Invited Conference Paper

Heavy metals in bottom sediments and suspended material from the Elbe, Weser and Ems Estuaries and from the German Bight (south eastern North Sea)

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Received September 20, 1982

Grain size effects, accumulation factors, chemical forms and remobilization processes of particle associated metals were studied on samples taken from estuary and coastal marine regions of the Northern Germany during the cruise of the R/V »Valdivia« in October, 1981. In addition the Institute of Marine Research in Bremerhaven obtained other data on the Weser Estuary.

Standardization of metal concentrations to the contents of aluminum (AAS) or scandium (INAA) is particularly useful for the reductions of grain size effects in monitoring studies. The strongest anthropogenic enrichment of metals is found for cadmium, lead and zinc in the sediments of the Weser and Elbe Rivers near Bremen and Hamburg, respectively; accumulation of lead and cadmium in the outer part of the German Bight is probably caused by the dumping of waste material.

Characteristic remobilization of cadmium was found with the initial increase of salinity in the Weser Estuary. Chemical extraction studies indicate that crystallized (moderately reducible) Fe-oxyhydrates are concentrated in smaller grain size fractions, whereas larger particles are preferably coated by (easily reducible) amorphous iron oxide. The latter seems to affect the sorption properties for other metals, such as manganese and zinc.

INTRODUCTION

It has been shown by numerous studies on the survey, assessment or monitoring of metal pollution in sediments that grain size effects can play a considerable role as they influence not only the extent of enrichment of pollutant components but also the natural background concentrations of certain metals on which the comparison is based. These effects have been investigated and methods of correction are proposed from sediment samples taken from the Elbe, Weser and Ems Estuaries as well as from the German Bight during the R/V »Valdivia« cruise.

In nearshore and estuarine areas redox changes and salinity effects may result in characteristic processes of remobilization of trace metals. The possible interactions have been studied by laboratory experiments and model

* Presented at the VII International Symposium »Chemistry of the Mediterranean«, organized by the Center for Marine Research, »Ruđer Bošković« Institute, Zagreb, and held at Primošten, Croatia, Yugoslavia, May 6—12, 1982.

calculations; another type of study is related to the analysis of interstitial water, which is also the medium of metal transport to surface sediments. A third, relatively new approach for the evaluation of chemical processes between dissolved and solid constituents in coastal marine and estuarine sediments is the differentiation of characteristic chemical forms in the particulates by means of sequential extraction.

In the present experiments it was attempted to investigate whether flocculation and coprecipitation occur in the estuaries of the Weser, Elbe and Ems Rivers. Therefore the oxidic association types of heavy metals on sediments and suspended material from the fluviatile, estuarine and marine environments of the three rivers were analyzed in an extraction sequence and compared. In addition, the influence of grain size on the chemical association form was determined.

MATERIALS AND METHODS

Sampling was carried out during the cruise of the R/V »Valdivia« from October 11—22, 1981 on the Weser, Elbe, and Ems Rivers and the North Sea. Sampling sites are indicated in Fig. 1.

The various parameters of sampling localities such as salinity, temperature, redox potential, *p*H, *etc.* are described in the official Cruise Report[1].

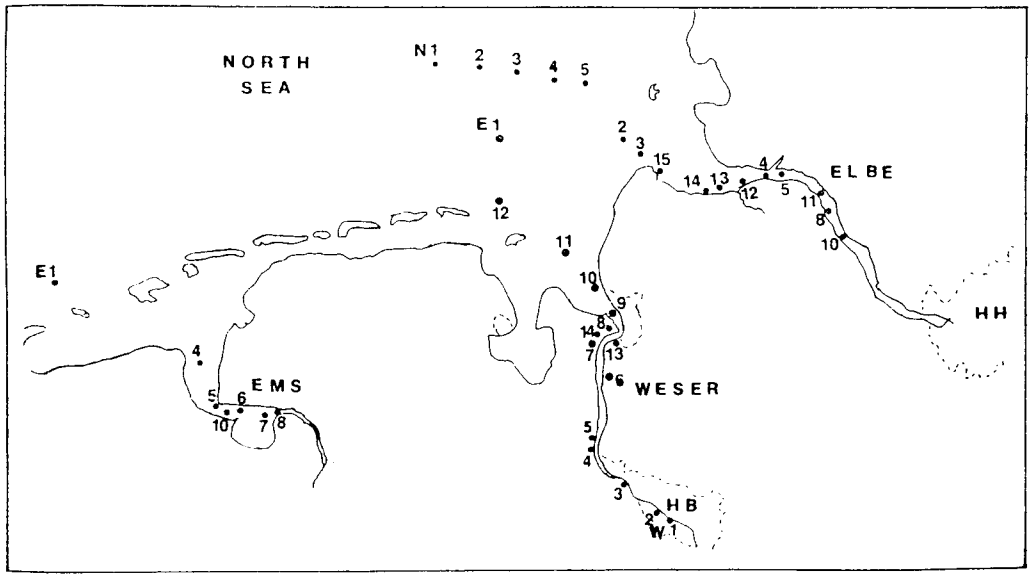

Fig. 1. Sampling sites of the Ems, Weser, and Elbe estuarine zones and German Bight.

Sediment sampling was done with a box grab and samples of suspended substance were isolated by continuous flow centrifugation or sedimentation and filtration from a 30 liter water sampling device. Initial data on the Weser Estuary study of the Institute of Marine Research in Bremerhaven were added by Calmano and colleagues[2].

For grain size analysis and sediment digestion for AAS analysis the samples were treated with ultrasonic. Subsequently the total fraction < 63 μm was separated in Atterberg tubes. The samples were then digested with concentrated HNO_3 and analyzed with AAS. In another method the total fraction < 63 μm was brought into solution with lithium metaborate ($Li_2B_2O_4$). Control was carried out with known »Rhine« and »Estuary« sediments[3].

For instrumental neutron activation ca. 100 mg of a dried and fractionated sample (< 63 μm) were filled into special polyethylene capsules that were tightly sealed and irridiated at a neutron flux of 2×10^{12} $cm^{-2} s^{-1}$ (10 hrs). 4—5 days after the end of irradiation the surface of the capsules was cleaned with 0.1 *M* HNO_3 and double distilled water and they were then inserted into larger polyethylene tubes.

Measurement of gamma-spectra was carried out for 6—13 and 20—25 days after the end of irradiation. Each sample was measured for 30 and 60 minutes, respectively.

The samples were irradiated together with an iron standard in the research reactor at the DKFZ, Heidelberg. Subsequent verification was accomplished with two multielement standards (»Rhine« and »Estuary« sediment from the Federal Institute of Hydrology in Koblenz). Evaluation of the gamma-spectra, accuracy of the analysis, interferences of gamma-lines and their influences on the results are discussed elsewhere[4].

Following a review of various procedures given in the literature we have used an extraction sequence for the assessment of chemical forms of particle associated metals[5]:

(a) *exchangeable cations* — 1 *M* ammonium acetate, *p*H 7, solid/solution ratio 1:20, 2 hrs shaking;

(b) *easily reducible phases* (Mn-oxides, partly amorphous Fe-oxyhydrates and carbonate phases) — 0.1 *M* $NH_2OH \cdot HCl$, *p*H 2, dilution 1:100, 12 hrs shaking;

(c) *moderately reducible phases* (*e. g.*, amorphous and poorly crystallized Fe-oxyhydrates) — 0.2 *M* ammonium oxalate + 0.2 *M* oxalic acid, *p*H 3, dilution 1:100, 24 hrs shaking;

(d) *organic fraction, including sulfides* — 30 % H_2O_2, 85 °C, extracted with 1 *M* ammonium acetate, dilution 1:100, 12 hrs shaking;

(e) *residual fraction* — concentrated HNO_3, 2 hrs at 120 °C, dilution 1:100.

Analysis of heavy metal concentrations in the extraction solutions was done with AAS. Flame and flameless methods were applied. The sum of heavy metal concentrations of the various association fractions agreed satisfactorily with the given means of the control samples. Deviations laid between 1.6 and 24.3 %, mean 12.4 %.

One reason for more significant differences may be the fact that digestion at the end of the extraction sequence was not complete; thus, total heavy metal contents of the samples could not be determined. Reproducibility of the described method was tested by repeating the same procedure three times on two samples with higly deviating compositions. Results were satisfactory.

For total metal contents relative standard deviations of 1.2 to 11.2 % were obtained. For the extraction steps the standard deviation remained generally under 10 %. Significant exceptions to this appeared only in fractions with very low metal contents.

RESULTS AND DISCUSSION

The results of the sediment and suspended matter investigations of the »Valdivia« cruise are summarized in the official Cruise Report. At sampling sites characterized by »flu« (= fluvial) electric conductivity was < 2 mS, for »est« (= estuarine) it ranged between 2 and 20 mS and sites at which electric conductivity attained 20 mS or more were designated »mar« (= marine).

Grain size effects

Results of the studies on grain size and metal contents in the silt and clay fractions are illustrated in Figs. 2 to 7. The individual samples are arranged according to their position in the estuaries and open sea, respectively; *i. e.*, the marine samples are on the left side of the graphs and the freshwater samples on the right side (see sketch map in Fig. 1 indicating the locations of the sampling stations).

