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F. M. G. Tack^a; H. A. H. Vossius^a; M. G. Verloo^a

^a Laboratory of Analytical Chemistry and Applied Ecochemistry, University of Gent, Gent, Belgium

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A COMPARISON BETWEEN SEDIMENT METAL FRACTIONS, OBTAINED FROM SEQUENTIAL EXTRACTION AND ESTIMATED FROM SINGLE EXTRACTIONS

F. M. G. TACK, H. A. H. VOSSIUS and M. G. VERLOO

*Laboratory of Analytical Chemistry and Applied Ecochemistry, University of Gent,
Coupure Links 653, B-9000 Gent, Belgium*

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We compared the sequential extraction according to Tessier *et al.* with the results, obtained from single extractions employing reagents and reacting conditions similar to these of the different Tessier steps. The aim was to investigate whether an approach involving fewer consecutive steps provides similar information as sequential extraction.

The estimates of the exchangeable, acid extractable and reducible fractions from the single extraction data were in good agreement with the fractions obtained using sequential extraction. The oxidizable fraction should be determined by extraction of the residue of a hydroxylamine-hydrochloride extraction.

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

INTRODUCTION

Sequential extraction or fractionation is applied to determine the chemical association of trace elements in soils and sediments¹⁻³. In particular the five-step sequential fractionation scheme of Tessier *et al.*⁴ is frequently used. The results obtained are operationally defined, i.e., the “forms” of metals are defined by the determination of extractable elements using a given procedure³. Consequently, sequential extraction does not provide hard evidence and always must be interpreted with extreme care and in the context of other observations. Yet sequential extraction has proven its value, despite of the severe restrictions⁵.

Apart from the conceptual problems associated with the use of sequential extraction, proper sample handling and preparation (e.g., freeze drying, oven drying) remains a major practical problem, because it critically influences the results of a sequential extraction⁶. For anoxic sediments, the necessity of maintaining anoxic conditions during sampling, sample treatment and extraction has been clearly evidenced^{6,7}. Sequential extraction, moreover, is a tedious and time-consuming procedure. This objection is even more relevant when considering the limitations of the results obtained in return for the effort.

An approach where the same information is gained from separate, single extractions would be advantageous. With the single approach, sample preservation is critical only before adding the reagent and during one extraction. There is no risk for sample losses

during consecutive phase separations and washing steps. Not all the work is lost when something goes wrong during an extraction step. Finally, results can be obtained faster because the extractions can be carried out simultaneously. Drawbacks include the fact that more sample is needed and that there is a possibility for errors due to sample heterogeneity.

We compared the sequential extraction according to Tessier *et al.*⁴ with the results, obtained from single extractions that used reacting conditions similar to these of the different Tessier steps. The aim was to investigate whether the sequential approach may be replaced by single extractions or at least an approach involving fewer consecutive steps.

MATERIALS AND METHODS

A reduced sediment sample from the Scheldt estuary (Table 1) was used for the experiments. The pH was measured in a 1/5 soil to water suspension after equilibration for 12 hrs. The redox potential was determined by immersion of a platinum electrode and a standard calomel reference electrode in the native sample and waiting for a stable reading⁸. For the analyses that follow, the sample was dried during 12 hrs at 120°C and ground to pass a 2-mm sieve. Organic C was estimated by the Walkley-Black method and converted ($1.72 \times C$) to percent organic matter⁹. Carbonate content was determined by back titrating an excess of 0.500 M HCl added to 1.000 g of the sample with 0.500 M NaOH¹⁰. Particle size fractionation was performed with dry and wet sieving techniques¹¹.

The wet, reduced sediment was sequentially extracted according to the Tessier method⁴. The residual fraction was determined after aqua regia destruction¹². Aliquots of the sample were subjected to single extractions using similar reacting conditions as the steps of the sequential extraction.

The extracting conditions applied are outlined in Table 2. The extractions were performed on 3.00 gram reduced wet sediment (dry matter percentage $35 \pm 1.5\%$) in 250 ml polyethylene centrifuge tubes. The sediment dry weight was determined on a separate portion by drying at 120°C until constant weight. To limit oxidation during extraction, the tube was sealed with laboratory film after flushing the headspace with N₂-gas. This precaution was taken during the first three steps of the sequential extraction procedure only. After each extraction step, the suspension was centrifuged (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.

Table 1 Characteristics of the sediment studied.

Granulometry (%)	
0–2 μm	34.5
2–50 μm	56.9
> 50 μm	8.6
pH-H ₂ O (1:5)	7.1
Redox potential (mV vs SHE)	2
Buffering capacity (to pH 4.3; mmoles HCl/kg dry sediment)	2357
Organic matter (%)	2.7
CaCO ₃ (%)	16.2

Table 2 Experimental extraction conditions used per gram reduced sediment.

