

CHEMICAL SPECIATION OF HEAVY METALS IN SOLID WASTE MATERIALS (SEWAGE SLUDGE, MINING WASTES, DREDGED MATERIALS, POLLUTED SEDIMENTS) BY SEQUENTIAL EXTRACTION

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ABSTRACT

Sequential extraction techniques are used to determine the chemical associations of heavy metals with specific solid phases, whereby the potential availability of toxic compounds in waste materials for biological uptake and possible remobilization effects into the aqueous phase may be estimated.

INTRODUCTION

The bonding of metals in particulate matter can be the result of the following mechanisms: (i) Heavy metals are transported and deposited as major, minor, or trace constituents in the detrital minerals of rocks and soils, in organic residues, and in solid waste material. The composition of the clay fraction is of prime importance for the natural background levels of fine-grained sediments. Three major types of detrital accumulative patterns can be distinguished: Most metal in "conglomerate" particles, i.e. in aggregates of ultrafine ($<1\mu\text{m}$) particles, most metal in the heavy mineral sub-fraction, and metal distributed over all subfractions¹. (ii) Sorption and cation exchange takes place on fine-grained substances with large surface areas. A generalized sequence of the capacity of solids to sorb heavy metals was found to occur in the order: manganese oxides \gt humic acids \gt hydrous iron oxides \gt clay minerals.² (iii) A rise in pH and the oxygen content - e.g. in the estuarine mixing zone - promotes the formation of metal hydroxides and carbonates. Hydrous Fe/Mn-oxides constitute significant "sinks" of heavy metals by the effect of co-precipitation³ (iv) In waters rich in organic matter solubilization and release of heavy metals is achieved by the combined processes of complexation and reduction⁴; incorporation into the sediment involves the mechanisms of adsorption, flocculation, polymerization, and precipitation⁵.

Since the availability of trace metals for metabolic processes is closely related to their chemical species in particulate matter, the type of chemical association between metals and sediment constituents has become of interest in connection with problems arising from the recovery and disposal of waste material. Chemical extraction procedures from soil studies⁶ and sedimentary geochemistry⁷, and on recent deposits of less polluted aquatic environments⁸ have been developed enabling the estimation of the toxicity potential of a sediment⁹. The basic rationale of these studies is that the non-lithogenic fractions of the sediment, dredged material, or sewage substances constitute "the reservoir for potential subsequent release of contaminants into the water columns and into new interstitial waters"¹⁰, thus being predominantly available for biological uptake. Criteria to predict the pollution potential of these substances must reflect the sediment fraction that has a detrimental effect on water quality and the associated biota¹¹.

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METHODS

The various single leaching steps (examples in Table 1) are combined into sequences of increasingly stronger extraction reagents. In that respect, the differentiation of oxidizable, reducible, and residual phases on polluted sediments near a sewer outfall of Los Angeles County was made by Bruland et al.²³.

Table 1 Methods for the extraction of metals from chemical phases in solid matter¹².

Adsorption and cation exchange

BaCl₂-triethanole-amine pH 8.1 (6)
MgCl₂ (8)
ammonium acetate, pH 7 (13)

Carbonate phases

CO₂-treatment of suspension (14)
acidic cation exchanger (15)
NaOAc/HOAc-buffer (pH 5) (16)

Reducible phases (in approximate order of release of iron)

hydroxylamine + 0.01 M HNO₃ (17)
ammonium oxalate buffer (18)
dithionite-citrate buffer (19)

Organic phases (incl. sulfides)

H₂O₂ - ammonium acetate pH 2.5 (13)
H₂O₂ - nitric acid (20)
organic solvents (21)
0.1 M NaOH (humic acid extract) (22)

Engler et al.¹³ devised a selective extraction procedure to functionally separate interstitial water, exchangeable, easily reducible, moderately reducible, organic and residual fractions from marine and fresh water sediments. The procedure precludes atmospheric oxidation at sensitive steps (during sampling, and during extraction of interstitial water, exchangeable and easily reducible phases.

Further modification of the Engler's scheme was performed by Gupta and Chen²⁰ and applied on sediments from Los Angeles Harbor. It is obvious from these studies and from the analyses performed by Brannon et al.²⁴ on harbor sediments from Mobile Bay, Alabama, Ashtabula on Lake Erie, and Bridgeport, Conn., that as the metal levels in the sediments rise (usually pointing to a rise in metal pollution) the metal concentrations in the residual fraction decrease. It can therefore be assumed that the additional metals which are carried into the

water systems are in relatively instable bonding forms.