The *grain size distribution* (Fig. 2) studies indicate that the percentage of the fraction <63 μm in the bulk samples varies widely from less than 1 % to more than 70 %. Within this fraction, which is separated from the bulk sample by sieving, the pelitic subfraction <2 μm is predominant in the sediments from the Ems River, in most studied samples from the Elbe and Weser Rivers and their adjacent marine areas. In the Weser River sediments there is even a relatively higher portion in the coarse silt fraction (20—63 μm).

Generally speaking, there is no evident homogeneous pattern, a fact which is important for the following considerations on grain size correction. The available data are insufficient to indicate characteristic changes in fresh water to — *via* the estuarine zone — the marine environment.

The highest *absolute metal contents* for iron and especially for the anthropogenically more affected elements such as Cd and Zn are found in the grain size fraction 2—6 μm (Figs. 3 and 4). This is true not only of samples that are slightly polluted by heavy metals but also of those that are subjected to a greater heavy metal contamination (*e. g.*, sample Wl from the Weser River section). For total metal concentrations the fraction <2 μm usually follows, which is contrary to data from previous investigations on river sediments, where the highest concentrations are usually found in the pelitic particles (<2 μm). Perhaps this is the result of the coarsening of the contaminated fine-grained particles under the influence of increasing salinities in the estuarine mixing zone. Also, the decrease of metal contents with increasing coarseness is less than expected to the mineral composition (chiefly quartz in the coarse silt fraction). An explanation for this in addition to the mentioned formation of aggregates, may be found in the formation of coatings — *e. g.*, of iron oxides, carbonates, organic matter — on the relatively inert (in respect to heavy metal contents) components; during separation procedures such as sieving and settling in Attenberg tubes the mechanical fractionation obviously does not accurately affect the release of these often extremely fine-grained and surface active compounds. This may allow increased metal concentrations to be carried over into coarser grain size fractions.

Lines in Figs. 3 and 4 indicate the *relative mass transport* of a certain metal in the various fractions of the sediment; metal concentrations are multiplied by the grain size portion and this value is equal to 100. As the grain size effect is dominant to metal concentration in the various fractions, the greatest metal transport usually occurs in the fraction <2 μm. Subsequently, there is a general decrease of metal contents at an increasing coarsening of grain size. On average, metal concentrations in the pelitic fraction (<2 μm) are 3 to 10 times greater than those in the coarse silt fraction (20—63 μm). These data clearly show that there is a great internal variability of metal data even after separation of the <63 μm fraction. Therefore this method has considerable disadvantages compared to the standardization with conservative elements (see below). Further observations on the particle behaviour in the estuaries of West Germany will be given elsewhere[6, 7].

Factors of enrichment

Most of the grain size corrections — extrapolation, separation of distinct grain size fractions, *etc.* — will reduce (not eliminate) the fraction of the sediment that is largely chemically inert, *i. e.*, mostly the coarse-grained

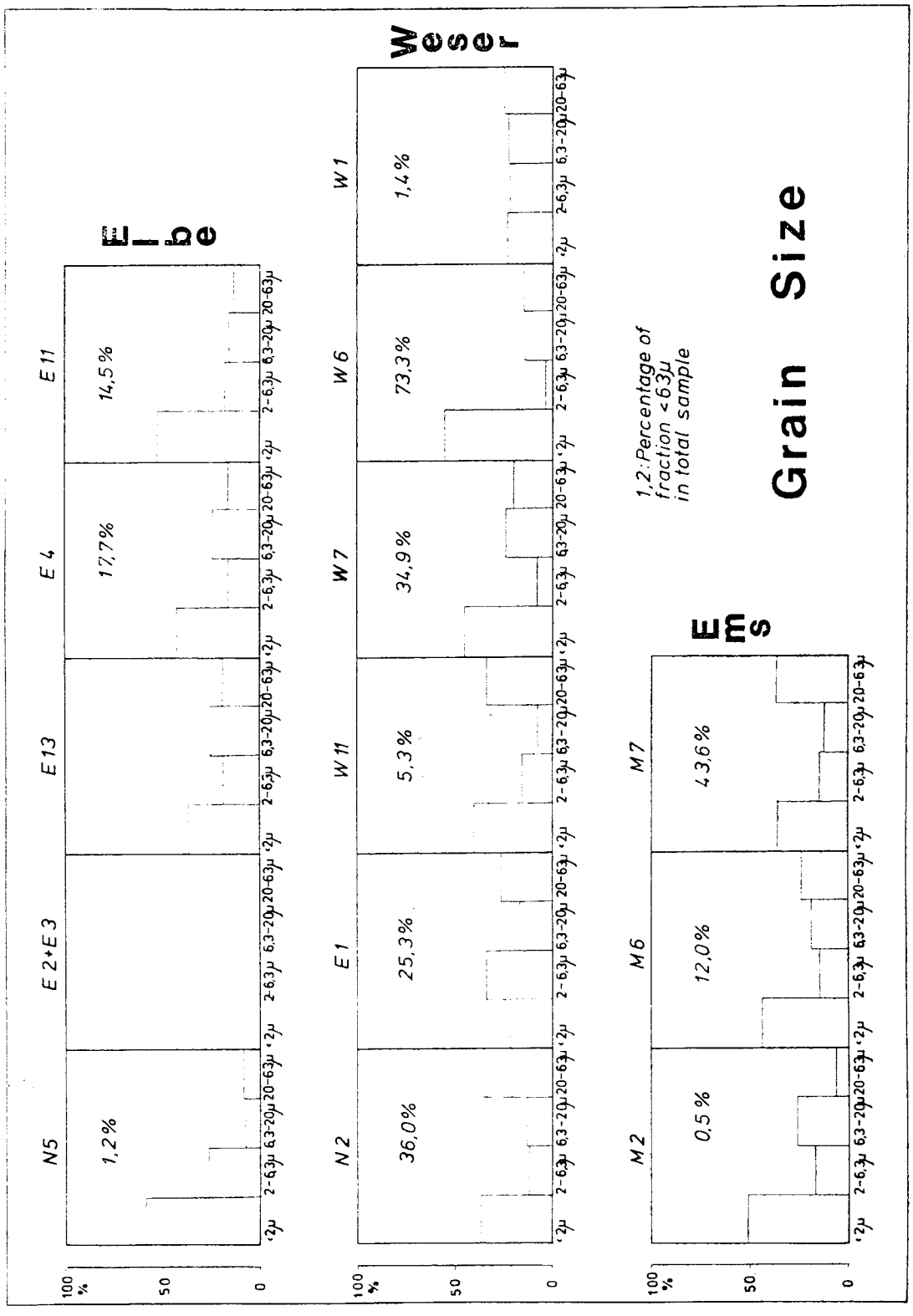

Fig. 2. Grain size fractions of the Elbe, Weser and Ems sediments.