MgCl ₂ -extraction	8 ml 1 M MgCl ₂ (pH 7), 1 hr, room temperature, continuous shaking ⁴
NaOAc-extraction	8 ml 1 M NaOAc + HOAc (pH 5), 5 hrs, room temperature, continuous shaking ⁴
NH ₂ OH.HCl-extraction	20 ml 0.04 M NH ₂ OH.HCl in 25% HOAc, 6 hrs, 95°C, intermittent shaking ⁴
H ₂ O ₂ -extraction	3 ml 0.02 HNO ₃ + 2 ml 30% H ₂ O ₂ (pH 2), 2 hrs, 85°C, intermittent shaking; 3 ml 30% H ₂ O ₂ (pH 2), 3 hrs, 85°C, intermittent shaking; 5 ml 3.2 M NH ₄ OAc in 20% HNO ₃ , 30 min, room temperature ⁴
Aqua regia	7.5 ml 37% HCl + 2.5 ml 65% HNO ₃ , overnight at room temperature, 2 hrs heating under reflux ¹²

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 6361). 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. All extraction sequences were replicated four times.

RESULTS AND DISCUSSION

According to the sequential fractionation scheme of Tessier *et al.*⁴, metals are categorised as "exchangeable", "bound to carbonates", "bound to iron and manganese oxides", "bound to organic matter" and "residual"⁴. In this discussion, we will refer to these fractions as "exchangeable", "acid extractable", "reducible", "oxidizable" and "residual", respectively.

The sequentially extracted metal amounts are listed in Table 3. There was a reasonable agreement between the sum of the sequentially extracted amount and the aqua regia extractable content. For some elements (Pb, Cu and Co), significant more metals were extracted with the sequential extraction procedure than with aqua regia (t-test,

Table 3 Sequential fractionation⁴ of metals (mg/kg dry sediment) (means ± standard deviation of 4 replicates).

Fraction	Cd	Co	Cu	Ni	Pb
Exchangeable	< 0.5	< 1	< 1	< 1	< 2
Acid extr.	< 0.5	4.2 ± 0.3	< 1	6.8 ± 0.6	10 ± 2
Reducible	9.6 ± 0.3	8.2 ± 0.8	22 ± 1	9.9 ± 0.8	64 ± 8
Oxidizable	7.2 ± 0.9	10.0 ± 0.1	115 ± 3	14.7 ± 0.3	92 ± 10
Residual	< 1	11.3 ± 1.3	27 ± 1	28 ± 3	23 ± 1
Aqua regia	11.0 ± 0.1	26.3 ± 0.3	123 ± 1	54 ± 6	168 ± 3

Fraction	Zn	Ca	Fe	Mn
Exchangeable	< 0.5	4140 ± 150	10 ± 2	37 ± 1
Acid extr.	49 ± 15	37000 ± 4600	4970 ± 1100	510 ± 45
Reducible	434 ± 26	10700 ± 3000	13600 ± 930	366 ± 36
Oxidizable	90 ± 2	670 ± 51	9500 ± 1200	49 ± 10
Residual	66 ± 2	328 ± 10	30670 ± 680	103 ± 4
Aqua regia	641 ± 6		57570 ± 520	1052 ± 4

$p = 0.05$). As aqua regia digestion is expected to extract between 70 and 90% of the total content of metals, it is not a real total analysis¹².

The extracted Ca and Fe amounts are indicative for the dissolution of carbonate and iron-manganese oxyhydroxide phases, respectively. A mayor part of Ca was released in the acetate buffer (Table 3). However, the portion extracted in the reducible step was still important. The experimental conditions of the acid extractable step thus were not suited to dissolve all of the carbonates. This problem is related to the particularly high carbonate content of the sample (Table I) and has been discussed elsewhere¹³.

The relatively large portion of Fe that was dissolved in the acid extractable step may be related to the reduced state of the sediment. The acid extractable and reducible Fe can also originate from amorphous sulphides. Conceptually, sulphides are expected to be dissolved during the oxidizable step⁴. However, it has been shown that amorphous sulphides are dissolved throughout the sequential extraction scheme^{6,14}.

Metal fractions estimated from the single extractions are presented in Table 4. The amounts extracted in $MgCl_2$ (exch. (A) in Table 4) are identical as the sequentially extracted amounts because the exchangeable fraction constitutes the first step in the sequential extraction scheme. Only Fe, Mn and Ca were detected in the extracts.

To estimate the 'acid extractable fraction' from the single extractions, the amounts extracted with $MgCl_2$ were subtracted from these extracted with NaOAc, thereby correcting for the 'exchangeable' metals (B-A). This correction made almost no difference as the $MgCl_2$ -amounts were small. The sequentially obtained acid extractable fraction (Table 3) corresponded well with the acid extractable fraction estimated from the single extractions. The $MgCl_2$ -treatment and the subsequent phase separation and washing steps during the sequential extraction therefore did not significantly alter the sediment matrix.

