

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 high amounts of contaminated sediments for which safe disposal areas on land or in the aquatic environment have to be found.

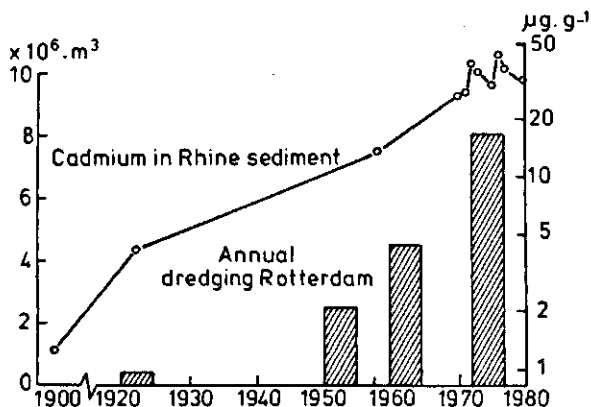


Figure 1: Increase in cadmium concentrations in Rhine sediments due to increased industrial use and the increase in annual dredging in the Rotterdam harbour due to harbour extension. Note that the cadmium concentrations are logarithmic.

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 manganese⁵.

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 fractions⁸. This method has subsequently been adopted for the study of heavy metals in sediments in Canada⁹ and in Norwegian fjords¹⁰. 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 matter⁹.

Chester and Hughes¹¹ 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 hydroxides¹³. 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 manipulations¹⁴. A single extraction method for the determination of trace metals associated with carbonates makes use of an acidic ion-exchanger¹⁵.

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 uptake¹⁷⁻²⁰.

Adsorption and cation exchange

Extractions with: BaCl³⁹, MgCl²⁴, NH₄OAc⁴²

Detrital/non-detrital; authigenous/lithogeneous fractions

Extractions with: EDTA⁶, 0.1 M HCl⁴¹, 0.3 M HCl¹⁴, 0.5 M HCl¹³, 0.1 M HNO₃⁴³

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

Extractions with (in approximate order of release of iron): Acidified hydroxylamine⁴⁴, ammonium-oxalate⁴⁵, hydroxylamine-acetic acid¹¹, dithionit-citrate¹³.

Carbonate phases

Extractions with: CO₂ treatment⁴⁶, acidic cation exchange¹⁵, NaOAc/HOAc (pH 5)²⁹

Organic phases; Humic and fulvic acids, solid organic material

Extractions with: H₂O₂³⁹, H₂O₂-NH₄OAc⁴², H₂O₂-HNO₃²⁶, organic solvents⁴⁷⁻⁵⁰, 0.5 N NaOH⁵¹, 0.1 N NaOH/H₂SO₄⁵², Na hypochlorite-ditionite/citrate²⁴

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" reagent¹¹, followed by an oxidizing step (30% H₂O₂)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 Columbia²¹, sediments from the Dead Sea in Israel²², and for sediments from Southern California²³. 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 harbor²⁶ 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