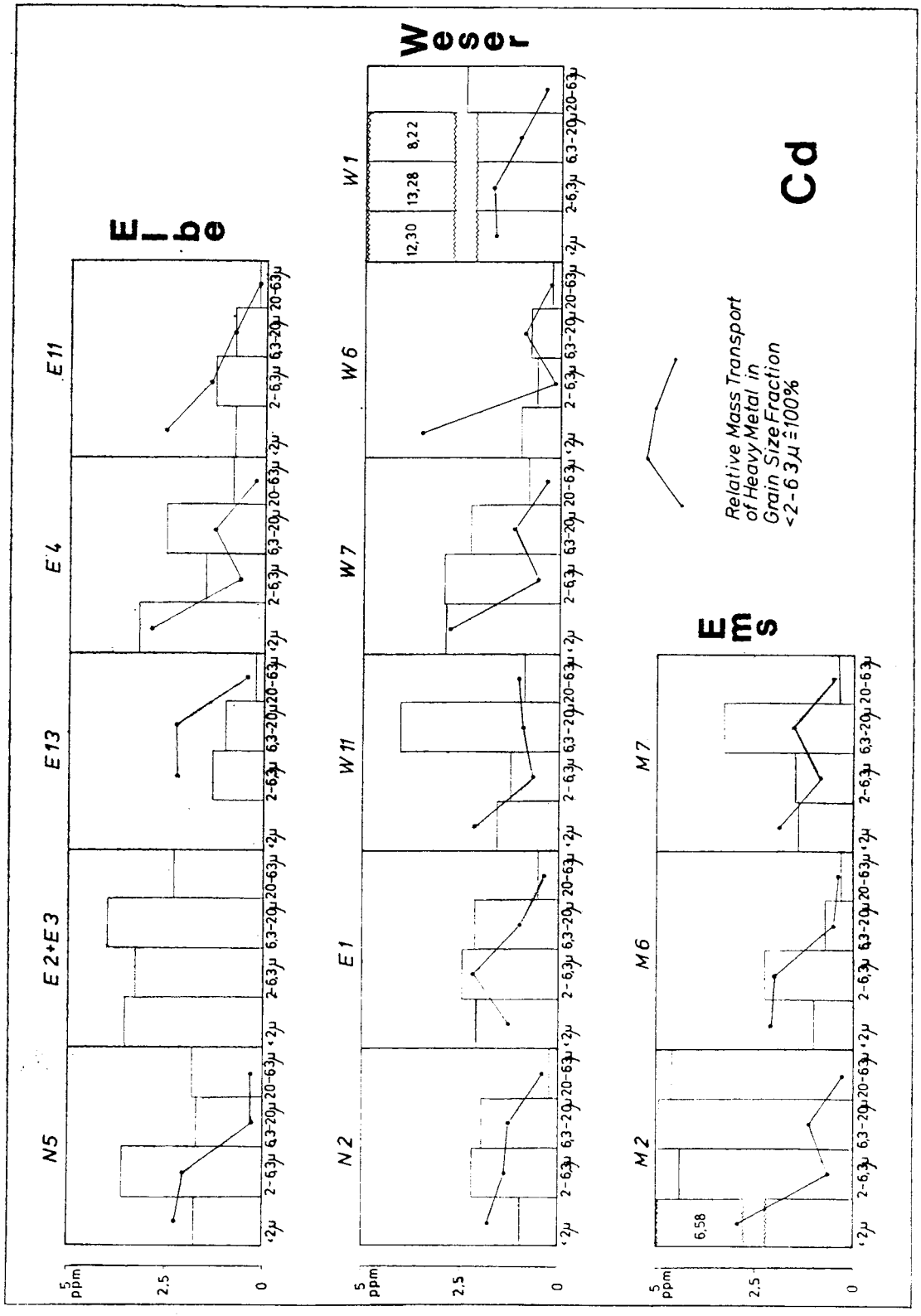

Fig. 3. Distribution of cadmium in grain size fractions < 2—63 μm.

quartz, feldspar and carbonate minerals, and increase the substances active in metal enrichment, *i. e.*, hydrates, sulfides, amorphous minerals and organic substances.

Standardizing anthropogenic (and »abnormal« natural) metal concentrations to the contents of »conservative elements« such as aluminum and potassium, *i. e.*, on the percentage of clay minerals, has at first glance one major disadvantage in that is given a ratio instead of real concentrations. But it can be attempted — as Li has done[10] — to standardize the contents to a standard material, defining the enrichment factor, *e. g.*, of the element »i« in the sample as the concentration ratio of »i« to Al(C^i/C^{Al}) compared to the ratio in the standard material.

With respect to the methods of standardizing for grain size correction, Ackermann[8] has provided an example from the Ems River Estuary, for which a series of potential reference elements (Cu, Eu, Fe, Sc, Sm and Th) were analyzed by neutron activation analysis. Sumarized in Table I are: percentage

TABLE I

Correlation coefficients »r« and concentration ratios s (100 %)/s (0 %) for some potential reference elements[8]

Element		Cs	Sc	Fe	Rb	Eu	Th	Sm
Fraction < 20 μm	»r«	0.987	0.982	0.858	0.958	0.945	0.932	0.878
	s (100 %)/(0 %)	14	7.3	6.4	3.4	3.1	3.2	3.1
Fraction < 63 μm	»r«	0.919	0.937	0.789	0.900	0.947	0.944	0.911
	s (100 %)/(0 %)	20	15	9.0	3.7	3.8	3.8	3.9

of the fraction <20 μm or <63 μm in the total sample (separated from bulk samples by plastic sieves), the correlation coefficient »r« and quotient s (100 %)/s (0 %), from the ordinate values of the regression lines at 100 % and 0 % of the grain fractions 20 μm and 63 μm (see Fig. 5 for Cs in grain size fraction <20 μm). The closer to 1.0 the correlation coefficient »r« for a specific reference element lies and the larger the quotients s (100 %)/s (0 %), the more exactly a grain size correction can be carried out according to the formula:

$$c_{HM}\ (\text{in fraction } 20\ \mu\text{m or } 63\ \mu\text{m}) = \frac{c_{HM}\ (\text{total sample})}{c_{CE}\ (\text{total sample})} \times F,$$

where c_{HM} and c_{CE} are the concentrations of the polluting heavy metal and conservative element, respectively, and F is a conversion factor, which is derived from the extrapolation of the regression line to 100 % of the grain size fraction <20 μm or <63 μm.

According to Table I, cesium appears to be the preferred referrence element for two reasons: it is particularly well correlated (r = 0.987) with the percentage of the 20 μm fraction and the quotient s (100 %)/(0 %) is greater than for the other elements. However, owing to the very close geochemical relation between aluminum and scandium, the latter element seems to be particularly recommendable when neutron activation techniques are used for metal analysis[9—11].

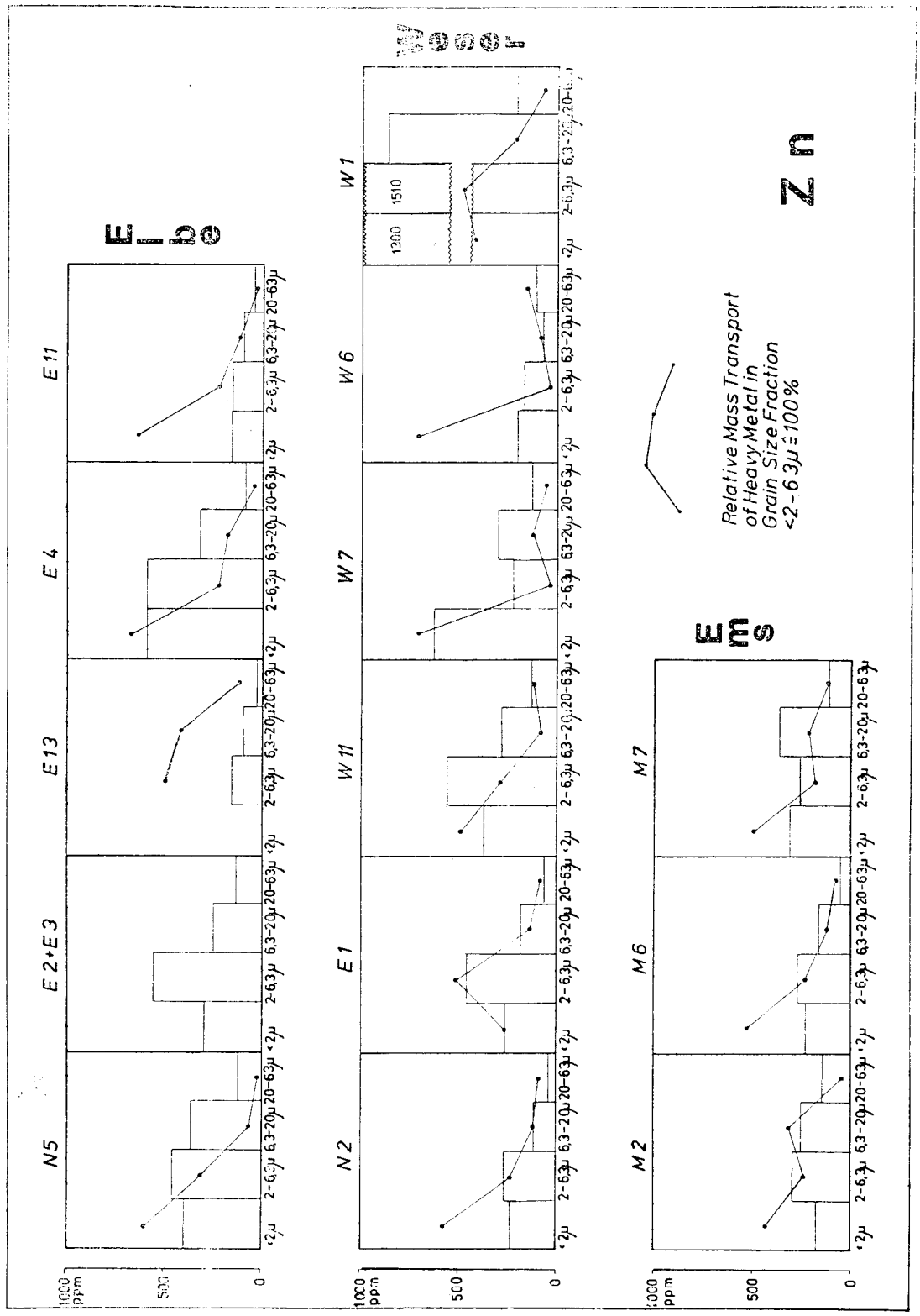

Fig. 4. Distribution of zinc in grain size fractions < 2—63 μm.

In Fig. 6 the trace elements Cd, Cu, Pb and Zn are shown, which are more or less strongly affected by anthropogenic inputs, for the fluviatile, estuarine and marine zones. The solid lines indicate the metal concentrations after correction for scandium. Average shale value[12] of scandium (13 mg/kg) is used as a standard reference and all corrected data show concentrations of metals that are higher than those in the original measurements of the fraction <63 µm because of the relative coarseness of the samples.

