trace metal analysis on polluted sediments

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TRACE METAL ANALYSIS ON POLLUTED SEDIMENTS

Part I: Assessment of Sources and Intensities

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ABSTRACT

Sediment analyses are used to pin-point major sources of metal pollution and to estimate the toxicity potential of dredged materials on agricultural land. For source assessments (Part I of the present review) standardization is needed with respect to grain size effects, commonly achieved by analyzing the sieve fraction <63 µm. Further aspects include sampling methods, evaluation of background data and extent of anthropogenic metal enrichment.

INTRODUCTION

Trace metals occur in different forms in the aquatic environment. Fig. 1 shows the four major abiotic and the three biotic reservoirs of heavy metals as well as their possible pathways[1].

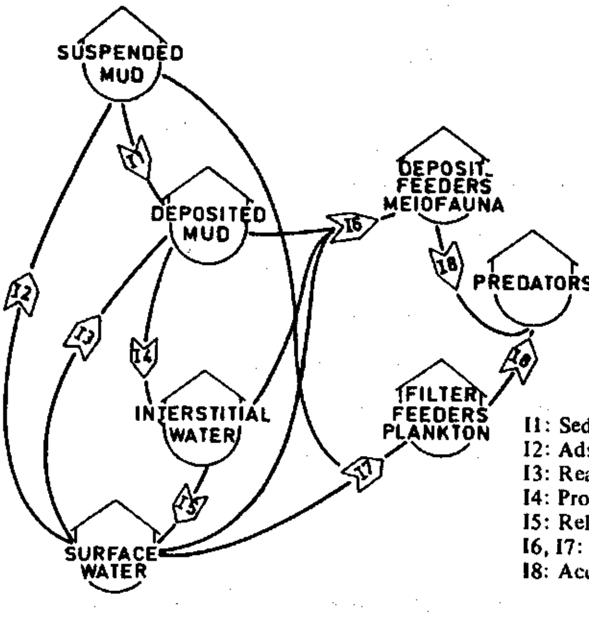

Figure 1: Pathways of metals in aquatic ecosystems.

I1: Sedimentation, transport, erosion.
I2: Adsorption of metals by suspended matter. Precipitation of dissolved metals.
I3: Reactions between surface water and deposited mud.
I4: Provision of the interstitial water with heavy metals.
I5: Release of metals from the interstitial water to the surface water.
I6, I7: Uptake of metals by organisms.
I8: Accumulation in the food chain.

Deposited sediment, interstitial water, suspended matter and surface water can be distinguished as abiotic reservoirs. Under changing redoxconditions, the deposited material can provide the interstitial water with higher concentrations of nutrients and trace metals. These may also affect the composition of the surface water. Through processes of diffusion, compaction, erosion and bioturbation, trace metals and nutrients may be released into the overlying waters. Apart from physical processes, biologically mediated reactions occur in the sediment, by which trace metals can be transformed into more toxic organo-metallic compounds.

The distinction between solid matter and aqueous constituents is operationally defined through a process of membrane filtration at 0.45μm pore size. This differentiation is often problematic due to the presence of organic and inorganic colloids in the filtered material, which may carry considerable contents of trace metals. Even the 0.45 μm fraction, however, indicates a high percentage of trace metals transported as solid material (Table 1):

Table 1: Percentage particulate-associated metals of total metal discharge (solid + aqueous)[2].

	Mississippi River[3]	Polluted U.S. Rivers[4]	Polluted FRG Rivers[5]	Rhine (Netherlands)[6]
Sodium	-	-	0.5	-
Calcium	-	-	2.5	-
Strontium	-	21	-	-
Boron	-	30	-	-
Cadmium	88.9	-	30	45
Zinc	90.1	40	45	37
Copper	91.6	63	55	64
Mercury	-	-	59	56
Chromium	98.5	76	72	70
Lead	99.2	84	79	73
Aluminum	-	98	98	-
Iron	99.9	98	98	-

In the less polluted Mississippi River[3], only 11% (Cd) to less than 0.02% (Fe) of the heavy metals discharged to the Gulf of Mexico is in a dissolved-complexed state.A similar sequence of the ratios of particulate and dissolved heavy metal phases has also been found for polluted systems, with the typical effect that the dissolved heavy metal percentages in polluted waters are significantly higher than in less polluted systems, particularly for metals such as cadmium, zinc and copper.

With respect to the following analytical approach on "polluted sediments", the aquatic solids are composed of a mixture of inputs from different sources, including eroded rocks and soils, sewage and solid waste particles, atmospheric fallout and autochthonous formations in the aquatic system, e.g. inorganic precipitates, biogenic matter, adsorbates on particles from solution, complexed and colloidal matter, etc. Although a differentiation of the components according to their origin is desirable, it has not as yet been possible to carry out such a differentiation satisfactorily (see Part II of the present review). For the methodologic aspects, it is important to note that heavily contaminated river sediments sometimes contain as much as 30% or even more sewage particles[7].

Two major uses of sediment analyses - especially on trace metals, but also on persistent organic chemicals such as polycyclic aromatic and halogenated hydrocarbons - can be defined:

- the identification, monitoring, and control of pollution sources;
- the evaluation of the environmental impact of polluted sediments, particularly with respect to the biological effects of dredged materials on agricultural land.

The two aims of this study vary in respect to their sampling, preparation of samples and analytical procedures and will therefore be discussed separately.

PART I ASSESSMENT OF SOURCES AND INTENSITIES OF TRACE ELEMENTS

It has been established from hundreds of investigations[8] that sediment analysis can be particularly usefull in detecting pollution sources and in the selection of critical sites for routine water sampling for contaminants that, upon being discharged to surface waters, do not remain solubilized, since they are rapidly adsorbed by particulate matter, and may thus escape detection by water analyses. During periods of reduced flowrates, suspended material settles to the bed of the river, lake or sea, becoming partly incorporated into the bottom sediment. By virtue of their composotion, sediments "express the state of a water body"[9]. With lateral distribution (quality profiles), local sources of pollution can be determined and evaluated. Vertical sediment profiles (cores) also are useful, because they often uniquely preserve the historical sequence of pollution intensities, and at the same time they enable a reasonable estimation of the background level and the input variations of a pollutant over an extended period of time; this approach is particularly useful if the rate of sedimentation is known.