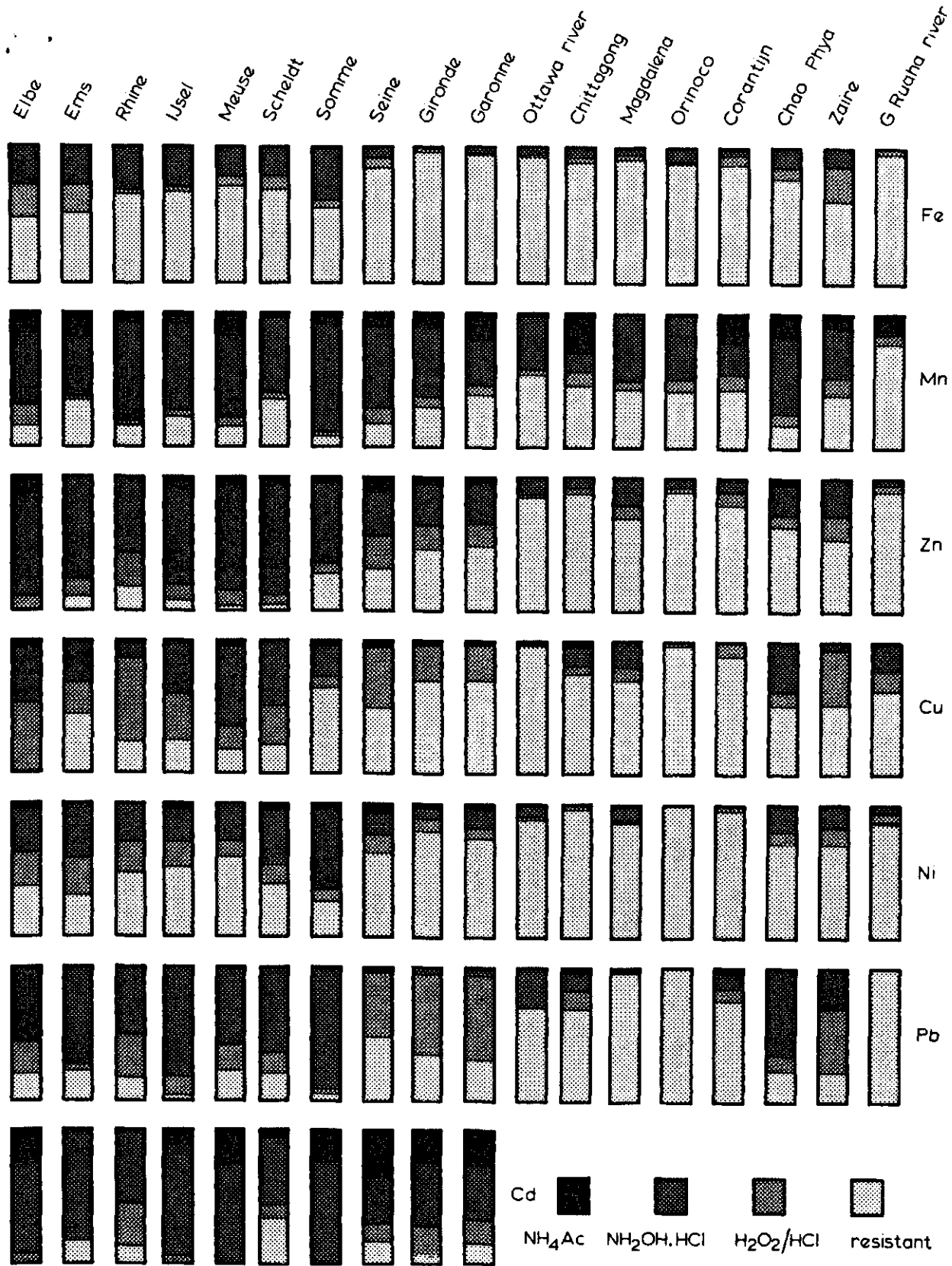


Figure 2: The speciation of trace metals in eighteen different river sediments. The rivers are arranged according to their approximate geographical position from north to south. Most tropical rivers contain low amounts of cadmium and here it was not possible to obtain a reliable speciation. For the Rio Magdalena and the Orinoco River, insufficient material was available for the determination of the exchangeable fractions; the acidified hydroxylamine 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 Michigan²⁸, the Yamaska and Saint Francois rivers in Canada²⁹, the Rio Grande³⁰, and Tokyo Bay³¹. 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 Sea³². 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-workers³³⁻³⁶. Examples of an elaborate fractionation scheme are presented in Tables 2 and 3.

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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 $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 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°) + 1 M NH_4OAc , pH 2
 - 7 Detrital silicates: HF/HClO_4 digestion
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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 data⁵⁴ 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.

Total conc. µg/g d.w.	Ni		Cu		Zn		Pb		Cd
	E-E	R-R	E-E	R-R	E-E	R-R	E-E	R-R	R-R
	42	84	26	209	227	922	66	144	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 Cu³⁵. 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 uptake³⁷.

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 PARTICULATE 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 occur³⁸; 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 sediments³⁹. 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 techniques³⁹. 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/HClO₄) 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 BaCl₂, MgCl₂ and NH₄OAc (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 silicates⁴⁰.

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-defined⁵⁵, the ammonium-acetate solution seems to offer an acceptable compromise.