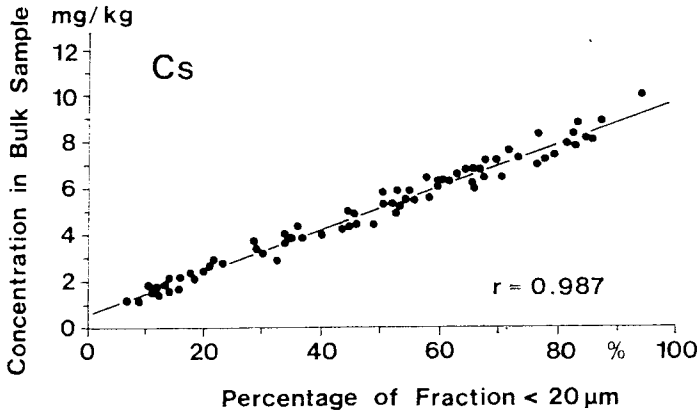

Fig. 5. Cs concentration in the total sample as a function of the percentage of the fraction ≤ 20 µm. The regression line and corresponding correlation coefficient »r« are also shown[8].

It is obvious that there are still significant variations of the metal concentration in the course of sediment transport from the fluvial to the marine zones which may be caused by local metal inputs or by hydrological effects such as shoaling and deposition processes.

In Table II factors of metal enrichment were calculated from the scandium corrected data compared to the natural background values[12, 13] of the respective element (Cd 0.2 mg/kg; Cu 31 mg/kg; Pb 20 mg/kg; Ni 32 mg/kg; Zn 95 mg/kg).

TABLE II

Enrichment factors of pollutant metals in sediments from different environments in the Elbe, Weser and Ems estuaries and the North Sea*

River Area	Environment	Cd	Cu	Pb	Ni	Zn
Elbe River	fluvial	6	2	6	2	4
	estuarine	9	2	9	1	4
	marine	5	1	6	1	2
Weser River	fluvial	22	2	10	3	7
	estuarine	7	1	3	2	3
	marine	10	2	6	1	3
Ems River	marine	4	1	5	1	2
German Bight	(North Sea)	4	2	8	1	2

* Metal in sample/Metal in background x Sc in sample/Sc in background (average shale or shallow water sediments) — mean values.

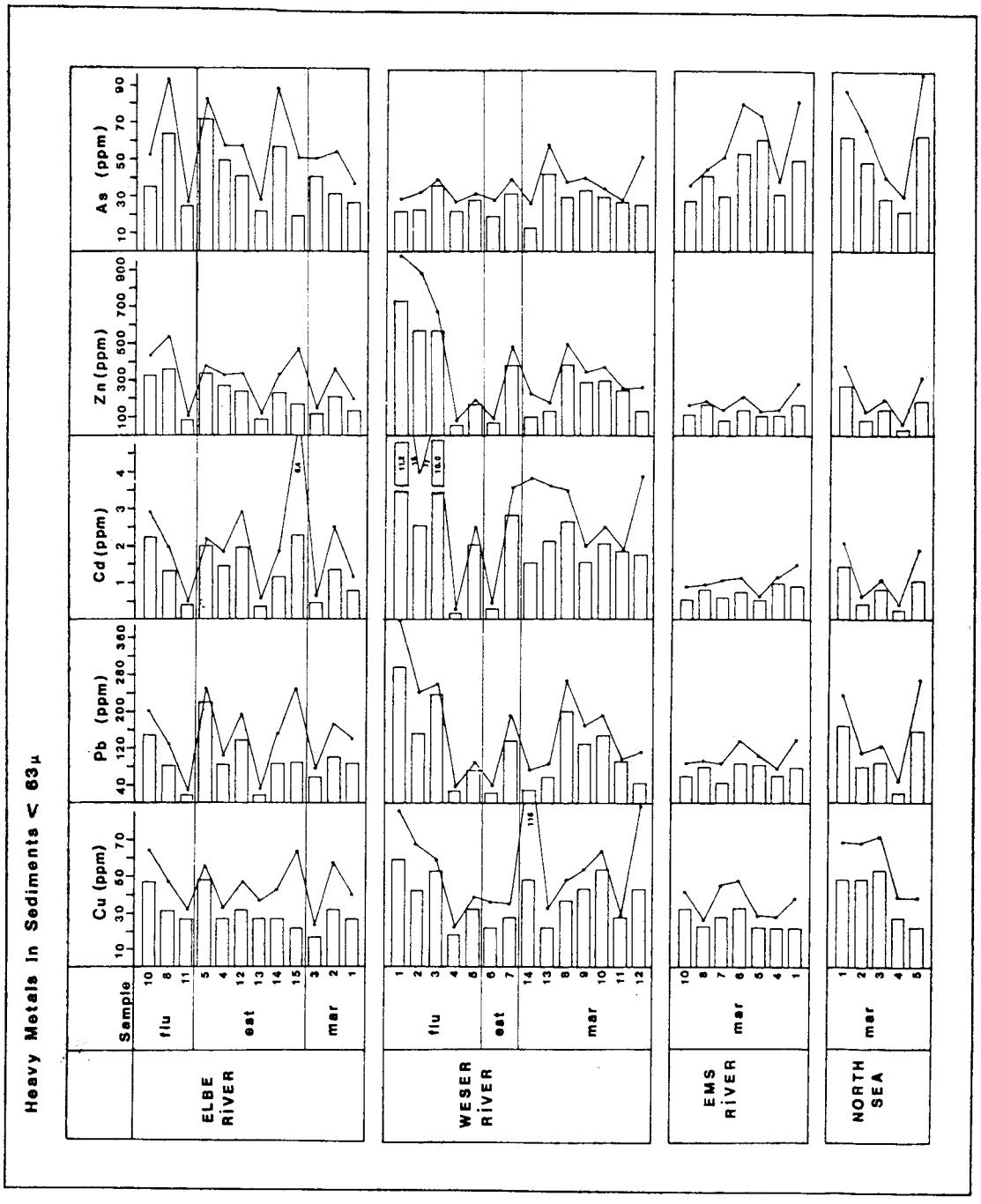

Fig. 6. Trace elements in sediments $< 63\ \mu$m. Solid lines indicate concentrations after correction for scandium.

The strongest enrichment for cadmium is found in the fluvial section of the Weser River, whereas the accumulation of copper and nickel is relatively small in all areas studied here. It should be noted, however, that the really strong metal pollution in the harbour area of Hamburg was not included in the present samples.

The study of the working group »Reinhaltung der Elbe«[14], which was performed on a long section profile of the whole Elbe River course within West Germany (also on the sediment fraction <63 μm) indicated values as high as 30—40 mg Cd/kg, 600—800 mg Pb/kg, 3000—5000 mg Zn/kg and 500—700 mg Cu/kg dry sediment from the Hamburg Harbour. This could result in a factor of enenrichment of about 100 for Cd, 30 for Pb and Zn and 20 for Cu (numbers in parentheses in Table II). The relatively strong enrichment of lead in the samples from the outer part of the German Bight (the North Sea) is probably caused by dumping of waste materials. Similar effects have been observed in a dated sediment core from the area near the island of Helgoland[15], where a characteristic increase of cadmium, lead, zinc and mercury takes place in the upper layers.

Remobilization of metals

One of the characteristic features in the sedimentary geochemistry of estuaries in industrialized regions is the sharp decrease of heavy metal concentration downstream in tidal areas. This effect has been explained[16, 17] to be due to mobilization processes, caused by decomposed organic matter and subsequent formation of organo-metallic complexes. The authors of this hypothesis based their strongest arguments on the obvious similarities in the order of sequence for both the rates of decrease during the estuarine mixing and their respective position within the Irving-Williams Series of the relative stability of metal chelates. On the other hand, after studying the Columbia River and Elbe River Estuaries Bothner and Carpenter[18] and Müller and Förstner[19] have pointed out that the simplest explanation for these developments is the mixing of highly polluted river-induced material with less contaminated sea-derived sediment particles. It has been shown that the higher the portion of a specific metal concentration is influenced by man, the greater its decrease in the estuarine mixing zone.

It should be noted that contrary to the »mixing theory« the authors of the ARGE-Elbe study[14] suggest a major effect of rapid sedimentation of highly polluted suspended solids at reduced flow velocities within the stream branching zone of the Hamburg Harbour area. This causes considerable dredging activities to be necessary within this section of the Elbe Rive[20]. According to the mass balances of the ARGE-Elbe study there should only be a minor net input of anthropogenic metal loadings into the estuarine zone.

The numerous investigations of the past years have shown that the above hypotheses, namely »remobilization« and »mixing«, are not cases that can be circumscribed by the implication inherent in the expression »either ... or«, as »not only ... but also« more accurately characterizes a differentiated view of individual metals. In a study on the Scheldt Estuary Salomons and Eysink[21] have measured the mixing ratio of marine to fluvial particulate matter with stable isotopic composition of the carbonate minerals. Conservative mixing was observed for Cs, Hg· Cr; positive deviations from the mixing curve, *i. e.*, precipitation/adsorption processes, are found for Fe, P, and Mn. For the

elements Co, Pb, Zn, Cu, Cd, and Ni negative deviations from the mixing curve were found, indicating the transfer of these elements from the particulate phase to the estuarine waters.