Sampling

Surface bottom sediments are usually taken with a grab sampler of the Van Veen or Ekman-Birge type from a depth of 15-20 cm. Material of the upper, flaky, light brown, oxidized layer is generally dissimilar to the layers below it, and are non-representative. It is suggested that the chiefly dark layers directly underneath (ca. 1-3 cm depth) must be removed with a plastic spoon for subsequent investigation. Material taken at this depth from river deposits often with rapidly fluctuating sedimentation rates can reflect the contamination over a period of years. To complement this, surface sediments (current contamination) as well as a sample from deeper sections (10-20 cm depth) could be examined. In environments with a relatively uniform sedimentation, e.g. in lakes and in the marine coastal basin, which is fine-grained and occurs at a rate of 1 to 5 mm/yr, a more favorable procedure involves the taking of vertical profiles with a piston corer. A core profile of approximately 1 m covers a historical period of at least 200 years and its development can be traced by virtue of the metal content in the individual layers. Suspended sediments are recovered by filtration, continuous-flow centrifugation, or by sediment traps. In rivers, water discharge rates must be known and sampling must be frequently repeated. Pore waters have been extracted from sediments by leaching, centrifugation and squeezing; oxidation must be prevented during these procedures. In situ methods are now considered most promising, particularly for studies on the sediment/water interface[10,11]. Storage of the solid materials under oxigen-free, cold conditions is necessary, particularly if speciation, organic extractable trace elements, etc. are to be studied[12]. Freeze-drying is the last strenuous treatment in use today, but ovendrying at 70°C to 105°C is also used.

Grain Size Effects

Two effects must be considered when sediment analyses are used for the identification of pollution sources. Firstly, under conditions of high water discharge erosion of the river bed takes place and generally leads to a lower degree of local contamination.[13,14] (For brief periods during the initial stages of storm runoff, there is often a very significant increase in the metal concentration in solution , which can be explained as a flushing [15].)

Secondly - a fact often overlooked - it is imperative to base metal analyses, particularly those from river sediments, on a standardized procedure with regard to particle size, since there is a marked decrease in the content of metals as sediment particle size increases. An example is given in Fig. 2, indicating the concentrations of cadmium in different grain size fractions of sediments from the highly polluted Rhine and Main rivers in the Federal Republic of Germany.[16]

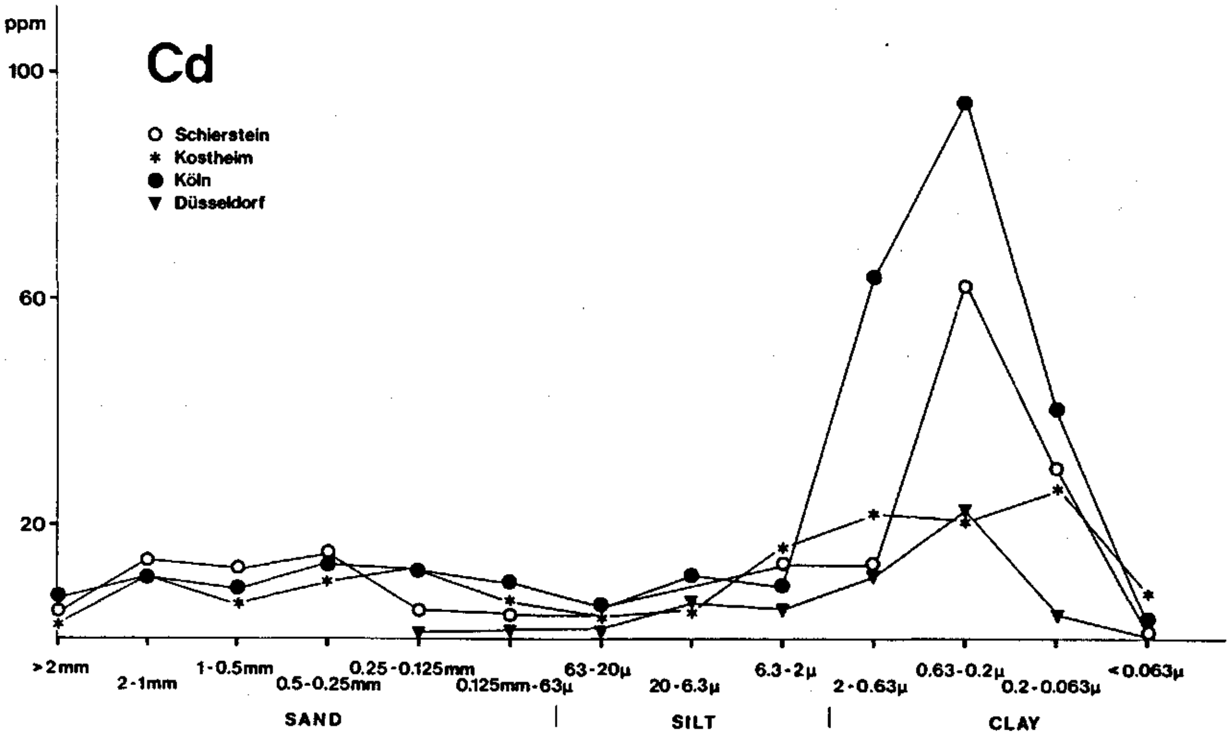

Figure 2. Grain size dependencies of cadmium concentration in sediment samples from the Main and Rhine rivers, West Germany. Samples collected by members of the working group "Metals", German Research Society.

Many different methods for grain size corrections are in use:

A. Separation of grain size fractions

204μm[17] ——— 175μm[18] ——— 63μm[19] ——— 2μm[20,21] ;

B. Extrapolation from regression curves

% <16μm[22] — %<20μm[23] ——— %<63μm[24] ——— specific surface area[25];

C. Correction for "inert" minerals

Metals in quartz-free sediment[26], carbonate/quartz-free sediment[27];

D. Comparison with "conservative" elements

Ratio element/aluminum[28]; sediment enrichment factor[29].

In respect to the characterization of metal pollution at a certain locality, the extrapolation techniques both for grain size and specific surface area of the material (method B) require a large number of samples (10-15). In addition, the calculation of the regression line is a time-consuming procedure. It is often not even possible to determine the regression line due to the limited range in grain size or specific surface area of the sediment at a certain locality.

The quartz correction method (method C) in some cases has to be extended to dilution effects caused by feldspar, carbonates, and opaline silica[30]. In order to apply such corrections, information is needed on metal concentrations in the various phases to judge whether the correction is justified. Normalizing of anthropogenic metal concentrations to the contents of "conservative" elements such as aluminum and potassium (method D), i.e. on the percentage of clay minerals, has one major disadvantage in that it gives a ratio value instead of real concentration data.

Separation of grain size (method A) is advantageous because only few samples from a particular locality are needed. However, separation of the fraction less than 2 µm (pelitic fraction) is time-consuming and a remobilization of metals might take place during settling in distilled water. The fractions less than 173 µm and 204 µm contain considerable percentages of large grains which are usually low in trace metals. Therefore, the fraction less than 63 µm is recommended for the following reasons:

- trace metals have been found to be present mainly in clay/silt particles;
- this fraction is most nearly equivalent to the material carried in suspension (by far the most important transport mode of sediments);
- sieving does not alter metal concentrations by remobilization (particularly when water of the same system is used);
- numerous metal studies have already been performed on the suggested <63 µm fraction.

