

## CHEMICAL EXTRACTION OF HEAVY METALS IN POLLUTED RIVER SEDIMENTS IN CENTRAL EUROPE

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### ABSTRACT

A five-step sequential extraction technique was used to determine the chemical association of heavy metals (Zn, Cd, Pb, Cu) with major sedimentary phases (exchangeable cations, easily and moderately-reducible compounds, organic/sulfidic phases, residual components) in samples from polluted rivers in Central Europe (Middle Rhine River, Lower Rhine/Rotterdam Harbor, Weser Estuary, Neckar River). Data gained suggest that the surplus of metal contaminants introduced into the aquatic system from anthropogenic sources usually exists in relatively unstable chemical forms. The more important accumulative phases for trace metals are found in the easily-reducible fractions. Extraction with acidified hydroxylamine solution seems to yield the metal fractions which may predominantly participate in short-term geochemical and biochemical processes. Rates of mobilization were significantly higher for zinc and cadmium than for copper and lead.

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### INTRODUCTION

The uptake of heavy metals by organisms occurs chiefly in the dissolved phase but in studying the concentration and availability of such trace substances, the interactions with solid phases must be considered with their mechanical and chemical processes such as bioturbation, sorption and desorption, diffusion and mobilization.

Availability of heavy metals depends greatly on the properties of the particle's surface, on the kind and strength of the bond and on external conditions such as pH, Eh, salinity and concentration of organic and inorganic complexation agents. The internal and external conditions may change during the transport of suspended particulate matter as well as during diagenesis after deposition as sediment. This process results in a still greater bonding strength which assists in the redistribution and remobilization of the heavy metals.

The relative bonding strength of metals in different phases can be determined through sequential extraction procedures. When combined with biological uptake data, these procedures could also enable estimation of the toxicity of metal pollutants. Although the determination of the relative bonding strength of metal ions is possible using chemical procedures, the correlation with the biological parameters is not yet satisfactory. The goal of this study was to establish a chemical extraction sequence for differentiating the major forms of metal associations in polluted river sediments.

The data were compiled from different research programs, e.g. on dredged sediments, suspended matter and bottom sediments from the Weser Estuary; on an intercalibration sample from the Rhine River supplied by the Federal Institute of Hydrology; on sediments from various locations in Rotterdam Harbor and on samples of Cd-contaminated mud dredged from the Neckar River, a tributary of the Rhine.

#### FORMS OF HEAVY METALS IN RIVER SEDIMENTS

Three groups of components occurring in fluvial systems are potentially able to enrich metals in the sediments [1,2]:

i) Detrital solids, which originate from weathering and erosion of soils and rocks as well as from anthropogenic sources, consist chiefly of inorganic particles such as clay minerals, metal oxidic carbonate, quartz and feldspar. These compounds are usually coated with hydrous manganese and iron oxides or with organic substances, which to a large extent affect the interaction processes [3].

ii) Endogenic fractions, which are substances originating from processes occurring within the water column, by precipitation, sorption, enrichment in organisms or organo-metallic interactions. Settling of particulates, filtering organisms and flocculation represent characteristic mechanisms for the enrichment of chemical compounds; endogenic processes are transitory, mainly as a result of the variation of the organic productivity.

iii) Diagenetic fractions, which consist of those substances that result from processes occurring within the sediments as a result of the decomposition of buried organisms.

Reactions in natural waters occur mainly on the interface water/solid phase. Influenced by the numerous components of which the solid matter consists, many variable and complex chemical interrelations exist which make it difficult to describe such a system in a standard way.

Table 1 summarizes the various mechanisms, products and substrates of metal enrichment and their estimated significance in aquatic systems; this scheme includes all major types of metal associations that occur in both natural and industrially-affected water systems.

### Diagenetic Reactions

Diagenetic reactions occur in sediment mainly as a result of the decomposition of buried organisms. Decomposition generally follows a definite succession in sediments depending upon the nature of the components supplying oxygen: oxygen consumption (respiration), nitrate reduction, sulfate reduction and methane formation. Environments corresponding to these processes are, respectively: oxic, post-oxic, sulfidic and methanic [12].