Generally two processes seem to be effective in the release of trace metals at the mixing of riverine (and mainly waste) particulates with seawater[22]:

(1) oxidation either of organic particles containing trace metals, or oxidation of metal sulfides and the surface desorption of trace metals caused by a high dilution ratio; and
(2) complexation of trace metals to form soluble complexes with organic ligands and of inorganic ligands such as Cl^-.

The relative high stability of chloro-complexes of cadmium and mercury seems to provide one possible explanation for the enrichment of dissolved species in interstitial water and the preferential release of these metals from estuarine sediments[23—27].

Experimental data of de Groot *et al.*[28] indicate significant remobilization of Cd from anoxic sediments after treatment with oxygen-rich seawater, while these effects were not observed with river water and for other metals studied (Table III).

TABLE III

Metal remobilization in laboratory experiments with strongly contaminated Rhine sediments[28]

Element	%				
	Cd	Zn	Cu	Ni	Pb
Seawater	49	2.2	2.0	2.5	0.1
River water	1	—0.8	0.9	—2.0	± 0

Another indication for the mobilization of particle bound Cd in the estuarine mixing zone was found in the radiotracer experiments of Calmano and Lieser[29]; about 95 % of the Cd-109 sorbed to natural supended matter (including organic particles) from the Main River was re-dissolved after treatment with NaCl-solution equivalent to seawater concentration.

The rate of mobilization in the experiments of de Groot *et al.*[28] is relatively slow and the maximum of metal liberation has been observed after 2—3 weeks (the reactions ended after about 4—5 weeks). Since dispersion of the dredged spoil is usually much faster than the release of metals one would not expect significant increase in the concentrations of dissolved metals, even of cadmium, at the dumping location. These conclusions are parallel to the findings of our field studies in the Weser Estuary, where during a dumping event no measurable increase in metal concentrations was observed[2].

From a long section of the Weser Estuary, however, direct evidence for the release of cadmium from particles has been found[7]. Relatively high values of dissolved Cd occur at the Weser River km 80 (downstream from Bremen) at salinity of approximately 6 ‰ (Fig. 7 a, b). Figure 7 c shows the distribution coefficient K_d of cadmium (K_d means µg metal/g particulate matter : µg metal/ml solution) as a function of salinity; the lower K_d the higher is the dissolved fraction of cadmium. A marked decrease of the K_d in the salinity

range between 1 ‰ and about 6 ‰ suggests intensive mobilization of Cd from riverine particles in the estuarine mixing zone. The increase of K_d-values in the outer estuary and in the marine zone (Fig. 7 c) can be interpreted by dilution of less contaminated seawater or by adsorption of Cd in the oxygen--rich seawater.

Mobilization processes such as in the example of the Weser Estuary must not necessarily take place to the same extent under natural (uncontaminated)

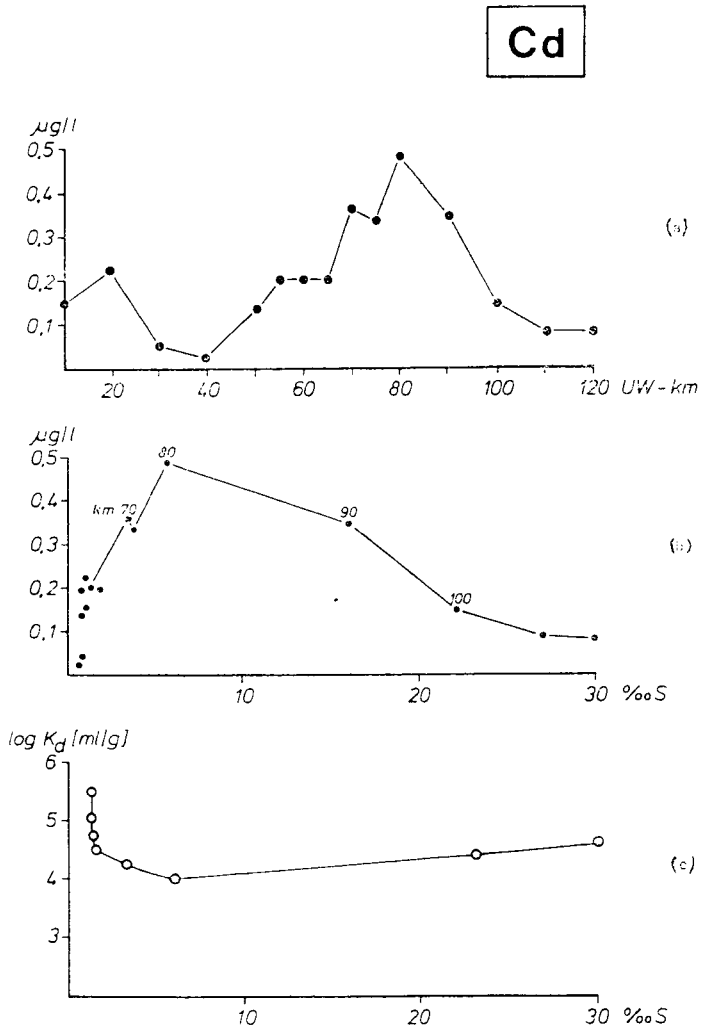

Fig. 7. Cd concentration in solution in the Weser Estuary (a) and *vs.* salinity (b). Distribution coefficient of Cd *vs.* salinity (c) (K_d means µg metal/g particulate matter : µg metal/ml solution).

conditions. Possibly the occurence of freshly adsorbed Cd-inputs — in the Weser Estuary from waste water emissions in the Bremen and Nordenham areas[2] and from dredge spoil, which is regularly dumped near the Lower Weser River km 80 where the maximum of dissolved Cd was observed — are the prerequisite of this phenomenon, which may establish detrimental effects on the aquatic biota in such areas.

Chemical extraction studies

The chemical leaching procedures are subject to much criticism particularly concerning their selectivity to specific chemical phases. Nevertheless the knowledge of the relative changes among the different — operationally defined — chemical forms may indicate how typical constituents enter the sediments and how they behave under changing conditions, for example, salinity or redox effects. In addition, these methods can provide information on the portion of a specific metal which may take part in short term geochemical processes and/or is potentially »bioavailable«.

Since there are various processes which may affect a release of metals from solid material some sort of compromise has been made with regard to a relatively simple distinction of major accumulative fractions and their behaviour under certain environmental conditions. One of the first proposals has been made by Gibbs[30] for the differentiation of typical metal species in relatively unpolluted sediments of the Amazon and Yukon Rivers:

(1) adsorptive bonding on fine-grained substances — comprising the metal ions which are physically sorbed, chemically sorbed and those which are ion-exchangeable;
(2) metals which are precipitated as discrete compounds, such as metal oxides, and hydroxides, carbonates, sulfides and phosphates;
(3) metals which are coprecipitated with Fe/Mn oxyhydrates or carbonates;
(4) metals in organic matter; and
(5) detrital forms of metals, bond in relatively inert structures of silicates and other residual components.

Generally the bonding strength for trace metals should increase from top to bottom in these chemical fractions and one possibility to study them would be the application of chemical extractants, either singly or in sequence. A number of chemical leaching procedures are presently employed for environmentally relevant metal investigations[31—34] and a sequence comprising five steps — exchangeable cations, easily reducible and carbonate fractions, moderately reducible phases, organic and sulfidic compounds and residual fractions — is used in our experiments (see section on Material and Methods).

Studies on polluted sediments and sludges revealed the following general developments:

— For all metal examples a clear decrease of the residual component is shown with increasing overall metal concentrations. These findings suggest that the surplus of metal contaminants introduced into the aquatic system from man's activities usually exists in a relatively unstable chemical form and should, therefore, be more accessible for short-term geochemical processes — including biological uptake — than the detrital, natural metal compounds.
— With the exception of cadmium the amount of heavy metals in exchangeable positions is very low. The most important enrichment phases in sediments are apparently the easily (Mn, Zn, Cd) and moderately (Fe, Pb, Cu, Cr) reducible components. Sewage sludges show higher percentages of metals in the organic extraction than do sediments. It seems that the treatment steps with ammonium acetate and acidified hydroxylamine are well suited for the estimation of the potential availability of metals for biochemical processes.