Problems are raised by the utilization of the dithionite-citrate couple¹⁶: (i) Dithionite is highly contaminated with metals and its purification proves difficult; (ii) frequent clogging of the burner is observed upon analysis of the aqueous extracts by flame atomic absorption spectroscopy due to the high salt content of the extraction solution; (iii) sulfide is formed as a result of the disproportionation of dithionite. Gupta and Chen's²⁰ findings on Los Angeles Harbor sediments, where copper is almost totally found in the residual fraction - despite strong anthropogenic enrichments - can possibly be explained by the latter effects. We propose replacing the dithionite/citrate extraction step for analysis of moderately reducible fractions (including all non-silicate iron) by Schwertmann's¹⁸ oxalate buffer reagent, which has successfully been tested by Heath and Dymond²⁵ in their comparative study on metalliferous sediments from the East Pacific Rise. We have inserted this step before the hydrogen peroxide extraction, due to the possibility of reduction effects of the latter.

Extraction sequences related to Engler's¹³ above-mentioned scheme have been used for the speciation of particulate metals in Lake Michigan²⁶ and the Rio Grande²⁷, as well as on sediments from Tokyo Bay²⁸. Sequential leaching by 1 M MgCl₂, dithionite buffer, hydrogen peroxide, and analysis by neutron activation was employed by Shuman et al.²⁹ on suspended particulates from control and polluted stations within a small drainage area of the Haw River,

North Carolina. Eisenreich et al.³⁰ studied the transport phases of dissolved and particulate metals in the upper Mississippi River. Their extraction scheme included 0.5 N MgCl₂ for exchangeable cations, 0.4 N sodium pyrophosphate for metals bound to particulate organics and 0.3 M HCl for the determination of metal oxides. Förstner and Patchineelam³¹ used the sequence of 0.2 N BaCl₂-triethanole-amine - 0.1 M NaOH - acidic cation exchanger - acidified hydroxylamine hydrochloride - H₂O₂/ammonium acetate - hydroxylamine/ acetic acid for their investigations of sediments from the Rhine River and from the German North Sea³². However, sorption/desorption experiments with copper and clay minerals have shown that true cation exchange (with BaCl₂) is relatively insignificant and that the triethanole-amine reagent (added to raise the pH of the solution) effects the release of additional metal compounds, which may be more appropriately designated as easily extractable phases³³. It has been shown by Burton³⁴ that while a solution of sodium pyrophosphate and sodium hydroxide powerfully attacks humic materials, the reagent as generally employed also attacks silicates to an appreciable degree. One of the major gaps in this kind of work presently is in the partitioning of metals in anoxic sediments as no extraction procedure is yet available to differentiate organic and sulfidic metal associations³⁵.

It should be clearly pointed out that the various extraction procedures are not as selective as sometimes stated. Readsorption of metals can occur³⁶, reactions are influenced by the duration of the experiment, the temperature, and by the ratio of solid matter to volume of extractant. Our experiments have demonstrated that 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 hydrochloride buffer (initial pH = 2) and oxalate/oxalic acid (pH 3) solutions³⁷.

Unfortunately there is a proliferation of extraction schemes, making an intercomparison of results difficult, if indeed not impossible. However, presently sufficient information and experience with different extraction techniques is available for a variety of sediments to propose a "standard" extraction method for the speciation of particle-associated trace metals. Based on an evaluation of the literature Salomons and Förstner¹² suggested 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 has been an inherent part of several extraction schemes on sediments. It also reflects the portion of elements which can be dissolved under the effect of minor redox gradients during diagenesis of metalliferous deep-sea sediments³⁷. The hydroxylamine step includes the reextraction of exchangeable cations and of carbonate-bound metals.
- B. An extraction with acidified hydrogen peroxide (30%). This method was originally used in soil extraction techniques⁶. The H₂O₂-treatment should be followed by an extraction of ammonium acetate to remove any readsorbed metal ions, a step as suggested by Engler et al.¹³.

The rather important "exchangeable phase" (important as it represents very loosely bound trace metals and may regulate and/or reflect the composition of the aqueous phase) is not included in this scheme. Although the ion-exchangeable fraction of trace metals is still ill-defined, the ammonium acetate solution seems to offer an acceptable compromise¹². Prior to the determination of exchangeable cations, the total water soluble and soluble complexed metals can be extracted and analyzed^{38,39}. The standard extraction scheme was employed in the speciation of particulate trace metals in 18 different river systems, including major rivers in France, the Magdalene, Orinoco, Zaire Rivers, and in the Ottawa River. In nearly all river systems the reducible phase is an important sink for trace metals.¹²

In addition to providing information on availability, chemical speciation data can also indicate the source of metal enrichments in sediments. We have investigated two areas from the region Wiesloch/Leimen south of Heidelberg, where synchronous problems with thallium have been encountered in plants⁴⁰. The source of the enrichment near Wiesloch was a lead-zinc mine that had been worked since the Middle Ages to be completely closed only in 1954. A portion of the waste material from this site was relatively widely spread, also reaching agricultural land. Such was the case for the Tl-emissions of a cement plant near Leimen (ca. 5 km further north) that had used sulfidic roasting residues as additives to special cements. Results of extraction experiments using 1 M ammonium acetate on soil samples from both areas show characteristic and statistically highly significant differences. Whereas the average extractable portion of 14 soil samples from the mine area was in the range $4.4 \pm 2.7\%$, the average values of soil in areas affected by the cement plant emissions (n=25) attained values of $17.5 \pm 10.7\%$ extractable with ammonium acetate (pH 7). The lower absolute concentrations in the latter area were therefore more available, leading also in some cases to increased concentrations of thallium in plants⁴⁰.