For the recognition of early diagenetic environments [13],  $\text{MnO}_2$ -type minerals constitute a good indicator of truly oxic conditions. Post-oxic (weakly reducing) conditions, which involve successively the reduction of nitrate, manganese and iron, are characterized by  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  silicates such as glauconite and the absence of sulfide minerals and minor organic matter. Sulfidic and methanic (strongly reducing) environments typically contain significant amounts of organic matter and either newly formed or pre-existing Fe minerals such as pyrite.

Oxic reaction conditions are predominant in river sediments. In estuarine regions these conditions could become post-oxic or reducing. Particulate matter precipitates in regions of maximum turbidity. The activities that occur in estuarine regions could be the source and cause of the release of heavy metals. Significant problems can be expected during dredging of such sediments, and especially if the sediments are applied to agricultural land.

### METHODS

Chemical extraction procedures have been used to differentiate chemical forms of metals in sediments. These procedures were applied on pelagic Mn/Fe deposits, particularly for the identification of diagenetic reactions [14, 15]. An acidified hydroxylamine hydrochloride buffer can be of advantage for the investigation of processes involved in the 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, both of which act as a reservoir for nodule formation [16].

Chemical fractionation of metal compounds was promoted by environmental studies, mainly for these phases of the sediment, dredged material or sewage substances, which "constitute the reservoir for potential subsequent release of contaminants into the water column and into new interstitial waters" [17] and are thus predominantly available for biological uptake [18]. The relative binding strength can be determined with the application of chemical extraction agents either singly or in sequence. Table 2 presents examples of chemical leaching reagents as presently employed for environmentally relevant metal investigations [19].

In spite of the clear advantages of a differentiated analysis over investigations of total sediment, it should be clearly pointed out that the various

TABLE 2.

Methods for the extraction of metals from major chemical phases in sediments.

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Adsorption and cation exchange

BaCl<sub>2</sub>-triethanoleamine, pH 8.1

MgCl<sub>2</sub>

Ammonium acetate, pH 7

Carbonate phases

CO<sub>2</sub> treatment of suspension

Acidic cation exchanger

NaOAc/HOAc buffer (pH 5)

Reducible phases (in approximate order of iron release)

Acidified hydroxylamine

Ammonium oxalate buffer

Hydroxylamine-acetic acid

Dithionite-citrate buffer

Organic fraction (including sulfides)

H<sub>2</sub>O<sub>2</sub>-NH<sub>4</sub>OAc (pH 2.5)

H<sub>2</sub>O<sub>2</sub>-HNO<sub>3</sub>

Organic solvents

0.1 M NaOH/H<sub>2</sub>SO<sub>4</sub>

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Examples from Gibbs [23]

extraction steps are not as selective as sometimes stated. The literature identifies the following problems:

- Labile metal phases could be transformed during sample preparation, which can occur especially for samples from reducing environments [20].
- Readsorption of metals can occur, and sometimes even precipitation [21].
- Reactions are influenced by the duration of the experiment, the temperature and by the ratio of solid matter to volume of extractant. Our experiments (Fig. 1 [16]) 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 pH values in a time-dependent test with hydroxylamine buffer (initial pH = 2) and oxalate/oxalic acid (pH 3) solutions.
- There are major objections to the use of BaCl<sub>2</sub>-triethanol amine [22] (the latter compound is used to raise the pH to 8.1) or MgCl<sub>2</sub> [23] for the determination of exchangeable trace metals: possible chelating effects of the organic agent and the formation of dissolved metal-chloro-complexes.
- Basic metal oxides may be formed during initially high pH conditions, e.g. for humic extraction, with sodium hydroxide or sodium pyrophosphate [24].