Sediment Digestion and Analysis of Trace Metals

Except for direct measurements on solid matter, e.g. by neutron activation analysis or X-ray fluorescence spectroscopy, it is necessary to bring the metals into solution for analysis. Complete digestion vertering usually is performed with hydrofluoric acid combined with perchloric acid, sulfuric acid or nitric acid. Numerous studies have shown that aqua regia (HNO_3-HCl; 1:3) or conc. nitric acid decomposition ontbinding of sediments is sufficient for trace metal analysis.[8] It has been suggested that for this type of study it is not necessary to obtain full digestion of all sediment components including minerals, since the pollution effects usually are associated with the surface of the sediment particles with which the autochtonous precipitates. Simple $HCl-HNO_3$ (1:1) digestion has therefore been proposed for the determination of trace metals by atomic absorption spectroscopy.[31] Leaching the samples with cold 0.3 N[32] or 0.5 N HCl[33] has been shown to provide a rapid, inexpensive way of "initially establishing the gross degree to which a sediment population has been subjected to trace metal pollution from the overlying waters" [34]. Chemical extractions in this manner may also offer some advantages compared to simple grain size separation (see above) and subsequent complete digestion: "coating", e.g. of Fe/Mn oxides, carbonate, and organic substances on relatively inert materials, such as quartz grains, still play a role in the bonding of heavy metals in coarser grain size fractions[35].

Recent reviews of metal contaminants in aquatic solids - e.g. "cadmium in polluted sediments"[36]-reveal a great variety of separation and digestion techniques used by the various laboratories. A greater degree of standardization will be needed in the future to obtain comparable data with regard to the assessment of the environmental impact of polluted sediments (see also Part II "Evaluation of Environmental Impact", which will describe chemical leaching techniques used mainly in the trace metal analysis of contaminated dredged materials).

Atomic absorption spectroscopy, either as the flame or the carbon furnace method, is widely applied for trace metal analysis of sediments, but other techniques such as neutron activation analysis, X-ray fluorescence, atomic emission spectroscopy and polarographic methods are also in use.
A comparison of costs and characteristics between some commercially available trace analytical instrumental methods is given by Nürnberg[37] (Table 2):

Table 2: Cost and characteristics of trace analytical instruments.

Method	Price 10^3U.S. d.	Samples/day (real time/h)	Remarks
Electrothermal AAS	8-15	50(8)	sequential
automated	30-45	50-100(12-24)	single element method
X-ray fluorescence	40		multielement method, depends on
energy dispersive		100(24)	sample type and program
multiple crystal	150		
Atomic emission ICP excitation multiple channel	70-120	100(24)	Multielement method for up to 60 elements
Pulse polarography	5-10	10-20(8)	up to 6 metals
automated	20-25	30-40(8)	simultaneous
(including DPASV)			species sensitive
NAA, multi-channel analyzer + tape + computer	90	10(24)	frequently radiochemical separation
Lead cell	50		

Geochemical Background and Man's Influence on the Concentration of Trace Metals in Sediments[38]

Trace metals in recent sedimentary deposits can generally be divided into two categories in accordance with their predominant source of origin - either as "lithogenic" or "anthropogenic". These categories are often simply referred to as "geochemical" and "man-made" ("civilization"), respectively.[39] Metals such as zirkonium, rubidium, and strontium, which are derived from rock material by natural weathering processes, constitute the first group. The second group is made up of metals which have become enriched chiefly as a result of man's activities, and includes among others chromium, cobalt, nickel, copper, zinc, cadmium, mercury, and lead. Between these two groups there are combinations: for example, the enrichment of mobile elements such as manganese and iron, which may well have had civilizational origins such as extreme eutrophication. By their own accumulation, these metals can cause other elements to accumulate. Even the precipitation of carbonates can be influenced by "civilizational" means and this can turn influence metal levels.

When attempting to determine the "extent of pollution" in a lake or river by means of the heavy metal load in sediments, it is of primary importance to establish the natural level of these substances, i.e., the "pre-civilization"[40] level and then substract it from existing values for metal concentrations in order to derive the total enrichment caused by anthropogenic influence.

In order to obtain an ideal comparative basis for environmental studies, the following criteria should be fulfilled so as to achieve representative values for metal concentrations: a large number of sediment samples must be analyzed which correspond with recent deposits in their (a) grain size distribution, (b) material composition and (c) conditions of origin. A fourth criterium states that the samples must be uncontaminated by civilizational influences. In practice all these criteria cannot be fulfilled simultaneously.

Several possibilities have been discussed to establish background values for trace metals:

(1) Average shale composition as a global standard value;
(2) Fossil lake and river sediments as a standard taking into account natural allochthonous and autochthonous factors and mechanisms as well as regional influences;
(3) Recent deposits in relatively unpolluted areas; and
(4) Short, dated sedimentary cores, providing a historical record of events occuring in the watershed of a particular river or lake. They would enable an estimation of both the background levels and the changes in input of an element over an extended period of time.

Table 3 gives a compilation of background values for trace elements evaluated according to methods (1) to (3). A summary of core studies (4) designed for the evaluation of different influences from natural and civilizational sources of trace metals in aquatic sediments is given by Förstner and Wittman[8].
A comparison of the metal values found in the sediments collected from several areas reveals that in industrialized and urbanized areas, the metal enrichment must be ascribed to anthropogenic influences rather than to natural enrichment of sediments by geological weathering (as evidenced by the analyses of the lower sections of sediment profiles).

Similar results are found from a comparison of the consumption rates of heavy metals with the natural concentrations of the respective elements in rocks, soils, and sediments. The "index of the relative pollution

Table 3: Concentration of metals (values in μg/g), organic carbon (%) and carbonate (%) in pelitic fractions (<2 μm) of fossil and recent aquatic sediments. Average shale composition after Turekian and Wedepohl[41]

	Fossil lake sediment (Ries-Lake)[a]	Fossil river sediment (Rhine)[b]	Recent lake sediments mostly from remote areas (n=87)[c]		Shale standard
Iron	18,200	32,350	43,400	(11,500 -67,300)	46,700
Manganese	406	960	760	(100 - 1,800)	850
Strontium	252	184	151	(60 - 750)	300
Zinc	105	115	118	(50 - 250)	95
Chromium	59	47	62	(20 - 190)	90
Nickel	51	46	66	(30 - 250)	68
Lithium	203	91	45	(15 - 200)	66
Copper	25	51	45	(20 - 90)	45
Lead	16	30	34	(01 - 100)	20
Cobalt	15	16	16	(4 - 40)	19
Mercury	0,5	0,2	0,35	(0.15- 1.50)	0.4
Cadmium	0.2	0.3	0.40	(0.10- 1.50)	0.3
Org. C	3.5%	1.8%	1.6%	(< 0.2%- 3.7%)	-
Carbonate	36%	11%	16%	(0 - 70 %)	-

[a] Arithmetic mean of 25 values

[b] Arithmetic mean of 4 values

[c] Metal = median of 87 values, organic carbon = arithmetic mean of 87 values

potential"[42] and the "technophility index"[43] show that particularly large man-made enrichments can be expected from emission of lead, mercury, copper, cadmium, and zinc in surface sediments and soils.

