to estimate the enrichment of a component in the sediments of a region is the comparison with an area, where sediments of the same type are very unlikely to have experienced changes in their natural heavy metal contents. PERTTILÄ, BRÜGMANN (1991) give background values for fine grained mud of the Baltic Sea as shown in Table 2. NIEMISTÖ, VOIPIO (1981) used the natural values given in Table 3 for the Baltic Sea sediments.

Table 2: Natural background values of heavy metals (ppm) in fine-grained muds of the Baltic Sea (PERTTILÄ, BRÜGMANN 1991).

Cu	Zn	Ni	C	Pb	Cd
20	100	30	80	25	0.2

MÜLLER (1986) uses the so called geoaccumulation index (I_{geo}) to estimate the grade of pollution of a sediment by inorganic or organic substances and bioelements that are of environmental relevance. This index relates the present concentrations of elements and compounds to concentrations prior to civilization and thus allows to derive sediment quality:

$$I_{geo} = \log_2 (C_n/B_n \times 1.5)$$

with

C_n = measured concentration of the element in the clay fraction of the sediment

B_n = geochemical background of the element in silt stone ("silt stone standard") or clay fraction respectively of sediments deposited in the same environment prior to civilization

Conclusions

Interpretations of heavy metal distributions in the sediments of the Baltic Sea have to be done with care. Besides detailed knowledge of the study area and its sedimentary environment as well as information about circles and processes which occur between the sediment and the water phase and in the sediments itself, it is also necessary to have information about sedimentation rates and age of sediment. Also interpretations using linear regression have to be done with care, because there can be differing environments at the different sample locations.

Quantitative estimations about a possible anthropogenic enrichment of heavy metals in Baltic Sea sediments can be made more reliable if total metal analyses are supported by special, sequential, leaching methods which can provide more reliable information on the binding forms of metals in the sediments. Also, when discussing both possible enrichment of metals at the sediment surface and migration processes, not only sedimentation rates but also physical property data of the sediments should be available to allow the calculation of flux rates of individual components. Many of the conclusions and statements presented in this paper can be applied more widely to lake and river sediments.

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Table 3: Heavy metal contents (ppm) in sediments of the Baltic Sea. The values in the sediments from the Ancylus and Litorina-periods are considered to be natural background values (NIEMISTÖ, VOIPIO 1981).

	Cu	Zn	Co	Ni	Cr	Pb	Cd
Ancylus	33.8	118	17.4	44	45.5	16.0	0.26
Litorina	31.4	120	18.9	45	45.5	17.5	0.35
At Present (>35 years)	47.5	245	25.9	34	37.9	51.0	3.48

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