The reducible fraction was estimated from the single extraction data by subtracting the NaOAc-extractable contents from the $NH_2OH.HCl$ -extractable contents (C-B). As the $NH_2OH.HCl$ -extraction proceeds in a more acidic medium, it is expected that all metals, released in a NaOAc-extract, are also released. The $NH_2OH.HCl$ -extracted Ca (exch. + acid + reduc.) supported this notion as it largely exceeded the amount extracted in NaOAc (exch. + acid) (Table 4).

Table 4 Estimated metal fractions from single extractions (means \pm standard deviation of 4 replicates; metal fractions: exch. = exchangeable; acid = acid extractable; reduc. = reducible; oxid. = oxidizable, extractions: A = $MgCl_2$ -extraction; B = NaOAc-extraction; C = $NH_2OH.HCl$ -extraction; D = H_2O_2 -extraction).

Fraction	Cd	Co	Cu	Ni	Pb
exch. (A)	< 0.5	< 1	< 1	< 1	< 2
acid (B-A)	< 0.5	3.4 ± 0.2	< 1	7.4 ± 0.5	13 ± 2
reduc. (C-B)	10.1 ± 0.4	7.6 ± 1.3	12 ± 1	11.0 ± 0.9	79 ± 3
oxid. (D-B)	11.0 ± 0.3	11.6 ± 0.3	104 ± 1	11 ± 2	152 ± 3
oxid. (D-C)	0.9 ± 0.5	3.9 ± 1.3	92 ± 1	6 ± 2	73 ± 3

Fraction	Zn	Ca	Fe	Mn
exch. (A)	< 0.5	3950 ± 95	10 ± 2	43 ± 2
acid (B-A)	55 ± 9	33300 ± 2500	3390 ± 720	463 ± 32
reduc. (C-B)	438 ± 21	22700 ± 3600	19600 ± 790	376 ± 48
oxid. (D-B)	449 ± 14	20600 ± 2600	20600 ± 1000	440 ± 35
oxid. (D-C)	11 ± 21	-2000 ± 2600	1000 ± 790	65 ± 37

For Zn, Cd and Ni, a close agreement was found between the reducible fraction of the sequential extraction and that, estimated from the single extractions. For Pb, Cu, Ca, and Fe, the differences were significant at the 5% level. The difference for Pb was rather small, being not significant at the 1% level. Copper was lower, and Ca and Fe were higher than in the sequential extraction. For Cu, the previous treatment of the sediment may have influenced the physical arrangement of the phases, resulting in a more efficient extraction of this metal during the sequential extraction than during the single extraction. For Ca and Fe, the reduced extraction efficiency in the single extraction may be a mass-law effect. The concentrations of Ca and Fe were 1049 and 402 mg/L in the single $\text{NH}_2\text{OH.HCl}$ -extract vs. 187 and 238 mg/L in the sequential extract, respectively. All carbonates were solubilised by the single $\text{NH}_2\text{OH.HCl}$ extraction, as evidenced by the high Ca extracted (Table 4).

The oxidizable fraction is the fourth fraction in the sequential procedure. In Table 4 two estimates of the oxidizable fraction are given. One was obtained by subtracting the NaOAc-extractable metals from the H_2O_2 -extractable amount (D-B), and the other estimate was calculated by subtracting the $\text{NH}_2\text{OH.HCl}$ -extractable fraction (D-C). The estimates obtained by subtracting the NaOAc-extractable amount agreed more or less for Cd, Co, Cu, and Ni. For the other elements, the sequentially determined reducible fraction was in between both estimates. This indicates that the single H_2O_2 -extraction released metals associated with the reducible fraction with a variable efficiency. The extracted Ca suggested that carbonates were solubilised efficiently in the H_2O_2 -extraction.

CONCLUSIONS

The data suggested that the estimation of the exchangeable, acid extractable and reducible steps from single extractions on separate subsamples was equivalent to performing the sequential extraction. This was not true for the oxidizable fraction. Because the previous fractions estimated from single extractions agreed with the sequential extraction, one can estimate the oxidizable fraction from a H_2O_2 -extraction on the residue of the $\text{NH}_2\text{OH.HCl}$ -extract. Precautions against oxidation after performing the $\text{NH}_2\text{OH.HCl}$ -extraction are not needed because the H_2O_2 -extraction involves a strong oxidation anyway.

This way, a fractionation scheme involving at most two consecutive extractions can be employed to replace the sequential extraction. The scheme involves MgCl_2 , NaOAc and $\text{NH}_2\text{OH.HCl}$ -extractions carried out on separate subsamples. The $\text{NH}_2\text{OH.HCl}$ -extraction is followed by a H_2O_2 -extraction. The acid extractable fraction is estimated from the difference between the NaOAc-extraction and the MgCl_2 -extraction and the reducible fraction from the difference between the $\text{NH}_2\text{OH.HCl}$ -extraction and the NaOAc-extraction. The residual fraction may be determined by subtracting the $\text{NH}_2\text{OH.HCl} + \text{H}_2\text{O}_2$ -extractable amounts from the results of a total analysis. These conclusions, however, should not be generalised before other soil and sediment samples have been tested in a similar way.

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