A quantitative measure of the metal pollution in aquatic sediments has been introduced by G. Müller[44], which he calls "the index of geoaccumulation":

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$$

where C_n is the measured concentration of the element 'n' in the pelitic sediment fraction (<2 μm) and B_n is the geochemical background value in fossil argillaceous sediments ("average shale"). This index reflects the relative enrichment of a certain trace metal in a given system or sub-system. A comparison of these sediment indices with the water quality classification of the International Association of Waterworks in the Rhine Cathment (IAWR) has been given by the same author, indicating particularly strong accumulation of cadmium in the lower section of the Rhine River (Table 4).

Table 4: Comparison of IAWR water quality index (based on biochemical data) and geoaccumulation index (I_{geo}) of trace metals in sediments of the Rhine River (after Müller[44]).

IAWR index	IAWR water quality (pollution intensity)	Sediment accumulation (I_{geo})	I_{geo}-class	Metal examples	
				Upper Rhine	Lower Rhine
4	very strong polluted	>5	6		Cd
3-4	strongly to strong poll.	4-5	5		
3	strongly polluted	3-4	4		Pb,Zn
2-3	moderately to strongly	2-3	3	Cd,Pb	Hg
2	moderately polluted	1-2	2	Zn,Hg	Cu
1-2	unpolluted to moderately	0-1	1	Cu	Cr,Co
1	practically unpolluted	<0	0	Cr, Co	

Sediment-Water Interrelations

Investigations performed by Aston and Thornton[45] on stream sediments of both mineralized and unmineralized areas in Great Britain have shown that sediment analyses may also provide a quantitative approximation of the metal concentration of associated waters. The salient factors are the degree of "contrast" and the assignment of "threshold" values. "Contrast" is defined as the highest anomalous concentration divided by the average background concentration. It was found that high contrast values are readily identified for contaminated areas and it is suggested that these data could be related to the "highest desirable level" (HDL) values for the particular trace element in water.

In the case of cadmium, the tentative grens threshold is reached at approximately 5 to 10 ppm Cd, depending on the drinking water standard; for zinc the value is approximately 2000 ppm, for copper 1000 ppm and for lead 500 ppm, respectively. However, because of considerable variations in the physical and chemical environments of the catchment areas as well as of the aquatic system properties, this approach can only be taken as a rough estimate, and has to be verified by detailed water analysis.

Acknowledgements

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TRACE METAL ANALYSIS ON POLLUTED SEDIMENTS

Part II: Evaluation of Environmental Impact

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ABSTRACT

Sequential extraction techniques are used to determine the chemical associations of heavy metals with specific sedimentary phases, whereby the potential availability of toxic compounds for biological uptake may eventually be estimated. The importance of such investigations in the classification of dredged materials is rapidly increasing. As in the case for the reduction of grain size effects (see Part I of the present review) a methodological standardization appears to be presently of special import. Available methods are discussed and a simplified scheme composed of two major extraction steps (acidified hydroxylamine and hydrogen peroxide) is proposed.

INTRODUCTION

Fluvial, marine, and estuarine sediments are becoming increasingly polluted with trace metals, phosphorus and other contaminants. The cadmium concentrations in the sediments from the Rhine River have increased more than 100-fold in eighty years (Figure 1). The problem of the polluted sediment is intensified by the closing of lagoons, the extension of harbour areas, the deepening of navigation channels and the channelization of rivers[1,2]. These human activities promote the accumulation of polluted sediments. The resulting increased maintenance dredging results in hugh amounts of contaminated sediments for which safe disposal areas on land or in the aquatic environment have to be found.

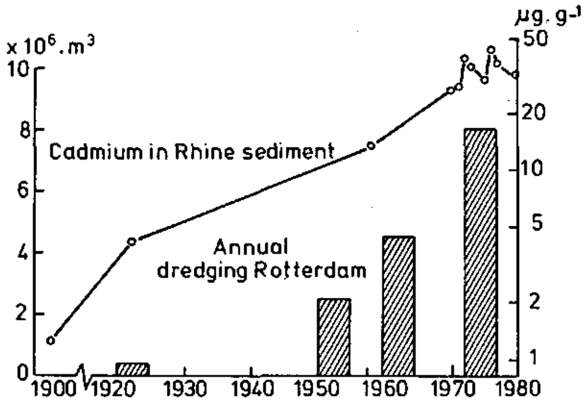

Figure 1: Increase in cadmium concentrations in Rhine sediments due to increased industrial use and the increase in annual dredging in the Rotterdam harbour due to harbour extension. Note that the cadmium concentrations are logarithmic.

Important problem areas with regard to the presence of contaminated sediments in the environment are:

- the behaviour of heavy metals and other contaminants in the sediments which are deposited in more or less permanent sedimentation areas (lakes, coastal environments): Are the sediments a permanent sink for trace metals or is remobilization possible?
- The bioavailability of the contaminants in the sediments for aquatic life;
- The behaviour of contaminants in dredged material during and after disposal in dumping areas either on land or in the aquatic environment;
- The availability of the trace metals in landfill areas for biological uptake.

To assess the environmental impact of contaminated sediments, information on total concentrations alone is not sufficient because trace metals are distributed over the various chemical compounds and minerals in sediments. Only part of the metals present may take part in short-term geochemical processes and/or are bio-available.

Five major mechanisms can be distinguished for metal accumulation on sedimentary particles: (1) adsorptive bonding on fine grained substances, (2) precipitation of discrete metal compounds, (3) coprecipitation of metals with hydrous Fe and Mn oxides and carbonates, (4) associations with organic compounds, and (5) incorporation in crystalline material.

METHODS FOR THE SPECIATION OF PARTICULATE TRACE METALS

Problems related to soil science have quite early led to the development of single leaching techniques to determine the availability of trace metals in soils for plants. Most of these earlier studies do not consider the various sinks for trace metals in soils. Some exceptions are the studies on the speciation of copper[3,4] and of copper, zinc, and manganese[5].

