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Testing Readsorption of Trace Elements during Partial Chemical Extractions of Bottom Sediments

Nelson Belzile, Pierre Lecomte, and André Tessier*

INRS-Eau, Université du Québec, C.P. 7500 Sainte-Foy, Québec G1V 4C7, Canada

■ The importance of postextraction readsorption of As, Cd, Cu, Ni, Pb, and Zn has been evaluated for each step of a sequential extraction procedure by measuring the recovery of small amounts of trace elements added during the extraction of oxic lake sediments. For all the cases examined but one, the trace element spikes (<100% of the amount present in control samples) were recovered within the limits given by the experimental errors. These results contrast with the large percentages of postextraction readsorption observed for these trace elements in previous studies, a consequence of the use by previous investigators of either large spikes (greatly exceeding the amounts present in the control samples) during extractions of natural sediments or simple model sediments.

Bottom sediments are complex mixtures that include detrital organic and inorganic substances as well as products formed in the water column or resulting from post-deposition (diagenetic) reactions. These diverse components that constitute the sediment matrix do not usually exist as separate particles but rather as aggregates. The modes of association of trace elements with the components of the sediment matrix are diverse; they can be adsorbed at particle surfaces, be present in the lattices of primary or secondary minerals, or be occluded in amorphous material. As these various trace element forms generally exhibit different chemical properties, measurement of their individual concentrations should prove invaluable for understanding their geochemical behavior (diagenesis, cycling, transport) and biological availability. However, the direct measurement of trace elements associated with a given sediment phase is seldom feasible, due to the complexity of the system and to the low concentrations of the trace elements involved. Therefore, indirect methods must usually be used. In this context, partial extractants (often called "selective" extractants) have been used to obtain information about the association of trace elements in sediments.

Methods involving single or multiple chemical extraction steps with reagents of various strengths have been developed for separating trace elements present in the sediment into broad geochemical classes (1–4). It is generally recognized that the partitioning of trace elements obtained by such procedures is operational, as it is influenced by experimental factors such as the choice of reagents, the time of extraction, and the ratio of extractant to sediment, as well as by inherent analytical problems such as incomplete selectivity and readsorption (5–8). Despite these drawbacks, partial extractions have been extensively used, with considerable success, to obtain information on the bioavailability (9–12) and the geochemistry (13–19) of trace elements.

Of particular interest in this context are recent reports that trace elements released during the attack of synthetic mixtures of substrates with a given partial extractant (and the concomitant dissolution of a target phase) can be readsorbed to a large extent on the remaining solid phases. The observation of a large postextraction readsorption (e.g. >90% readsorption of Cu; ref 20) for relatively simple systems has led to a questioning of the usefulness of partial chemical extractants in determining meaningful partitioning of trace elements in the more complex natural sediments (20–23). If, as suggested, such an extensive readsorption occurs in natural sediments, the concentration and type of surface sites available after the extractions, rather than the extractants themselves, would be responsible for the partitioning observed (22). However, most of the approaches used to date to evaluate the importance of postextraction readsorption of trace elements during extractions of natural sediments have yielded ambiguous results, notably because the experimental conditions have differed greatly from those prevailing during normal extractions of natural sediments (24, 25). In this study, we use a standard addition technique to examine the degree of readsorption of As, Cd, Cu, Ni, Pb, and Zn during various extractions performed on oxic lake sediments, and we show that the studies to date have overestimated the general importance of readsorption in partial extractions of natural sediments.

Experimental Section

Sampling. The sediments used in the experiments were obtained from two lakes differing in geological setting and trace element concentrations (Table I): Lakes Joannes (48°12′ N, 78°40′ W) and Brompton (45°25′ N, 72°10′ W). Lake Joannes is located in the vicinity (25 km) of the Rouyn-Noranda (northwestern Quebec) mining and smelting complex, a major source of Cu, Pb, and Zn contamination (12). In this area, the bedrock is covered by locally derived till overlain by lacustrine clay deposits from the proglacial Lake Barlow-Ojibway. Many Cu, Pb, and Zn anomalies have been observed in the lacustrine clays (26). No point sources of trace elements to the lake have been identified. Trace element concentrations found in the sediments of this lake may thus be considered to have been introduced both by the airborne smelter emissions and by natural processes of weathering and erosion. Lake Brompton is located in the Eastern Townships, Quebec. It lies in the Appalachian Mountains in an ophiolitic complex where Ordovician and Cambrian sedimentary rocks consisting of shales, calcareous shales, sandstone, and volcanic rocks are covered by unconsolidated deposits of glacial tills and marine clays. Only nickel mining, on a small scale, has been reported in the lake basin. Thus, trace element concentrations in the sediments of Lake Brompton, with the exception of nickel, are expected to originate from natural processes.