A direct consequence of these heavy metal problems south of Heidelberg was that a greater number of soil and sediment samples were then investigated with the standard extraction sequence¹². Selected data for zinc, cadmium and lead are presented in Table 2 for a sediment sample from (A) an unpolluted river sediment ($\leq 63\mu\text{m}$), (B) sediment from the above-mentioned mining area, (C) a soil sample near a former ore washery⁴¹, and (D) sediment downstream of a purification plant in which earlier problems with cadmium had been encountered⁴². The data showed that for all three metals the exchange-

Table 2 Chemical extraction studies on sediment and soil samples from the former mining area near Wiesloch (Baden/FRG). Reagents see Table 3
 Sample A: Unpolluted sediment from Leimbach upstream from Baiertal
 Sample B: Sediment affected by mining waste - Leimbach/Altwiesloch
 Sample C: Soil sample near the former lead-zinc mine (Wiesloch-NE)
 Sample D: River sediment from Landgraben/Leimbach - sewer outflow

	zinc				cadmium				lead			
	A	B	C	D	A	B	C	D	A	B	C	D
total(ppm)	230	3019	9450	1019	1.2	16.2	91.6	45.9	46.2	85.5	340	178
NH ₄ OAc (I)	5	3	1	3	6	1	2	3	1	1	4	1
NH ₂ OH (II)	32	13	36	26	34	4	23	26	1	2	9	1
H ₂ O ₂ (IV)	31	64	43	25	47	47	27	41	2	5	67	1
HNO ₃ conc (V)	32	20	20	46	13	48	48	30	96	92	20	97

able portion is relatively small. However, as middle-term reactions of the easily reducible component between soils and plants can well occur, the relatively high portion of zinc and cadmium in the fraction II of samples B, C, and D is of concern if it should reach agricultural land⁴³. Whether or not and to what extent the component extractable with H₂O₂ actually is part of such reactions is unknown - the organic metal fractions contain as much stably bound as relatively mobilizable components⁴⁴. It is assumed here that the high portion of zinc and cadmium in samples B and C and of lead in sample C represent the sulfidic-bound portion and is less probably in association with organic substances. On the other hand it may be that the H₂O₂ extractable parts of zinc and cadmium in sample D reflect the association with organic material, indicating the influence of the purification plant located upstream.

The present extraction sequence can probably be justified by the graduation of easily available components (exchangeable with ammonium acetate) and the short- to middle-term available metal portions (easily reducible fraction, including the carbonate phases). The standard method is still somewhat unsatisfactory later in the sequence as with H_2O_2 leaching, the moderately reducible components are also partially extracted on the one hand, and a part of the moderately reducible fraction, which may well be partly from anthropogenic sources, is not extracted by these reagents on the other. As to the question of biological availability, this aspect could very well be of secondary importance, concerning as it does relatively stably bound phases. It appears, however, that for other fields of application, for example the determination of origin and distribution as well as of the diagenetic effects, it is a valuable additional extraction step for moderately reducible metal components. We introduced the application of the Schwertmann¹⁸ oxalate buffer reagent directly after leaching with acidified hydroxylamine hydrochloride. In the present volume we showed examples from sand filter columns⁴⁵ and core sediments from lakes affected by acid rain⁴⁶, where this sequence was used to demonstrate the relative mobility of particle-associated trace metals.

In Table 3 examples were selected from other research programmes, e.g. on dredged sediments, suspended matter and bottom sediments from the Weser Estuary (1-3) in the framework of a project sponsored by the Federal Ministry of Research and Technology⁴⁷. The sediment sample from the Rhine River is an intercalibration sample of the Federal Institute of Hydrology (4), the study of metal associations in contaminated river sediments (5-8) and in sewage sludges (9-13) is in a program sponsored by the German Research Council^{41,42,48}. Here too (as in the data from the standard extraction) 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 (also for Cr, which is not listed in Table 3) and good extractability of Zn-Cd. Studies on the mobility of heavy metals in sludge-amended soils with step-by-step acidification of soil-water suspensions⁴⁹ showed the same sequence. The present extraction experiments show for all metal examples a clear decrease of the residual component (step V) with increasing overall metal concentration. In comparison with the standard extraction (Table 2) the portion following in the H_2O_2 extraction clearly decreases after the "oxalate-buffer" extraction has been applied. The organically bound portions of Cu and Pb are clearly enriched in the sewage sludges in comparison with the sediment specimen. Three samples (Table 3) deviate: Rotterdam Hr. (6) with relatively higher portions of copper and lead in the easily extractable fraction; the same is true for the sewage sludge sample No. 12 that still shows a remarkable high portion of exchangeable cadmium. Another sewage sludge sample (11) is notable for its low portion of cadmium and zinc in the easily reducible fraction. The source of these effects as well as the possibility of a chemical assessment system on the basis of these differentiations will be investigated further.