In the sediment-petrographic field, interest was focussed initially on differentiating between authigenic and detrital phases using single step leaching techniques. By chemical leaching with EDTA, dilute hydrochloric acid and acetic acid, the distribution of elements in detrital igneous minerals and authigenic phases in pelagic sediments could be determined[6,7]. Extraction with 25% (v/v) cold acetic acid has been used to separate trace elements in carbonate rocks into detrital and non-detrital fractions[8]. This method has subsequently been adopted for the study of heavy metals in sediments in Canada[9] and in Norwegian fjords[10]. The treatment with acetic acid removes metals present in carbonates and easily soluble amorphous compounds of manganese and iron held in ion-exchange positions and weakly attached to organic matter[9].

Chester and Hughes[11] introduced a combined acid-reducing agent of 1 M hydroxylamine hydrochloric acid and 25% (v/v) acetic acid for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace metals (non-lithogeneous fraction) from marine sediments. It should be noted that no concise nomenclature is possible in view of the different leaching agents and extreme variety in sediment composition. Both the acetic acid attack and the hydroxylamine acetic acid method do not liberate metals that form strong complexes with organic matter (e.g. copper)[12]. Therefore these two leaching solutions do not differentiate between detrital and non-detrital fractions in lake, river and certain estuarine deposits, which often contain high amounts of organic matter.

A dithionite-citrate extraction method has been proposed for the removal of metals present in hydrous manganese and iron hydroxides[13]. However, for routine investigations an extraction with 0.3 M HCl seems to produce the same results and is thus preferable because this procedure requires fewer manipulations[14]. A single extraction method for the determination of trace metals associated with carbonates makes use of an acidic ion-exchanger[15].

Further differentiation of the non-detrital or non-lithogeneous metal fraction was mainly promoted by environmental studies, since these phases of the sedimentary dredged material, or sewage substances, constitute "the reservoir for potential subsequent release of contaminants into the water column and into new interstitial waters"[16], thus becoming predominantly available for biological uptake[17-20].

Adsorption and cation exchange

Extractions with: $BaCl$[39], $MgCl$[24], NH_4OAc[42]

Detrital/non-detrital; authigeneous/lithogeneous fractions

Extractions with: EDTA[6], 0.1 M HCl[41], 0.3 M HCl[14], 0.5 M HCl[13], 0.1 M HNO_3[43]

Manganese and iron phases; reducible, easily and moderately reducible phases

Extractions with (in approximate order of release of iron): Acidified hydroxylamine[44], ammonium-oxalate[45], hydroxylamine-acetic acid[11], dithionite/citrate[13].

Carbonate phases

Extractions with: CO_2 treatment[46], acidic cation exchange[15], NaOAc/HOAc (pH 5)[29]

Organic phases; Humic and fulvic acids, solid organic material

Extractions with: H_2O_2[39], H_2O_2-NH_4OAc[42], H_2O_2-HNO_3[26], organic solvents[47-50]
0.5 N NaOH[51], 0.1 N NaOH/H_2SO_4[52], Na hypochlorite-dithionite/citrate[24]

Table 1. Summary of common methods for the extraction of metals associated with different chemical phases in sediments.

The various single leaching steps (Table 1) are combined into leaching schemes to determine the sinks for trace metals in sediments. A sequence beginning with the "Chester-Hughes" reagent[11], followed by an oxidizing step (30% H_2O_2)[21] resulting in a differentiation of trace metals into a reducible, oxidizable and resistant fraction, has been used for the study of reduced fjord sediments in British Columbia[21], sediments from the Dead Sea in Israel[22], and for sediments from Southern California[23]. A distinction between exchangeable metals, metals present in metal hydroxide coatings, organic solids, and the crystal phases was made for sediments from the Amazon and Yukon rivers[24,25]. Studies on sediments from Los Angeles harbor[26] and on contaminated sediments from Lake Erie, Mobile Bay, and the harbour of Bridgeport, Conn.[27] were performed by applying sequential extraction techniques to include the determination of the