In spite of the clear advantages of these differentiations over the study of total sediment, it should be clearly pointed out that the various extraction steps are not as selective as sometimes stated. Several problems may arise:

(1) Labile metal phases could be transformed during sample preparation, especially for samples from reducing environments (see discussion by Jenne *et al.*[35]);

(2) Processes of re-adsorption and precipitation have to be considered (see discussion by Rendell *et al.*[36]);

(3) Reactions are influenced by the duration of the experiment and by the ratio of solid matter to the volume of extractant. Some of the extractants are more specific than others, as shown by repeated experiments. Our experiments[37] demonstrate that a too high solid content together with an increased buffer capacity may cause the system to overload. Such an effect is reflected by raising *p*H values in a time dependent test with hydroxylamine buffer (initial *p*H = 2) and oxalate/oxalic acid (*p*H = 3) solutions (Fig. 8);

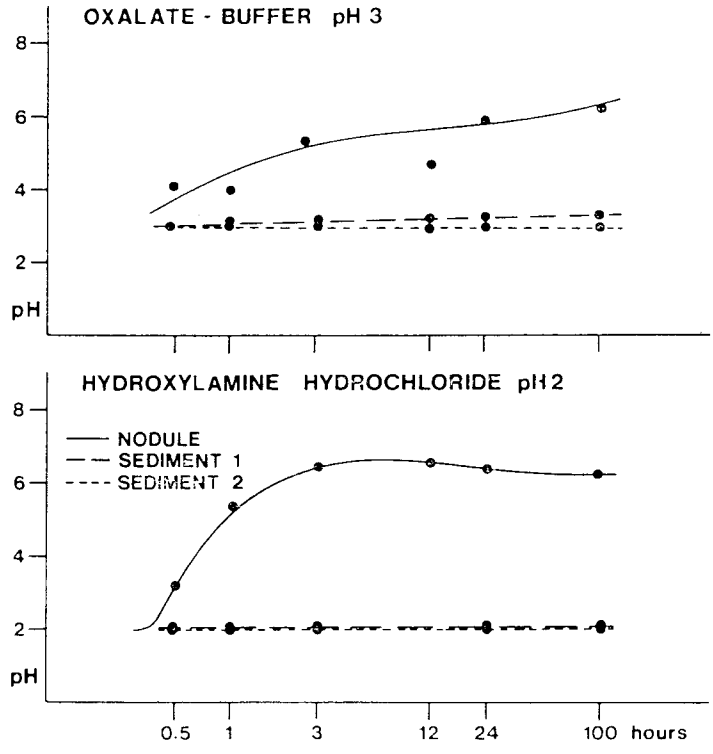

Fig. 8. Changes of the *p*H-values during the experiments with leaching solutions »oxalate buffer« and »hydroxylamine buffer«.

(4) There are major objections to the use of barium chloride/triethanolamine[38] (the latter compound is used to raise the *p*H to 8.1) or magnesium chloride[30] for the determination of exchangeable trace metals; there are chelating effects of the organic agent and the formation of dissolved metal-chlorocomplexes. Although the ion-exchangeable fraction of trace metals is still ill-defined, the ammonium acetate solution seems to offer an acceptable compromise[39];

(5) Basic metal oxides may be formed during initially high *p*H conditions, for example, for humic extraction with sodium hydroxide or sodium pyrophosphate[40];
(6) Difficulties occur with all carbonate extractions; reprecipitation under oxygenated conditions following CO_2 treatment, adsorption of organic compounds on exchanger resin[42], *p*H effects on labile oxyhydrates[34] (however the one major advantage of this step lies in the reduction of the buffer capacity of the sample before applying the following leaching steps);
(7) Problems are encountered particularly with the utilization of the dithionite/citrate extraction[34] : contamination by metals in the reagent, clogging of the burner during atomic absorption analysis, decomposition of the extractant and formation of sulfides (most of them highly insoluble);
(8) Treatment with hydrogen peroxide affects both labile as well as relatively stably bound metal components[43];
(9) Treatments with organic solvents are poorly suited for routine applications[39];
(10) The differentiation of organic and sulfidic metal associations is not as yet possible.

Figure 9 shows a selected example from the extraction experiments for cadmium in suspended material of the Weser Estuary between the Lower Weser River km 50—80[7]. Metals, such as Cd, Zn and Mn have a relatively large potentially mobilizable portion. It is apparent that Cd portions in exchangeable positions increased on the way downstream, which means that possibility of mobilization was easier at the Lower Weser River km 80. As considered before, the maximum of dissolved Cd at this position may be understood by this phenomenon.

Forms of iron and trace metals in marine sediments

Various authors have described the behaviour of »dissolved« iron in the estuarine zone as »non-conservative«, which means the reduction of iron contents as a function of salinity is not only due to dilution of riverine waters (higher iron contents) by marine waters (lower iron concentrations) but also to an elimination process of dissolved iron[44, 45].

It is thought that the cause of this estuarine process is a flocculation of the »dissolved« iron, which is present in most river systems as colloidal Fe-hydroxide[46], as a result of the decrease of repulsive forces between the colloidal particles originating from the increasing electrolytic concentration.

Other researchers have discussed the possibility that this elimination process is not restriced only to iron and that coprecipitation and adsorption of heavy metals on colloidal surfaces may occur[47,48].

Of particular importance for the study of these processes is, therefore, the differentation of the reducible sediment fractions. Chemical procedures for the distinction of oxidic and hydroxidic metal components have mainly found application on pelagic deposits where significant accumulation of metals takes place. According to recent data of Emerson *et al.*[49] and Klinkhammer[50] diagenetic processes in which the oxides (and to a lesser extent Fe-oxyhydrates) with their associated elements can be fractionally dissolved under the influence of minor redox gradients from the oxidation of organic

matter, lead to a manifold increase of Mn, Ni, Co, Cu, Zn, and Fe contents in the marine interstitial water[50,51]. The growth and enrichment of these metal compounds in concretions is thereby most probably favoured.

Extraction procedures with emphasis on reducible phases best reflect the processes involved in diagenetic remobilization of various elements in sediments[37]. In a composition study of various extractants for deep-sea sedi-

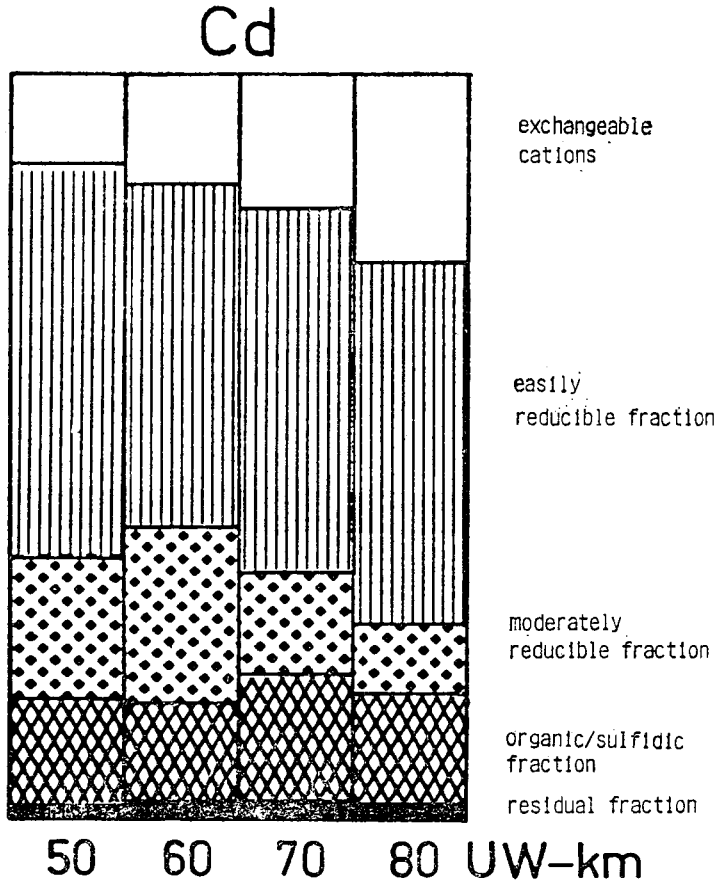

Fig. 9. Speciation of Cd in suspended matter of the Weser Estuary (UW-km = Lower Weser River kilometer).

ments Heath and Dymond[52] proposed the use of the oxalic acid leach developed by Schwertmann[53] — 0.2 *M* ammoniumoxalate + 0.2 *M* oxalic acid, *p*H 3 — which is considered to be a favourable method of removing amorphous ferric hydroxides and poorly crystalline goethite.

A weakly acidic reduction — 0.1 *M* hydroxylamine hydrochloride, *p*H 2 — introduced by Chao[54] for soil related metal studies, has been inserted by Pfeiffer *et al.*[37] in their investigations on the reducible metal compounds in pelagic sediments before the »Schwertmann leach« to extract the easily reducible components, mainly authigenic manganese oxides. According to the reaction formulae of these reduction processes

$$2\,NH_2OH + 2\,Fe_2O_3 + 8\,H^+ \leftrightarrow 4\,Fe^{2+} + N_2O + 7\,H_2O$$

$$2\,NH_2OH + 2\,MnO_2 + 4\,H^+ \leftrightarrow 2\,Mn^{2+} + N_2O + 5\,H_2O$$

$$C_2O_4^{2-} + Fe_2O_3 + 6\,H^+ \leftrightarrow 2\,Fe^{2+} + 2\,CO_2 + 3\,H_2O$$
$$C_2O_4^{2-} + MnO_2 + 4\,H^+ \leftrightarrow Mn^{2+} + 2\,CO_2 + 2\,H_2O$$

protons are used up, which means that solution becomes more alkaline. However, since Mn and Fe are precipitated in alkaline solutions (as hydroxides or oxides) buffering is necessary. The reaction products should not exceed the buffer capacity. It was shown by Pfeiffer *et al.*[37] that the oxalate buffer is most suited for determining the facies type and for the estimation of relation amounts of authigenic and detrital components due to the low rate of release in duplicate experiments.