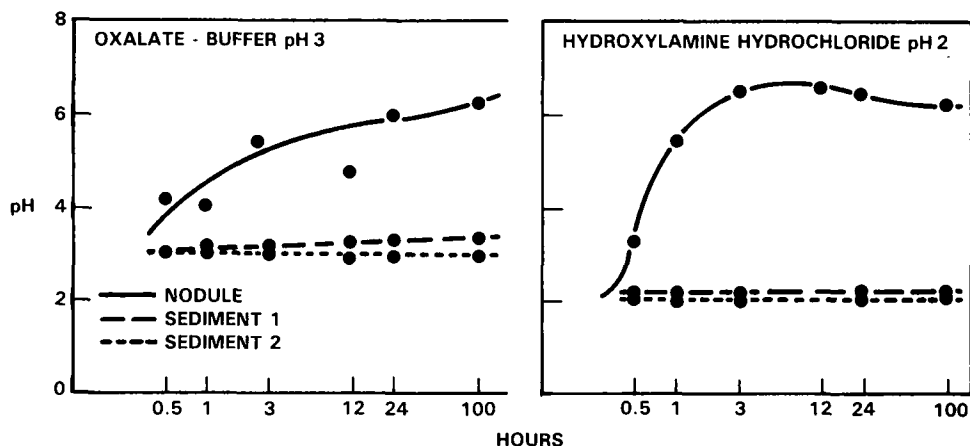


Fig. 1. Changes of pH values during chemical treatment of nodule and sediment material (Peru Basin /19/) with oxalate and hydroxylamine buffer solutions. Solid/solution ratio: 500 mg/50 ml.

- Difficulties occur with carbonate extractions: reprecipitation under oxygenated conditions following  $\text{Co}_2$  treatment [25], adsorption of organic compounds on exchanger resin [26], pH effects on labile oxyhydrates [27]. (However, the one major advantage of this step lies in the reduction of the sample's buffer capacity before the leaching of the remaining acid-reducible phases).
- Problems are encountered particularly with the utilization of the dithionite/citrate couple: contamination by metals, clogging of the burner during AAS-analysis, disproportionation of the reagent and sulfide formation [27].
- Treatment with hydrogen peroxide affects both labile as well as relatively stably bound metal components [28].
- Treatment with organic solvents (Table 2) are poorly suited for routine applications [19].
- The differentiation of organic and sulfidic metal associations is not yet possible [29].

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. This scheme including an additional step for exchangeable cations (although this fraction is still ill-defined, the ammonium acetate solutions seems to offer an acceptable compromise) was used to study the speciation of particulate trace metals in 18 different river systems, including major rivers in France, the Magdalene, Orinoco and Zaire Rivers in other countries, and in the

Ottawa River in Canada [19]. The results for European rivers in Fig. 2. show relatively small percentages for the ion-exchangeable fractions (maximum 30% for Cd, 7% for Zn), high concentrations in the hydroxylamine fraction for Zn, Pb (except for the Seine, Gironde and Garonne Rivers) and Cd, in the  $H_2O_2$  fraction for copper and in the residual fraction for nickel. There is an increase in the relative amount of metals present in the resistant (lithogenous) fraction for less polluted and unpolluted river systems.



Fig. 2. Speciation of trace metals in sediment samples from 10 rivers in Central and Western Europe. Analyses by W. Salomons [23].

The standard extraction scheme as proposed by Salomons and Forstner [19] comprising four steps (ammonium acetate - hydroxylamine hydrochloride pH 2 - hydrogen peroxide/ammonium acetate - conc. nitric acid) is still somewhat unsatisfactory later in the sequence as compared with  $H_2O_2$  leaching; the moderately reducible components are partially extracted and a part of the moderately reducible fraction, which may well originate to a certain extent from anthropogenic sources, is not extracted by these reagents. The same pertains to the method of Tessier et al. [27] which is similar to the procedure proposed here, except for the use of  $MgCl_2$  for cation exchange and the lack of a step concerning the moderately reducible phases. As to the question of biological availability, this aspect could very well be of secondary importance, concerning as it does relatively stably bound metal phases (see below). It appears, however, that for other fields of application, for example, the determination of origin and distribution as well as diagenetic effects, it is a valuable additional extraction step for moderately reducible metal components.