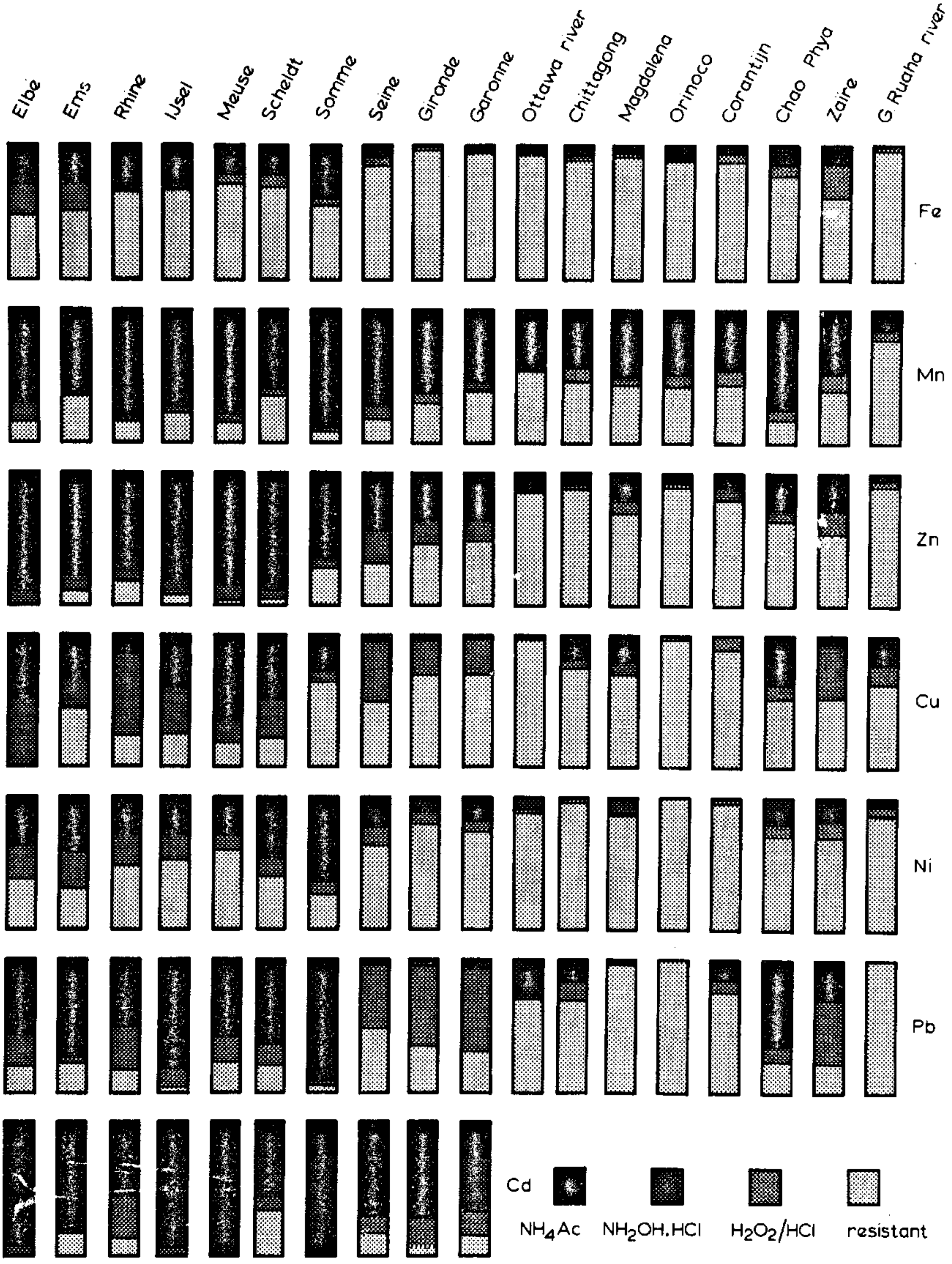

Figure 2: The speciation of trace metals in eighteen different river sediments. The rivers are arranged according to their approximate geographical positions from North to South. Most tropical rivers contain low amounts of cadmium and here it was not possible to obtain a reliable speciation. For the Rio Magdalena and the Orinoco River, insufficient material was available for the determination of the exchangeable fractions; the acidified hydroxyl-amine step therefore contains also the "exchangeable metals.

metal contents in interstitial water and in exchangeable, easily reducible, moderately reducible, organic, and residual fractions. Extraction schemes related to the above-mentioned ones have been used for the speciation of particulate metals in Lake Michigan[28], the Yamaska and Saint Francois rivers in Canada[29], the Rio Grande[30], and Tokyo Bay[31]. A simplified scheme consisting of an extraction with 0.1 M hydroxylamine-HCl (pH 2) followed by an extraction with hydrogen peroxide (30%, pH 2.5)-ammonium acetate was used for the study of sediments from the Rhine, Meuse, Ems and Scheldt rivers and from the North Sea[32]. This scheme including an additional step for exchangeable cations was used to study the speciation of trace metals in 18 different river systems (Figure 2). The results show the increase in the relative amount of metals present in the resistant (lithogeneous) fraction for less polluted or unpolluted river systems. In nearly all river systems the "reducible phase" is an important sink for trace metals. Copper more than other trace metals shows a tendency to prefer the "organic phase".

Elaborate schemes have been developed by Förstner and co-workers[33-36].

An example of an elaborate fractionation scheme is presented in Table 2.

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1 Exchangeable cations: 1 M ammonium acetate, pH 7

2 Carbonate fraction: acidic cation exchanger

3 Easily reducible phases:(Mn oxides; amorphous Fe oxyhydrates); 0.1 M $NH_2OH \cdot HCl$ + 0.01 M HNO_3, pH 2

4 Moderately reducible phases: (poorly crystallized Fe oxyhydrates): 0.2 M ammonium oxalate + 0.02 M oxalic acid, pH 3

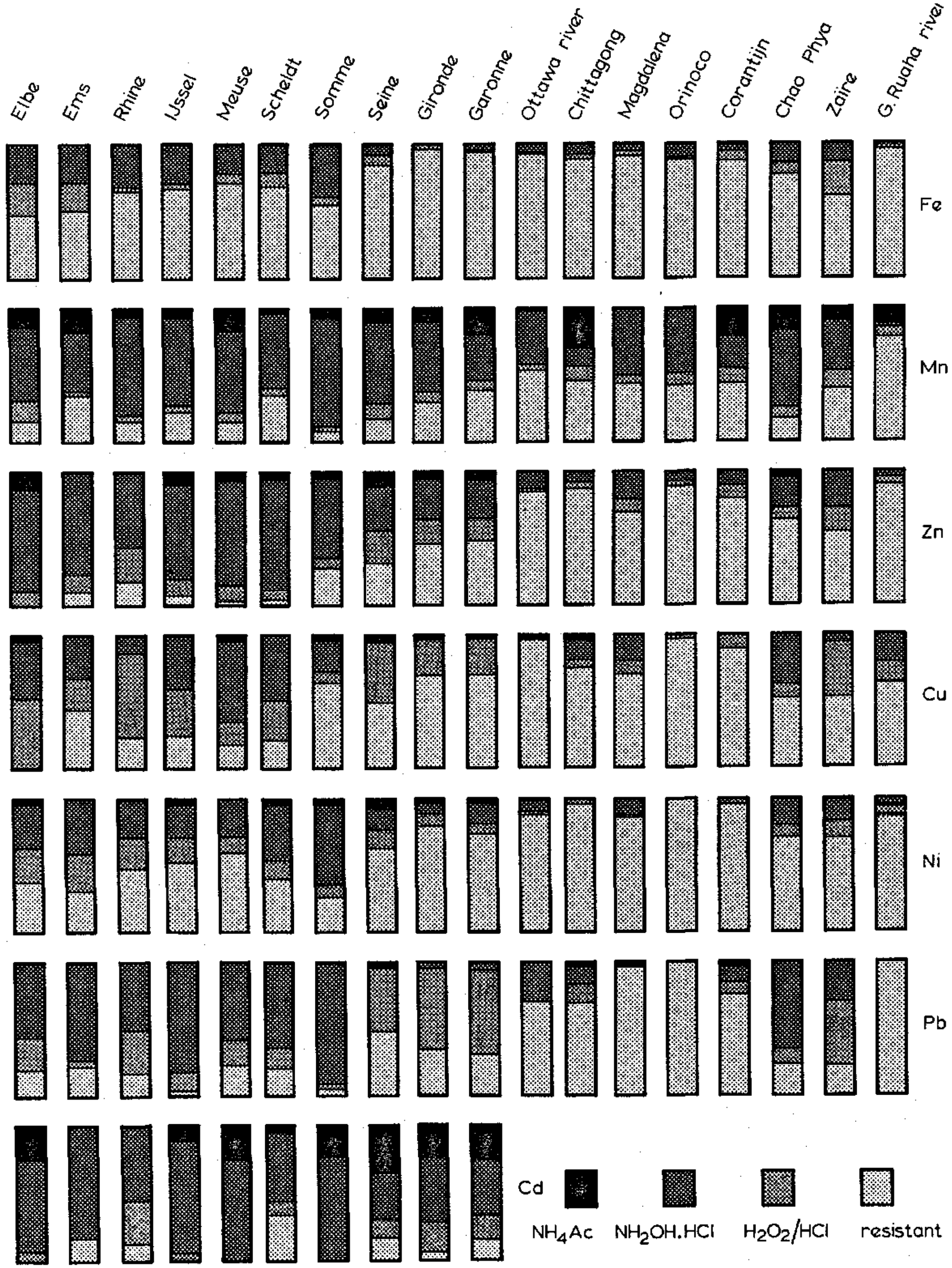
5 Non-silicate iron phases: citrate-dithionite extraction

6 Organic fractions: 30% H_2O_2(90 C^{o})+ 1 M NH_4OAc, pH 2

7 Detrital silicates:$HF/HClO_4$ digestion

Table 2: Example of elaborate scheme for the speciation of particulate trace metals.