ACKNOWLEDGEMENTS

We would like to show our appreciation to Dr. W. Salomons, Delft Hydraulics Laboratory, Haren Branch, for his cooperation in the development of methods. T. Zapf and U. Nagel aided in sediment analyses (Nos. 5-8, Table 3). The Ministry of Environment of State of Baden-Württemberg, the Federal Ministry of Research and Technology as well as the German Research Council supported our studies financially. Mr. D. Godfrey helped prepare the English version of this abstract.

Table 3 Sequential chemical extraction of metals from polluted sediments and sewage sludges (percent extracted; underlined: total content)

Step I: Exchangeable cations - 1 M ammonium acetate, pH 7, solid/solution-ratio 1:20, 2 hrs shaking

Step II: Easily reducible phases (Mn oxides; partly amorphous Fe oxyhydrates) and carbonate phases - 0.1 M NH₂OH·HCl + 0.01 M HNO₃, pH 2, dilution 1:100, 12 hrs shaking

Step III: Moderately reducible phases (e.g. poorly crystallized Fe oxyhydrates) - 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3, dilution factor 1:100, 24 hrs shaking time

Step IV: Organic fraction, incl. sulfides - 30% H₂O₂ + HNO₃, pH 2, 85°C, extracted with 1 M ammoniumacetate, dilution factor 100, 24 hrs shaking

Step V: Residual fraction - conc. HNO₃, 180°C, 1:100

	<u>Weser Estuary</u>			<u>Rhine R./Rotterdam</u>				<u>Neckar</u>	<u>Sewage sludges (activ.)</u>				
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
<u>Zinc</u>	<u>272</u>	<u>546</u>	<u>350</u>	<u>921</u>	<u>153</u>	<u>1130</u>	<u>3072</u>	<u>610</u>	<u>1267</u>	<u>6064</u>	<u>2998</u>	<u>830</u>	<u>1791</u>
I	5	4	4	10	4	1	5	3	4	3	1	12	7
II	49	43	45	35	23	59	85	48	69	68	19	44	49
III	33	38	38	34	50	37	7	34	14	20	65	16	25
IV	2	1	1	8	5	1	1	2	7	6	12	19	15
V	11	14	12	13	18	3	2	13	6	3	3	9	4
<u>Cadmium</u>	<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>	<u>1.8</u>	<u>8.5</u>	<u>9.5</u>	<u>9.7</u>	<u>41.8</u>
I	8	18	18	27	17	16	12	13	17	1	41	45	9
II	32	49	47	42	67	60	61	64	61	67	1	39	64
III	45	14	24	2	1	16	13	10	6	5	14	2	9
IV	12	17	9	17	11	6	12	12	11	26	80	10	18
V	3	2	2	12	5	2	2	1	5	1	5	3	41
<u>Copper</u>	<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>	<u>516</u>	<u>446</u>	<u>236</u>	<u>421</u> *	<u>478</u>
I	1	1	1	3	2	9	3	3	9	3	1	5	16
II	41	1	41	41	41	47	41	41	5	1	41	46	41
III	57	60	57	48	79	37	80	72	63	43	3	32	51
IV	1	1	1	15	7	4	4	9	16	43	82	13	27
V	41	38	41	34	12	3	13	16	7	10	14	4	6
<u>Lead</u>	<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>	<u>110</u>	<u>167</u>	<u>204</u>	<u>244</u>	<u>449</u>
I	1	1	2	41	41	41	41	41	41	41	41	14	1
II	2	1	2	1	3	66	1	2	11	2	1	55	2
III	56	41	41	39	46	18	19	22	29	25	36	25	18
IV	2	5	2	5	11	1	22	28	16	58	37	4	66
V	39	53	53	54	40	15	58	48	44	15	26	1	13
dredged sediment				standard sample BFG	sample No 3 Broekpolder	sample No 1 Broekpolder	sample No 2 Broekpolder	dredged sed. Lauffen/N.	Landau/Pfalz 1.4.1980	Landau/Pfalz 29.4.1980	Heidelberg 5.2.1981	München 7.8.1979	München 20.7.1979

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