The acidified hydroxylamine hydrochloride buffer can be of advantage for the investigation of processes involved in diagenetic remobilization and enrichment of metals in Mn/Fe concretions as it indicates the relative availability of the metals in the easily reducible fractions of micronodules and sediments.

Detailed investigations on the chemical forms of Fe, Mn, Cu, and Zn in suspended particulate matter (SPM) were performed on samples from the estuaries of the Weser and Elbe Rivers (Fig. 1) using the five-step extraction sequence described in the section »Materials and Methods«. Evaluation of the data given by Schoer and Eggersgluess[6] indicates characteristic changes of the various chemical forms of iron in the longitudinal sections ranging from fluvial to marine conditions. With increasing conductivity the portion of the easily reducible fraction in the Weser River increases about 15 %; at the same time the contents in the moderately reducible fraction decrease by about 25 %, while the portion in the residual fraction nearly doubles.

Similar results are shown in the investigation of the Elbe River SPM. The increase of easily reducible and residual Fe portions is even more marked than for the Weser River; the easily reducible portion, for example, doubles from the fluviatile to marine range.

Statistical analysis confirms the presence of highly significant (> 99 %) positive correlations between the data for conductivity and easily reducible fraction of iron in the Elbe River SPM; these findings suggest that dissolved or complexed iron from the Elbe River is precipitated at the interface with the marine environment in the form of amorphous or microcrystalline Fe-oxyhydrates. Figure 10 indicates that this process takes place mainly in the conductivity range between 1 and 4 mS, *i. e.*, in the upper reaches of the estuarine mixing zone.

Complementary investigations concerning the alteration of the chemical form of iron, manganese, copper and zinc in respect to grain size were carried out on samples N—3, M—5, E—5 and W—10 (*cf.* Fig. 1). Using Atterberg separation techniques the grain size fraction < 63 µm was partitioned further into the fractions < 2 µm, 2.0—6.3 µm, 6.3—20 µm and 20—63 µm. The additional samples gained with this method were then investigated as described above. Results are presented in Fig. 11.

A distinct increase in iron percentages in the easily reducible fractions with increasing grain sizes is observed. A parallel development is shown by the portion of the residual fraction. At the same time, the other chemical forms, especially the contents of the moderately reducible fraction, distinctly decrease.

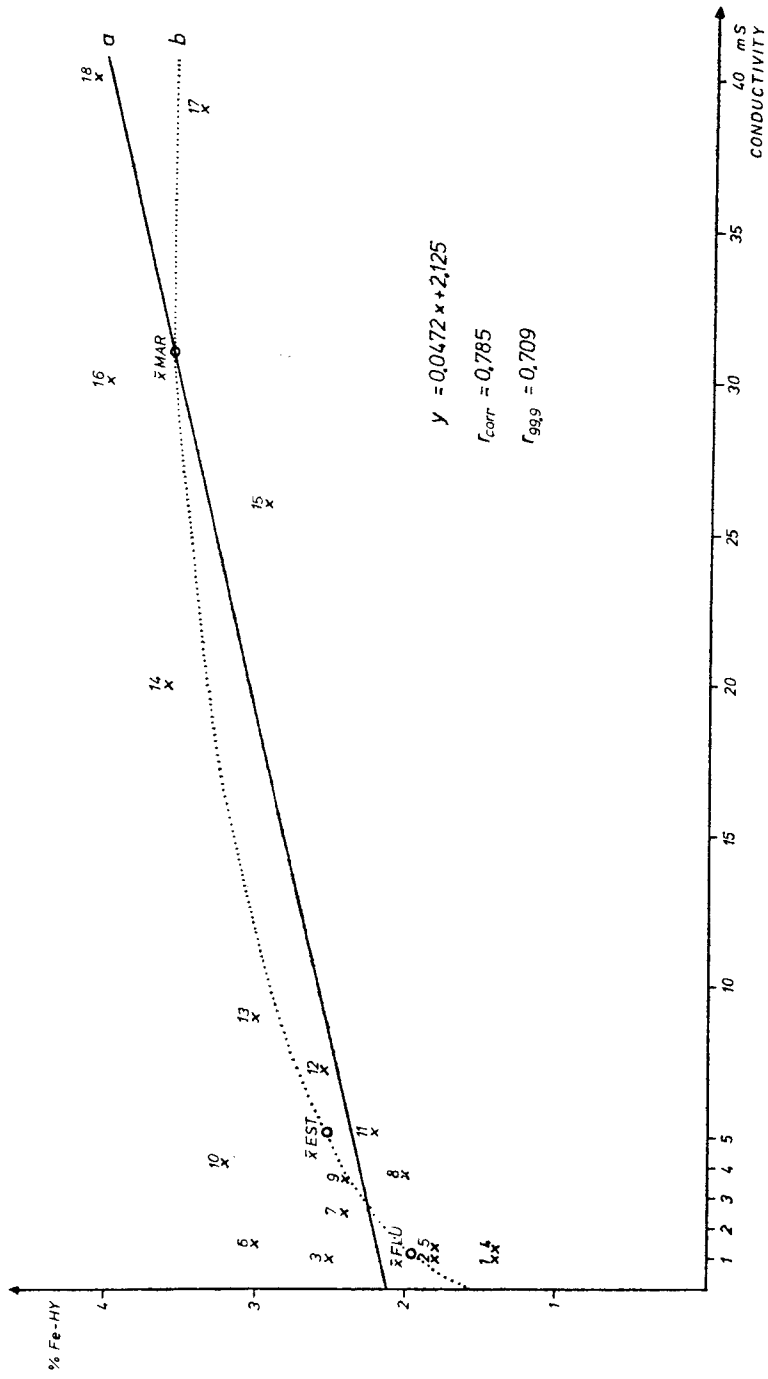

Fig. 10. Percent Fe in hydroxylamine-fraction *vs.* conductivity in the Elbe River. (a) linear regression line, (b) best mean fit.

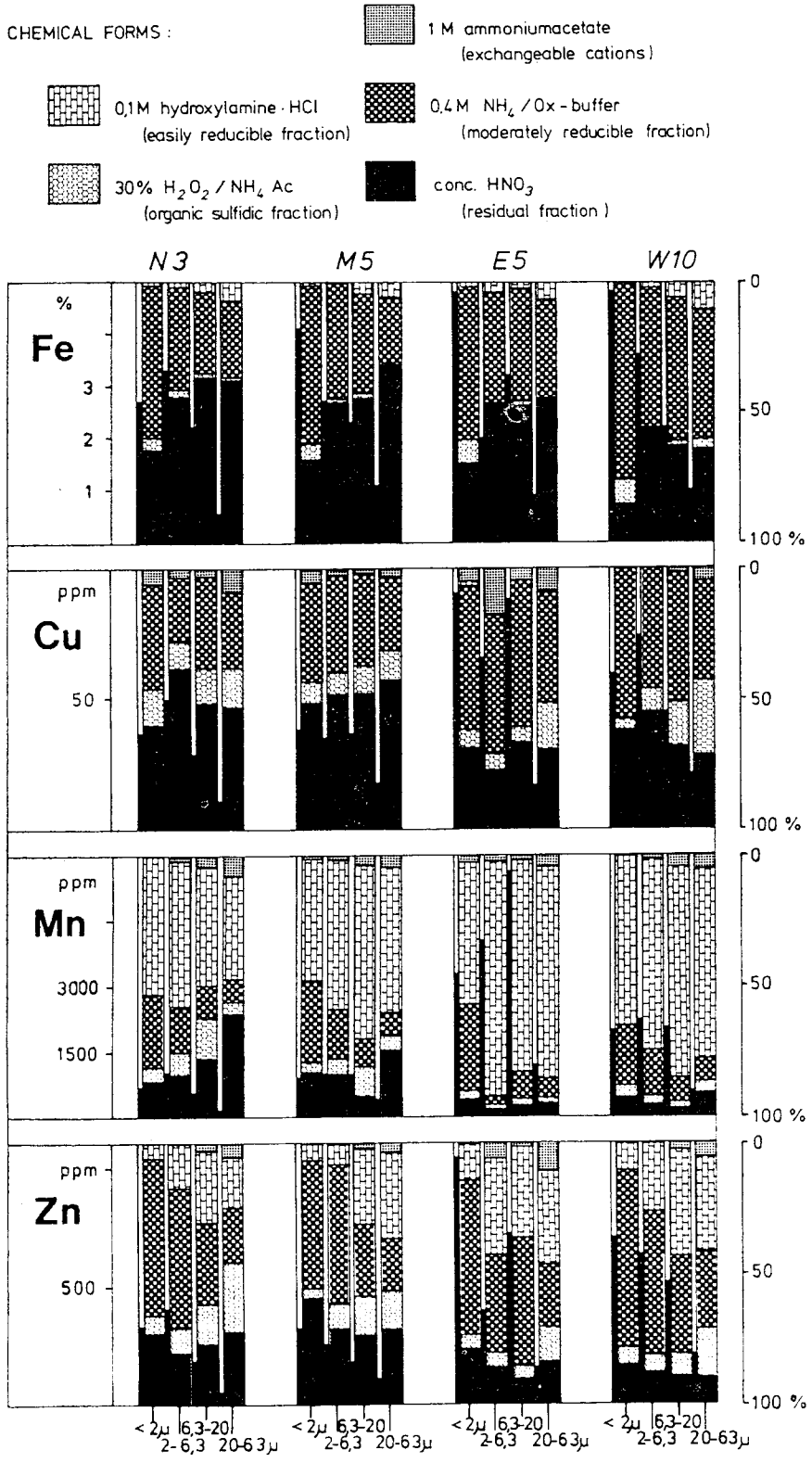

Fig. 11. Chemical forms of heavy metals in different grain size fractions (total = 100 %). Small black columns represent absolute concentration.