This scheme was applied to two intercalibration sediment samples of the Federal Institute of Hydrology (FRG)[53] from the Rhine River and Ems Estuary. Selected data[54] given in Table 3 indicates a significant decrease of residual associations for Cu, Zn, and Pb as the total metal concentration increases due to anthropogenic pollution. There is a considerable amount of Cu, Zn, Pb, and Cd bound in the carbonate fraction, whereas the exchangeable form is significant only in the case of Cd.


Elbe
Ems
Rhine
IJssel
Meuse
Scheldt
Somme
Seine
Gironde
Garonne
Ottawa river
Chittagong
Magdalena
Orinoco
Corantijn
Chao Phya
Zaire
G.Ruaha river
Fe
Mn
Zn
Cu
Ni
Pb
Cd
NH4Ac
NH2OH.HCl
H2O2/HCl
resistant

	Ni		Cu		Zn		Pb		Cd
Total conc. µg/g d.w.	E-E 42	R-R 84	E-E 26	R-R 209	E-E 227	R-R 922	E-E 66	R-R 144	R-R 9.9
1 Exchang.cat.	3%	6%	2%	1%	2%	9%	<1%	3%	18%
2 Carbonate fract.	10%	13%	19%	28%	31%	37%	35%	52%	38%
3 Easily reduc.	28%	25%	3%	3%	24%	39%	4%	6%	23%
4 Moderately reduc.	15%	17%	29%	30%	12%	5%	29%	23%	1%
5 Non-silic. Fe	-	6%	5%	2%	2%	1%	11%	6%	-
6 Organics, sulf.	6%	3%	3%	4%	3%	<1%	<1%	<1%	6%
7 Residual fract.	38%	40%	39%	32%	26%	9%	20%	10%	14%

Table 3: Chemical extraction of selected trace metals in sediment samples from the Rhine River (R-R) and the Ems Estuary (E-E) according to the methods of Table 2.

For most extraction phases a distinct reduction of the metal content is usually seen as grain size increases. The effects are particularly evident for the Zn and Pb associations with carbonates, easily and moderately reducible fractions, but can also be observed in the residual organic fractions for Cr, or in the humate fractions, for Fe, Pb and Cu[35]. In Part I of the present review we have shown that such effects should be even more pronounced if the mechanical fractionation would more accurately separate individual particles according to their grain size; the deposition of coatings on inert materials is one of the major reasons for the still relatively high contents of non-residual metal associations within coarse-grained sediment fractions.

The above-mentioned studies all show that the surplus metal contaminants introduced by man's activities into the aquatic system usually exists in relatively unstable chemical associations and is, therefore, predominantly available for biological uptake[37].

Unfortunately there is, as indicated, a proliferation of extraction schemes, making, as in the case of total metal concentrations in sediments, an intercomparison of results difficult, indeed if not impossible. However, presently sufficient information and experience with different extraction techniques is available for a variety of sediments, making it possible to propose a "standard" extraction method for the speciation of particulate metals.

PROPOSAL FOR A "STANDARD EXTRACTION METHOD" FOR THE SPECIATION OF PARTCULATE METALS

A "standard extraction method" should be relatively simple, in order to make routine analysis of large numbers of sediments possible, yet at the same time, it should provide sufficient information for a tentative assessment of the environmental impact of particulate metals. However, it should be clearly pointed out that the various extraction procedures (Table 1) are not as selective as sometimes stated. Readsorption of metals can occur[38]; reactions are influenced by the duration of the experiment, the temperature, and by the ratio of solid matter to volume of extractions.

Based on our experience and an evaluation of the literature we suggest the following procedure:

A. An extraction with acidified hydroxylamine hydrochloride. This extraction had originally been proposed for the selective dissolution of manganese compounds in soils and sediments[39]. It has been an inherent part of several extraction schemes[26,27,32]. The hydroxylamine step includes the extraction of exchangeable cations and of carbonate-bound metals.

B. An extraction with acidified hydrogen peroxide (30%). This method was originally used in soil extraction techniques[39]. The extraction should be followed by an extraction of ammonium acetate to remove any reabsorbed metal ions, a step as suggested by Engler et al.[42]

C. A total analysis ($HF/HClO_4$) of the residue remaining after the first two extractions.

The rather important "exchangeable phase" (as it represents very loosely bound trace metals and may regulate and/or reflect the composition of surface waters) is not included in this scheme. In determining the amount of exchangeable metal ions, an extractant is used which contains cations more strongly bound to the exchange positions as compared with the metals. Common extractants in use are $BaCl_2$, $MgCl_2$ and NH_4OAc (Table 1). Theoretically, after one or two extractions no more exchangeable metal should be released, since all the exchange sites have been "taken over". For calcium, which is mainly present in carbonates in the sediments used, the released amount reaches a constant value (Figure 3), due to the solubility of the carbonates in the extractant. The released amounts of manganese and nickel also reach a constant value due to the solubility of their metal compounds in the extractant. Magnesium alone reaches very low values, because it is mainly present in highly insoluble silicates[40].

Notable differences are found for the extraction with $MgCl_2$ and NH_4OAc; the former releases much more nickel and also more manganese, probably due to the formation of metal-chloride complexes in solution. Although the ion-exchangeable fraction of trace metals is still ill-defined[55], the ammonium-acetate solution seems to offer an acceptable compromise.