Keeping the above considerations in mind, we introduced the application of the Schwertmann [30] oxalate buffer reagent directly after leaching with acidified hydroxylamine hydrochloride and while maintaining as good a practicability as possible, we suggest the following scheme:

- Step I: Exchangeable cations - 1 M ammonium acetate, pH 7, solid/solution ratio 1:20, 2 hrs shaking;
- II: Easily reducible phases (Mn oxides, partly amorphous Fe-oxyhydrates and carbonate phases - 0.1 M  $NH_2OH \cdot HCl$  + 0.01 M  $HNO_3$ , pH 2, dilution 1:100, 12 hrs shaking;
- III: Moderately reducible phases (e.g. amorphous and poorly crystallized Fe oxyhydrates) - 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3, dilution 1:100, 24 hrs shaking time;
- IV: Organic fraction, including sulfides - 30%  $H_2O_2$  +  $HNO_3$ , pH 2, 85°C, extracted with 1 M ammonium acetate, dilution 1:100, 24 hr shaking;
- V: Residual fraction - concentrated  $HNO_3$ , 180°C, dilution 1:100.

Apart from this experiment on river sediments, this scheme has been applied to demonstrate the relative mobility of particle-associated trace metals in sewage materials [31], in sediments affected by acid rain [32] and in sand filter column experiments [33]. The river sediment samples consisted of material that was in all cases of clayey silt texture. It was homogenized and freeze-dried before extraction.

## RESULTS AND DISCUSSION

Table 3 summarizes the data of 8 selected examples from the Weser, Rhine and Neckar Rivers and from Rotterdam Harbor which were treated according to the five-step extraction scheme described above.

TABLE 3

Sequential chemical extraction of metals from polluted sediments (percent extracted; underlined: total contents)

Samples <sup>a</sup>		Weser Estuary			Rhine R.		Rotterdam H.	Neckar R.	
		1	2	3	4	5	6	7	8
	Step	<u>272</u>	<u>546</u>	<u>350</u>	<u>921</u>	<u>153</u>	<u>1130</u>	<u>3072</u>	<u>610</u>
Zinc	I	5	4	4	10	4	1	5	3
	II	49	43	45	35	23	59	85	48
	III	33	38	38	34	50	37	7	34
	IV	2	1	2	8	5	1	1	2
	V	11	14	12	13	18	3	2	13
		<u>3</u>	<u>4.3</u>	<u>2.6</u>	<u>9.0</u>	<u>1.8</u>	<u>7.9</u>	<u>18.1</u>	<u>33.6</u>
Cadmium	I	8	18	18	27	17	16	12	13
	II	32	49	47	42	67	60	61	64
	III	45	14	24	2	1	16	13	10
	IV	12	17	9	17	11	6	12	12
	V	3	2	2	12	5	2	2	1
		<u>23</u>	<u>45.7</u>	<u>26.7</u>	<u>202</u>	<u>42.8</u>	<u>1062</u>	<u>191</u>	<u>242</u>
Copper	I	1	1	1	3	2	9	3	3
	II	<1	1	<1	<1	<1	47	<1	<1
	III	57	60	57	48	79	37	80	72
	IV	1	1	1	15	7	4	4	9
	V	41	38	41	34	12	3	13	16
		<u>63.7</u>	<u>104</u>	<u>69.0</u>	<u>118</u>	<u>35.1</u>	<u>256</u>	<u>203</u>	<u>150</u>
Lead	I	1	1	2	<1	<1	<1	<1	<1
	II	2	1	2	1	3	66	1	2
	III	56	41	41	39	46	18	19	22
	IV	2	5	2	5	11	1	22	28
	V	39	53	53	54	40	15	58	48