It has already been pointed out that amorphous iron hydroxide alone is partially dissolved in the easily reducible phase. Oxalate buffer is, on the contrary, able to dissolve amorphous $Fe(OH)_3$ completely and hematitic as well as goethitic phases up to 10 % (dependent on the preparation of the minerals). This portion can be greatly increased upon treatment with nitric acid.

These findings can be interpreted as follows: Particles of smaller grain size most likely consist of discrete, poorly mineralized iron-oxo-hydroxides, whereas larger particles are present as amorphous $Fe(OH)_3$ as coatings or contain iron that is bound in inert systems. The fact that smaller grain sizes possess much higher concentrations of iron seems to corroborate this assumption.

These results have been substantiated also by studies of Eisma and Emeis[55]. These authors have found small massive Fe-oxo-particles and larger silicate nuclei with Fe-coatings in sediments of the Orinoco River Estuary. Similar investigations are planned for Elbe River samples.

A correlation analysis of heavy metal contents of the indicated grain sizes with concentrations in the various chemical fractions resulted in a highly significant dependency (> 99.9 %) between iron and zinc as well as copper. Upon closer study of the various correlation coefficients given constant locality or grain size or chemical form, it can be determined that for the ratio iron/ /copper the concentrations of the elements in the grain size fraction 6.3—20 μm and 20—63 μm in the residual fraction are chiefly responsible for this significance at all four sampling sites.

It should be noted, however, that the good correlation between conductivity data and easily reducible iron of the Elbe River SPM is not found for the Weser River sample as well. This may be due to different contributions of allochtonous Fe-oxides from the catchment areas, as has been discussed by Gibbs[56]. Distinct increases in the thickness of the iron-hydroxide coatings and in the trace metal/Fe-oxide ratios in the medium to coarse silt fractions are considered among other factors to be a result of the weathering environment, where coarser material in the soil would have a higher permeability, bringing about a greater supply of the precipitating (and co-precipitated) ions. Possibly the autochtonous Fe-formations in the Weser Estuary are masked by a stronger input of detritally bound iron phases, which is suggested by a significant positive correlation between the conductivity data and the percentages of residual (nitric acid extractable) iron fraction.

Acknowledgements. Professor E. T. Degens, University Hamburg, is thanked for his invitation to join the Valdivia cruise and the captain and crew for their hospitality and technical asssistance. Financial support from the Federal Ministry of Research and Technology in the programme »Metal Forms in Polluted Marine Sediments (BMFT MFU 0514) is gratefully acknowledged. Dagmar Eggersgluess and Ulrich Nagel are thanked for analytical data; thanks are due to Petra Wallitzer for the drawings and to Ulrich Kästner for the photographic work. David Godfrey assisted in the preparation of the English version of the manuscript. The Organizing Committee of the Symposium is cordially thanked for their kind invitation to U. F. and for the great hospitality during the Meeting.

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DISCUSSION

R. BREDER (F. R. Germany):

In. Fig. 2 a very high values appear just next to low values. How do you explain this phenomenon?

U. FÖRSTNER:

These differences are mainly due to grain size effects and, therefore, demonstrate the strong need for a correction or standardization — some of the methods have been indicated in our presentation.

R. P. EGANHOUSE (U.S.A.):

Two questions:

1. *Have you made comparison between the metal yield from sediments by the $HClO_4/HF$ digestion and the cumulative total for the succesive extraction scheme (*i. e., *a mass balance)?*
2. *Have you compared the yield of metal from total sediment using one of the selective extractions and the yield obtained by the same step during succesive extractions?*

U. FÖRSTNER:

1. After some years of experiments with these procedures, we have now reached quite satisfying coincidence of the data of acid digestion and cumulative total for the sequential extraction for most metals. Presently, only cadmium (too high values in the residual fraction) and lead (relative high variability in replicate analysis) are still problematic.

2. We have done this for several steps. Hydroxylamine extraction (step 2) includes the contents of ammonium acetate treatment (step 1); oxalate buffer (step 3) gives similar data, if applied direct or in sequence. The position of the H_2O_2-

treatment, however, is still controversial — and it seems, that the use of the H_2O_2-step before the extraction of the moderately reducible fraction (with oxalate buffer solution) may results in an overestimation of the metal fraction bound to organic substances or to sulfides.

W. STUMM (Switzerland):

It is very important to assess the strength of the binding of metal ions to the sediment phases and to gain insight into the surface speciation of the solid phases. Such work should be carried out by carefully studying the processes on defined surfaces. One needs to consider that much of the binding at surfaces occurs chemically:

$$> R—OH + Me^{2+} \rightleftarrows > R—OMe^{+} + H^{+} \quad (1)$$

$$> R—OH + HA \rightleftarrows > RA + H_2O \quad (2)$$

I do not think that Cd(II) and Zn(II) are »bound« to surface phases by ion exchange (merely an electrostatic association at ion exchange sites of aluminium silicates). Cd(II) and Zn(II) may be bound chemically to the surface of Al-oxides on other oxides (see reaction (1) above). A treatment with NH_4^+ -acetate would release such cations, because acetate would react according to reaction (2).

U. FÖRSTNER:

The exchangeable fraction is in fact not satisfactory defined, even in the present context of an operational approach to estimate the major groups of chemical forms. Our experiments have shown that ammonium acetate solutions (step 1) can remobilize significant portions of carbonate-associated metals.

E. K. DUURSMA (the Netherlands):

A comment. I would like to support this kind of investigation to elucidate the surface reactions on sedimentary materials. From earlier studies with radionuclides, it became clear that the kind of rections on the surfaces and the binding inside the crystal lattices are specific for the radionuclide involved and (sometimes) the composition of the sedimentary particles. Processes cannot be easily explained by grain size or distribution of natural elements, and such studies as yours should clear up these very important chemical processes.

T. C. LODER (U.S.A.):

A question: what is the mechanism of increase in the % of Fe (easily extractable) on the suspended particles as go from river to ocean?

U. FÖRSTNER:

Our data from longitudinal profiles of suspended matter in the Elbe Estuary and from the grain size variations of chemical forms suggest that the increase of easily reducible iron is mainly due to the formation of Fe-coatings on river-borne particles in the upper reaches of the estuarine environment (approx. 5 permil salinity).

D. DYRSSEN (Sweden):

You use a rather »hard« procedure to remove the organic coating (30 % H_2O_2 at 85 °C). Have you tried milder procedures such as UV irradiation? Do you have any method to check the removal of the coatings?

U. FÖRSTNER:

We have not performed experiments on the removal of the organic coatings although this seems to be very important for the interpretation of our data. We have tried to strip off the iron oxyhydrates with different leaching agents and there is — at least qualitatively — a reduction of the sorption capacity for trace metals.

IZVOD

Teški metali u sedimentima s dna i suspendiranom materijalu iz rijeke Elbe, Weser i Ems te iz Njemačkog zaljeva (jugoistočni dio Sjevernog mora)

U. Förstner, W. Calmano i J. Schoer

Na uzorcima koji su uzeti iz estuarija i priobalnog mora sjeverne Njemačke za vrijeme krstarenja R/V »Valdivia« u listopadu 1981. godine proučavani su efekti veličine čestica, faktori akumulacije, kemijske forme i procesi remobilizacije. Institut za istraživanje mora iz Bremerhavena sakupio je i podatke koji se odnose na teške metale u estuariju rijeke Weser.

Standardizacija koncentracija metala na sadržaj aluminija (AAS) ili skandija (INAA) je posebno korisna za smanjivanje efekata veličine čestica u studijima monitoringa. Najjače antropogeno obogaćenje metala pronađeno je za kadmij, olovo i cink u sedimentima rijeke Weser i Elbe kraj Bremena odnosno Hamburga, dok je akumulacija olova i kadmija u vanjskom dijelu Njemačkog zaljeva uzrokovana uskladištenjem otpadnog materijala.

Pronađeno je da je karakteristična imobilizacija kadmija praćena početnim rastom saliniteta estuarija rijeke Weser. Studije koje obrađuju kemijsku ekstrakciju ukazuju na to da su kristalizirani (umjereno reducirani) ferooksihidrati koncentrirani u frakcijama manjih čestica, dok su veće čestice obično obložene amorfnim oksidom željeza koji se lako reducira. Čini se da amorfni oksid željeza utječe na sorpciju drugih metala, kao što su na primjer mangan i cink.