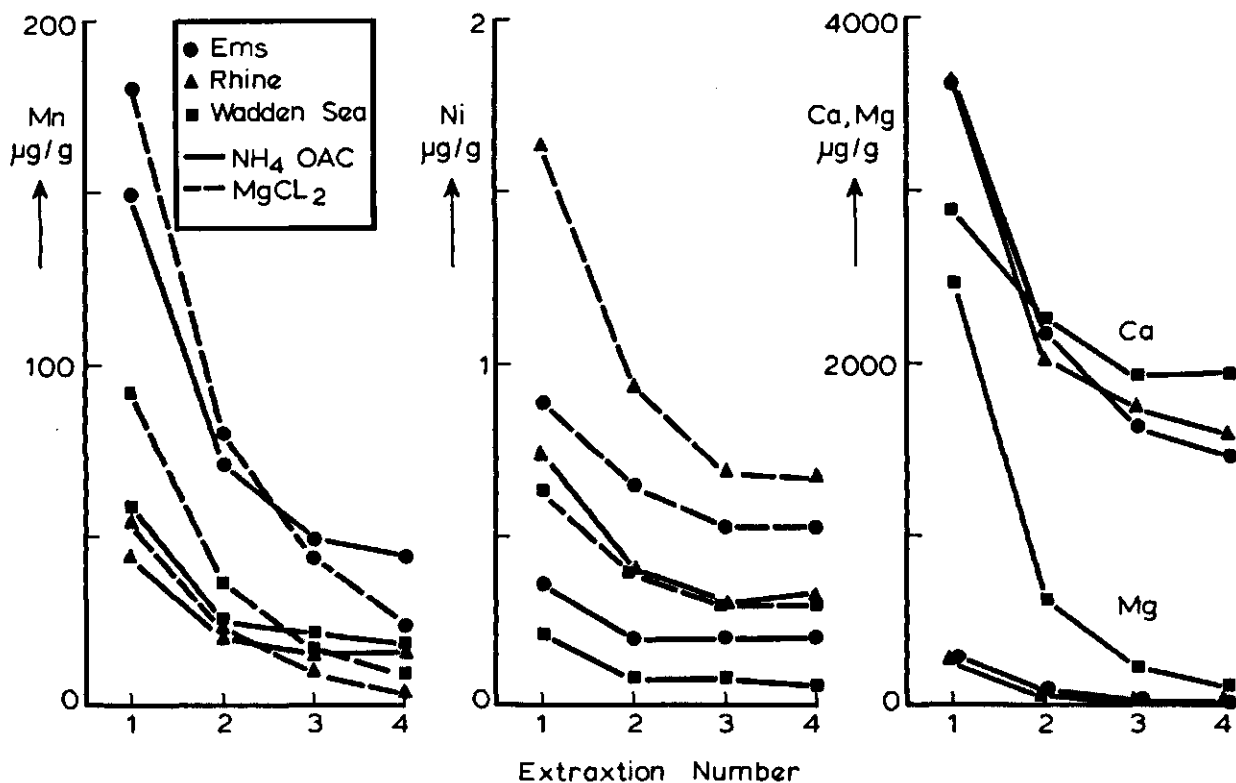


Figure 3: The amount of trace metals released after successive extractions with NH_4OAc and $MgCl_2$. For comparison data for magnesium and calcium are also given (extractions with NH_4OAc).

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 experiments⁵⁴ on pelagic sediments and nodules rich in iron and manganese have shown that the ammonium oxalate-oxalic acid reagent⁴⁵ 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

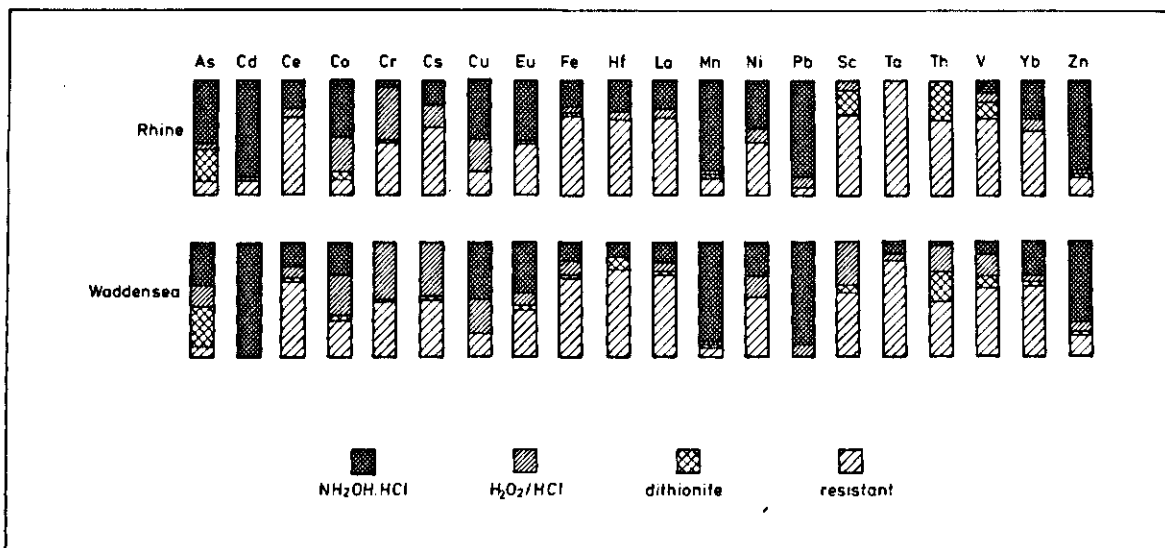


Fig. 4: Speciation of trace elements in samples from the Rhine River and from the Wadden Sea.

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's²⁶ 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 experiments⁵⁴ 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 oxalate-oxalic acid (initial pH 2) and citrate-dithionite (pH 3) solutions. Despite many difficulties with the carbonate extraction - reprecipitation under oxygenated conditions⁴⁶, adsorption of organic compounds on exchanger resin¹⁵, 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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