<sup>a</sup>

- 1 - dredged sediment
- 2 - suspended sediment
- 3 - bottom sediment
- 4 - standard sample BfG
- 5 - sample No 3 Broekpolder
- 6 - sample No 2 Broekpolder
- 7 - dredged sediment Lauffen/Neckar



In comparison with the 4-step standard extraction scheme [19] the portion of metals in the hydrogen peroxide step clearly decreases after the oxalate buffer has been applied. However, it appears that the organically bound portion of most metals in "normal" river sediments has been overestimated [34, 35]. On the other hand, data from sewage materials, using the same extraction sequence, indicate significantly higher percentages of metals in the peroxide fraction than was found for the sediments [31].

For all metal examples, a clear decrease of the residual component (step V) is shown with increasing overall metal concentrations. These data suggest that the surplus of metal contaminants introduced into the aquatic system from anthropogenic activities usually exist in relatively unstable chemical forms and should, therefore, be more accessible for short- and middle-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. Thus, the processes of metal enrichment in solid substances are insignificant. The most important enrichment phases in sediments are apparently the easily and moderately reducible components, e.g. Fe/Mn oxyhydrates. It is assumed that relatively high enrichment rates occur in carbonate phases upon heavier metal pollution [22]; these phases are also included in the present sequence of acidified hydroxylamine hydrochloride treatment.

There is a marked difference between the low extractability in steps I and II (ammonium acetate and acidified hydroxylamine) of the metal pair Cu-Pb and good extractability of the pair Zn-Cd. Studies on the mobility of heavy metals in sludge-amended soils with step-by-step acidification of soil-water suspensions showed the same sequence [36]. Soil experiments with weak extraction agents: ammonium acetate, ammonium nitrate, 0.05 M HCl and 0.1 M HCl - show a better correlation for cadmium and zinc to metal uptake in plants than, for example, for lead [37, 38].

Since there are various processes which may affect both the release and uptake 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 behavior under certain environmental conditions.

The estimation of bioavailability can only be performed by combination of chemical extraction and biological experiments, the latter using specific organisms. A comprehensive discussion was given by Jenne and Luoma [39] and Luoma and Bryan [40, 41, 42]. These studies indicate that the bioavailability of heavy metals was inversely related to the strength of metal-particulate binding in the sediments. Despite many unanswered questions this new approach may be useful as "a statistical interface between more sophisticated chemical and biological models" [40].

The important extraction mechanisms with which plant roots actively participate in the removing of nutrients from soil include redox [43], pH alteration [44] and organic complexing [45] processes. From the simulation of these basic mechanisms, which could vary greatly according to plant or soil type and climatic conditions, it is possible to make conclusions to the biological availability. For complexing processes from soil, the DTPA reagent introduced by Lindsay and Norvell [46] appears to be a good indicator of the reservoir of labile metal compounds. Its disadvantage lies in its poor phase specificity.

In our present extraction sequence the treatment with ammonium acetate gives the easiest available fraction. The subsequent acidified hydroxylamine treatment includes those metal portions occluded in a Mn-oxide matrix that may be released during redox changes. In the third stage (oxalate buffer) the simulated dissolution of iron compounds in comparison may amount to a relatively small portion during normal metabolic processes.

The potential processes of metal released from polluted sediments may play a role under the following conditions:

- influence of increasing salinity in estuaries
- pH alterations, locally caused by acid mining effluents or caused by acid rain in carbonate poor regions
- redox changes
- influence of natural and synthetic organic complexing agents.

In the estuarine environment the easily-exchangeable fraction might be affected; pH alterations influence according to the strength of the exchangeable, easily-reducible, and, occasionally, parts of the moderately-reducible fraction. Redox changes under post-oxic conditions concern the easily-reducible fraction, e.g., nitrate and manganese reduction. In strongly reducing environments the moderately-reducible fraction is of concern too, if the compounds are present as coatings and not lattice bound. The influence of organic complexation and interaction with solid organic materials is still a matter of controversy.

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