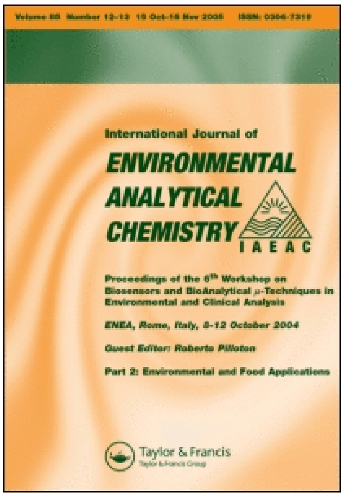

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Estimated Solid Phase Distribution of Metals Released in the Acid Extractable and Reducible Steps of a Sequential Extraction

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ESTIMATED SOLID PHASE DISTRIBUTION OF METALS RELEASED IN THE ACID EXTRACTABLE AND REDUCIBLE STEPS OF A SEQUENTIAL EXTRACTION

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The distribution of metals as determined by means of sequential extraction does not necessarily reflect their association with discrete sediment phases, but is operationally defined by the method of extraction. Sequential extraction was performed on a sediment as such and after extraction with NH_4OAc-EDTA to remove sorbed and complexed metal forms. From the data, we estimated a presumed solid phase distribution of the metals released in the acid extractable and reducible fractions. The metal fractions were subdivided in (1) sorbed, (2) carbonate associated and (3) ironoxihydroxide associated metals. Metals, associated with ironoxihydroxides, but extracted in the acid extractable fraction, were negligible. An important portion (10 to 25%) of the reducible fraction was estimated to consist of metals associated with carbonates, not released during the previous acid extractable step. In both sequential fractions, a significant portion (at least 10%) of the metals was identified as sorbed, rather than specifically associated with carbonates or iron-manganese oxihydroxides.

KEY WORDS: Heavy metals, fractionation, speciation, sequential extraction, sediment.

INTRODUCTION

For the fractionation of solid phase associated elements, either single or sequential extraction techniques are applied[1–4]. The application of sequential extraction has been subjected to much controversy. Non-selectivity of the extractants and redistribution of trace element among phases during extraction are the main problems of sequential extraction procedures[5–14]. Serious redistribution effects (Pb, Cu) and non-selectivity (Zn) have been observed in experiments with synthetic sediments[9,10,15,16] and with spiked metals in uncontaminated sediments[5]. These validation studies point out the importance of sample to sample differences. They argue against the indiscriminate use of selective extractions and the operationally defined phase associations[17]. Despite all these restrictions, sequential extraction has proved to be useful in the field of environmental analytical chemistry[4,18].

According to the frequently applied scheme of Tessier *et al.*[19], metals are categorised as "exchangeable", "bound to carbonates", "bound to iron and manganese oxides", "bound to organic matter" and "residual". The distribution of a metal, however, does not

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necessarily reflect its association with discrete sediment phases, but is operationally defined by the method of extraction[20]. We will therefore designate these fractions as "exchangeable", "acid extractable", "reducible", "oxidisable" and "residual", respectively.

A sediment was treated with NH_4OAc-EDTA to remove sorbed and complexed metals. On both the untreated and the NH_4OAc-EDTA-extracted sediments, sequential extraction was performed. From the data, we estimated a presumed solid phase distribution (sorbed, associated with carbonates, associated with Fe-oxides) of the metals, released in the acid extractable and reducible fractions.

MATERIALS AND METHODS

Sample characteristics

A sediment sample from the Scheldt estuary (Table 1) was used for the experiments. Sample preservation (e.g. freeze drying, oven drying) critically influences the results of sequential extraction[20]. It was intended to evaluate the performance of the analytical technique rather than to study the actual speciation of the reduced sediment. To avoid the problems related with handling and conservation of wet, reduced sediment samples, the experiments were performed on the 120°C dried sample.

The sediment pH was measured potentiometrically in a suspension of 10 g sediment in 50 mL distilled water after 12 hrs. The buffering capacity was read from a titration curve, obtained by adding constant volumes of standardised 0.1 or 0.01 mol/L HCl to a sediment suspension (10 g sediment in 50 mL of distilled water).

The sample was dried during 12 hrs at 120°C and ground to pass a 2 mm sieve. Carbonate content was determined by back titration of an excess of 0.5 mol/L HCl added to one gram of the sample with 0.5 mol/L NaOH[21]. Organic matter was estimated by the Walkley-Black method and converted $(2 \times C)$[22] to percent organic matter[23]. Particle size fractionation was performed with dry and wet sieving techniques[24].