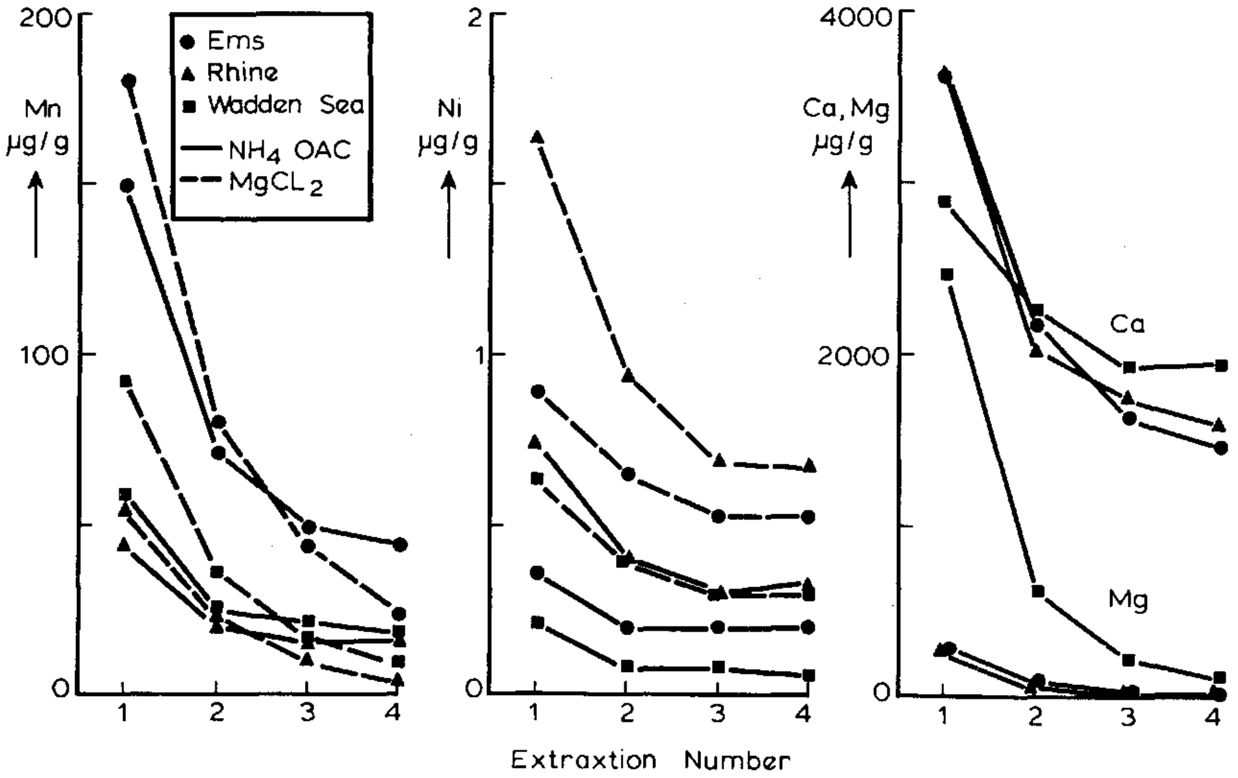


Figure 3: The amount of trace metals released after successive extractions with NH_4OAc and $MgCl_2$. For comparison data for magnesium and calcium are also given (extractions with NH_4OAc).

Comments on Other Extraction Procedures

In cases where sediments contain high concentrations of iron it may be advantageous to include additional acid-reducible extractive steps following the hydroxylamine extraction (Table 2) such as ammonium oxalate-oxalic acid and/or citrate-dithionite. The results of experiments with the citrate-dithionite agent on Rhine River and Wadden Sea sediments in Figure 4 indicate that significant amounts of arsenic, scandium, thorium and vanadium are still present in reducible phases after $NH_2OH{\cdot}HCl$ treatment; however, only small percentage of the heavy metals were found in the dithionite extract. Our experiments[54] on pelagic sediments and nodules rich in iron and manganese have shown that the ammonium oxalate-oxalic acid reagent[45] is particularly useful for the extraction of moderately reducible phases; considerable amounts of Fe, Cu, Zn, and Ni are released by this agent from all samples after $NH_2OH{\cdot}HCl$ treatment, whereas

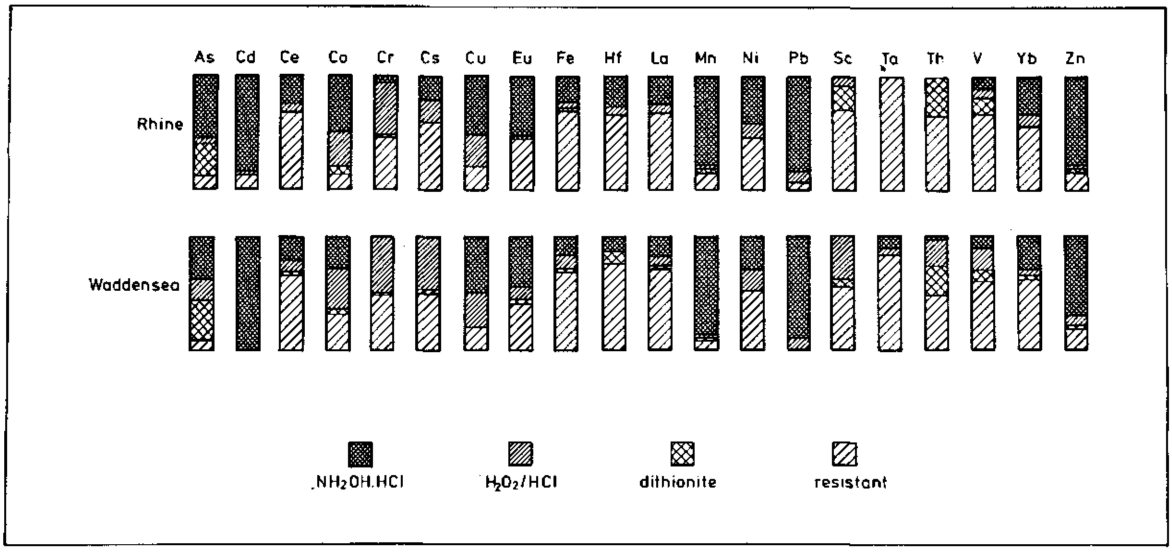


Fig. 4: Speciation of trace elements in samples from the Rhine River and from the Wadden Sea.

the subsequent extraction with citrate-dithionite is inadequate for additional release from the (fully authigenic) nodule material and only extracts significant amounts of iron, zinc, and manganese from the sediments. It seems that with the dithionite treatment copper is reduced to its less soluble univalent form; Gupta and Chen's[26] findings on Los Angeles harbour sediments, where copper is almost totally found in the residual fraction (despite strong anthropogenic enrichments),can possibly be explained by such effects.

Our experiments[54] have demonstrated characteristic effects of the solid/solution ratio. A too high solid content together with an increased buffer capacity may cause the system to overload, which is reflected by rising pH values in a time-dependent test with hydroxylamine-HCl (initial pH 2) and oxalate buffer (pH 3) solutions. Despite many difficulties with the carbonate extraction – reprecipitation under oxygenated conditions[46], adsorption of organic compounds on exchanger resin[15], pH effects on labile oxides – this step's one major advantage lies in the reduction of the samples' buffer capacity before the leaching of the remaining acid-reducible phases.

Extraction procedures with sodium hydroxide commonly used for the disintegration of humic and fulvic acids will no longer be applied in our leaching sequences due to the initial high pH conditions, which may promote the formation of basic metal hydroxides. Treatment with organic solvents (Table 1) are poorly suited for routine applications. The differentiation of organic and sulfidic metal associations is not as yet possible.

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