Sequential extraction

The sediment was sequentially extracted according to the Tessier method[19], except that the exchangeable fraction was omitted. The residual fraction was determined after aqua regia destruction of the residue[25]. The extractions were performed on three gram air dry

Table 1 Characteristics of the sediment studied.

Granulometry (%)	
0–2 µm	36.2
2–50 µm	41.1
> 50 µm	22.7
pH-H_2O (1:5)	7.7
Buffering capacity to pH 4.3 (mmol H^+/kg dry sediment)	3090
Organic matter (%)	6.5 ± 0.1[a]
$CaCO_3$ (%)	16.2 ± 0.7[a]

[a] Mean ± standard deviation of 3 replicates.

sediment in a 250 mL polyethylene centrifuge tube. After each extraction step, the suspension was centrifuged applying a centrifugal force of 1500 × g during 20 minutes. The supernatant solution was removed using a syringe. The remaining solids were resuspended in 24 mL deionised water, that was separated in a similar way and discarded.

A separate portion of the sediment was extracted with 15 mL NH_4OAc-EDTA pH 4.65 (38.5 g NH_4OAc + 25 mL of glacial acetic acid + 5.845 g EDTA in 1 L) for 30 minutes under continuous agitation at room temperature in a 250 mL centrifuge tube[22]. The liquid was separated and the solid rinsed with distilled water as described above, and then subjected to the sequential extraction.

Metal concentrations in the supernatant solution were determined with flame atomic absorption (Varian AA-1475 or SPECTRAA-10). Calcium was measured with flame emission (Eppendorf ELEX 631). For each extract, external standards, prepared in the corresponding extraction solution, were used for calibration. The exact volume of the extract after each extraction step was determined by weighing the centrifuge tube just before sampling the supernatant liquid. The experiment was duplicated.

RESULTS AND DISCUSSION

Sequential extraction

The distribution of the metals over the different fractions is shown in Table 2 and reveals clear differences between the elements. Copper was mainly released in the oxidisable fraction. The strong association of Cu with the oxidisable phase has been

Table 2 Fractionation of metals in the sediment, not extracted (a) and previously extracted with NH_4OAc-EDTA (b) (AmAc = NH_4OAc-EDTA-extractable, Acid = acid extractable, Red = reducible, Ox = oxidisable, Res = residual, Σ = sum of all fractions)[a]

		AmAc	*Acid*	*Red*	*Ox*	*Res*	Σ
				(mg/kg dry sediment)			
Cd	(a)		2.7 b	5.9 b	0.7 a	0.5 a	9.8
	(b)	2.3	1.1 a	4.4 a	0.7 a	0.6 a	9.1
Co	(a)		4.1 b	6.2 b	3.3 a	6.1 a	19.7
	(b)	3.8	1.6 a	4.2 a	3.3 a	6.6 a	19.5
Cu	(a)		1.9 a	6.6 a	64.3 a	20.4 a	93.2
	(b)	11.6	1.1 a	3.7 a	48.3 a	25.4 a	90.1
Ni	(a)		6.7 b	13.4 b	6.7 a	16.7 a	43.5
	(b)	7.3	2.5 a	8.8 a	7.0 a	18.4 a	44.0
Pb	(a)		24.2 b	46.1 b	35.9 a	31.5 a	138
	(b)	62.3	5.6 a	18.7 a	19.1 a	25.4 a	131
Zn	(a)		143 b	324 b	59.9 a	47.0 a	573
	(b)	126	55 a	229 a	58.8 a	57.9 a	527
Fe	(a)		106 a	9756 a	5784 a	23269 a	38915
	(b)	1262	191 b	8771 a	5462 a	27584 a	43270
Mn	(a)		201 a	497 b	88 a	132 a	919
	(b)	168	180 a	337 a	87 a	132 a	905
Ca	(a)		34889 b	21959 b	1339 b	131 a	58318
	(b)	15263	18009 a	7961 a	625 a	165 a	42023

[a] Means for an element and a fraction that are not significantly different are denoted with the same letter (Duncan multiple range test at the 95% level of significance).

frequently reported[26–28]. Zinc and Cd, which have a comparable environmental behaviour[29], were released mainly in the acid extractable and in the reducible fractions. Lead was extracted equally in the four fractions. Iron was predominantly found in the residual fraction, while Mn was mainly present in the acid extractable and in the reducible fractions. The acid extractable and reducible fractions were significantly affected when the sediment was previously extracted with NH_4OAc-EDTA[30].

Metal associations

From the sequential extraction data of the sediment as such and after extraction with NH_4OAc-EDTA, a presumed solid phase distribution of the metals, released in the different fractions, was estimated. We considered the elements Ca and Fe to be indicators for the release of carbonate and ironoxihydroxide phases, respectively. If one assumes that the metal contents, coprecipitated within these solid phases, are rather homogeneous, a release of Ca or Fe from carbonates or ironoxihydroxides should be accompanied by a proportional release of the metals in these phases.

With these assumptions, mass balances for the acid extractable and reducible fractions can be expressed as:

$$m_{Ca} \cdot Ca_a + m_{Fe} \cdot Fe_a + M_{s,a} = M_a$$

$$m_{Ca} \cdot Ca_r + m_{Fe} \cdot Fe_r + M_{s,r} = M_r$$

with:

Ca_a, Ca_r = Ca released in the acid extractable fraction (subscript *a*) or in the reducible fraction (subscript *r*) (mg/kg),
Fe_a, Fe_r = Fe released in the acid extractable fraction (subscript *a*) or in the reducible fraction (subscript *r*) (mg/kg),
$M_{s,a}$, $M_{s,r}$ = sorbed forms of an element, released in the acid extractable fraction (subscript *a*) or in the reducible fraction (subscript *r*) (mg/kg),
M_a, M_r = metal released in the acid extractable fraction (subscript *a*) or in the reducible fraction (subscript *r*) (mg/kg),
m_{Ca}, m_{Fe} = ratio between metal released and Ca (subscript *Ca*) or Fe (subscript *Fe*) released.

The ratio between metals released and Ca or Fe released (m_{Ca} and m_{Fe}) was estimated from the sequential extraction data of the sediment that previously was treated with NH_4OAc-EDTA. Ammoniumacetate-EDTA removes exchangeable and adsorbed metals[31,32] and partially dissolves carbonates and ironoxihydroxides because of the weak acid and the presence of EDTA. Therefore, it can be assumed that sorbed metal forms were largely removed from the sediment that was previously extracted with NH_4OAc-EDTA. The mass balances simplify to:

$$m_{Ca} \cdot Ca_a + m_{Fe} \cdot Fe_a = M_a$$

$$m_{Ca} \cdot Ca_r + m_{Fe} \cdot Fe_r = M_r$$

and m_{Ca} and m_{Fe} can be obtained by:

$$m_{Ca} = \frac{M_a \cdot Fe_r - M_r \cdot Fe_a}{Ca_a \cdot Fe_r - Ca_r \cdot Fe_a}$$

$$m_{Fe} = \frac{M_r - m_{Ca} \cdot Ca_r}{Fe_r}$$

The amount of metals in the acid extractable and reducible sequential fractions, associated with the dissolution of Ca or Fe, were estimated using the factors m_{Ca} and m_{Fe}. The remaining metals were assumed to be sorbed. This way, the acid extractable and reducible fractions were differentiated into (1) sorbed metals (exchangeable, adsorbed or complexed on various solid phases in the sediment system), (2) carbonate associated metals and (3) ironoxihydroxide associated metals. This is depicted in Figure 1.

For both the acid extractable and reducible fractions, significant portions (> 10% of the fraction) were estimated to consist of "sorbed" metals. Sequential reagents have been primarily designed to dissolve specific solid phases, thereby releasing the associated metals. Because the pH decreases throughout the sequence of extraction steps, these reagents may also release metals, specifically sorbed at the surface of various solid phases – iron-manganese oxihydroxides, organic matter or clay minerals[16,33].

The "sorbed" portion in the acid extractable step obviously includes metals associated with the "exchangeable" fraction, which was omitted in these experiments. It may also include more strongly sorbed metals, as the pH during the acid extractable step is

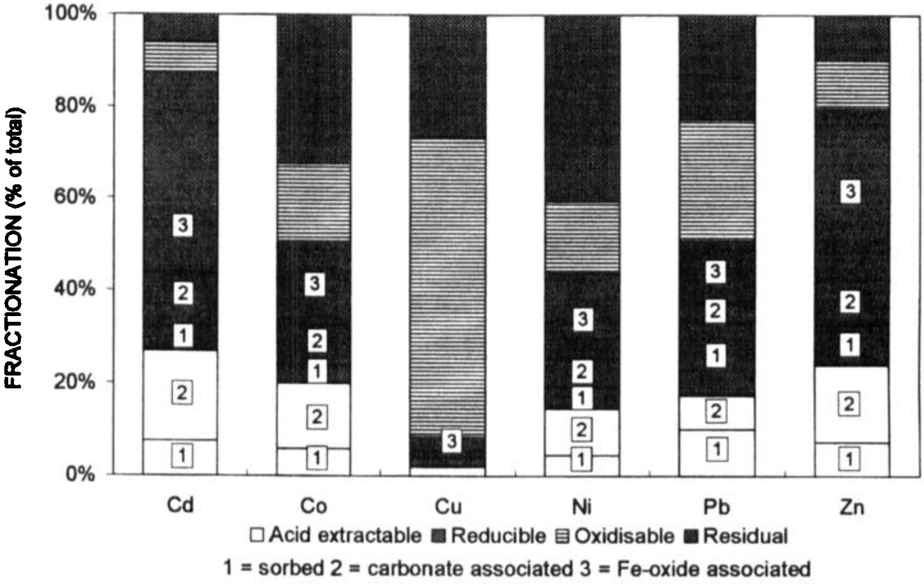

Figure 1 Sequential extraction of the sediment with indication of the calculated association of metals.

maintained at 5[16,18]. Likewise, the reducible fraction includes a significant portion of "sorbed" metals, released at a pH of approx. 2. For Pb, this portion represents more than 50% of the reducible fraction. It is likely that this Pb is largely associated with ironoxihydroxides, but adsorbed rather than coprecipitated. In adsorption experiments with iron oxihydroxides, 50% of Pb was retained on the solid at pH 3.1[34].

In this context, Kim and Fergusson[16] pointed out that the classification of the sequential fractions as first proposed by Tessier *et al.*[19] may lead to confusion: for example, metals sorbed on organic matter are indeed "bound to organic matter" but may be released in the exchangeable through the reducible steps, depending on their binding strength. Similarly, iron oxihydroxide sorbed Cd or Zn actually is "iron-manganese oxide bound" but may partially be released at pH 5 during the acid extractable step[34].

The acid extractable step was designed to release the heavy metals associated with carbonates[19]. The carbonate content of the sediment was high, at 16% (Table 1). The Ca amounts extracted (Table 2) suggested that the carbonates were only partially dissolved. The remaining carbonates and associated metals were released in the subsequent reducible step. This leads to an overestimation of the "iron-manganese bound fraction" with approx. 10% for most metals.

A slow dissolution of carbonates may be related to an increase in pH from 5 to 5.7 during the acid extractable step. Dissolution kinetics moreover may depend on the characteristics of the carbonate phases concerned. The buffering intensity of carbonates varies and is to a large extent influenced by the particle-size distribution and reactive surface area of the solid-phase carbonates[35]. Coatings and/or precipitated ions in the calcitic materials also affect the dissolution kinetics of carbonates[36].

From the relative low amounts of iron in the acid extractable step (Table 2) it may be concluded that ironoxihydroxides were affected to a minor extent in the acid extractable step. Consequently, no appreciable amounts of ironoxihydroxide-coprecipitated metals were estimated to be released in the acid extractable fraction. The acid extractable step hence exhibits a good selectivity, but lacks efficiency in dissolving the carbonates.

Changes in extracting conditions to enhance the dissolution of carbonates during the acid extractable step may result in other metal fractions being affected as well. Extending the extraction duration did not result in a significant increase of Ca in solution[19,37]. Increasing the extraction ratio or maintaining the extraction pH at 5 to enhance the dissolution of carbonates may bring more Fe and associated metals into solution[38]. It is hence advised not to alter the extracting conditions. Rather, one should be aware of the performance and limitations of the extraction technique applied. Sequential extraction data always must be interpreted with extreme care and in the context of other observations[4].

SUMMARY AND CONCLUSIONS

Using sequential data of a sediment as such and after extraction with NH_4OAc-EDTA, we estimated a presumed solid phase distribution of the metals extracted in the acid extractable and reducible steps. Metals coprecipitated in ironoxihydroxides but extracted in the acid extractable fraction were negligible. Because not all carbonates were dissolved during the acid extractable step, an important portion of metals in the reducible fraction (10 to 25%) originated from the dissolution of the remaining carbonates. A significant portion (at least 10%) of both the acid extractable and reducible steps was designated as "sorbed" on various solid phases of the system, rather than specifically associated with carbonates or ironoxihydroxides, respectively.

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