Precautions were taken to ensure that the sediments used in the experiments were oxic. Sediment cores were collected in Plexiglass tubes (9-cm diameter) in each lake at littoral stations (depth ≃3 m) by a diver. The tubes were tightly closed to minimize perturbation of the sediments during their transport to the shore. The sediment cores were extruded on the shore, and only the top first centimeter containing oxidized sediments was retained; these samples were kept at 4 °C during transport to the laboratory and then frozen until needed for the experiments. Vertical porewater profiles of dissolved iron and sulfate concentrations were obtained by dialysis (27, 28) at the coring sites to verify that the sediment layer retained

Table I. Geochemical Composition of Sediment Samples

| | total concentration on a dry weight basis | | | | | | | | | | |
| | % | | | | μg/g | | | | | | |
lake	C_{inorg}	C_{org}	Fe	Ti	Mn	As	Cd	Cu	Ni	Pb	Zn
Joannes	<0.1	5.9	2.47	0.37	1400	14	8	65	48	110	220
Brompton	<0.1	5.3	3.61	0.41	1500	12	1	12	220	69	147

	mineralogical composition
Joannes	major: quartz; minor: feldspar, chlorite, amphibole
Brompton	major: quartz; minor: feldspar, chlorite, mica, amphibole

was confined to oxic zone. The in situ porewater samplers used (1-cm vertical resolution) were similar to those described by Hesslein (27) and Carignan (28); a sheet of polysulfone filtration membrane (Gelman HT-450; 0.45-μm nominal pore size) was used. Prior to their insertion vertically in the lake sediments by a diver, the samplers were bubbled with nitrogen for at least 24 h in Plexiglass cylinders filled with demineralized water. After a 2-week equilibration period in the sediments, the samplers were retrieved by a diver, who at this time also collected the sediment cores. Samples for dissolved iron analysis were collected in the field from the samplers by piercing the membrane with a micropipet; these samples were injected into prewashed and preacidified (30 μL of 1 N Ultrex HNO_3; final pH < 2) Teflon vials. Samples for dissolved sulfate analysis were also collected in the field from the samplers with a syringe and injected into prewashed polypropylene tubes.

Standard Addition Experiments. The experiments were designed to evaluate the importance of postextraction readsorption of various trace elements at each step of a sequential extraction procedure under conditions similar to those normally found when such a procedure is applied to natural sediments. The tested procedure partitions the trace elements, M, into the following operational fractions:

(a) M(F1). The sediment sample is extracted for 30 min with a 1 N $MgCl_2$ solution initially at pH 7.

(b) M(F2). The residue from (a) is extracted for 5 h with a 1 M CH_3COONa solution adjusted to pH 5.0 with CH_3COOH.

(c) M(F3A). The residue from (b) is extracted for 30 min at room temperature with 0.1 M $NH_2OH \cdot HCl$ in 0.1 N HNO_3.

(d) M(F3B). The residue from (c) is extracted for 6 h at 96 °C with 0.04 $NH_2OH \cdot HCl$ in 25% (v/v) CH_3COOH.

(e) M(F4). The residue from (d) is extraced for 5 h at 85 °C with 30% H_2O_2 adjusted to pH 2.0 with HNO_3 and then a second time at room temperature with 3.2 M NH_4OAc in 20% (v/v) HNO_3. The details of steps a, b, d, and e have been published elsewhere (4); step c has been included to distinguish between manganese and iron oxyhydroxides as suggested by Chao (29). Owing to the inherent lack of selectivity of the extraction procedure, the fractions have henceforth been assigned numerical designations [M(F1)...M(F4)]. The procedure attempts to distinguish between trace elements that are exchangeable (F1), bound to carbonates or specifically adsorbed (F2), bound to Mn oxides (F3A), bound to Fe oxides (F3B), and bound to organic matter and sulfides (F4).

Prior to the standard addition experiments, the two sediment samples were thawed, centrifuged to remove excess water, thoroughly mixed to homogenize them, and subjected to the sequential extraction procedure to determine the natural concentrations of As, Cd, Cu, Ni, Pb, and Zn in each operational fraction of the original sediments. Triplicate subsamples of wet sediment were

weighed, dried, and weighed again to allow reporting the results on a dry weight basis. The extractions served to establish the amounts of each trace element that had to be added as standard additions during each extraction. Ideally, to preserve the conditions of normal extractions, the additions should be infinitely small quantities that will not change the natural concentrations; also, they should be easily detected. Use of radiotracers was considered for this purpose, but this could lead to artifacts as the systems have not reach a solid–solution equilibrium when the extracts are removed, i.e., at the end of the extractions. Time necessary for dissolved trace elements to reach equilibrium with natural sediments may indeed be much longer than the duration of the extractions (30). The difference between forward and backward reaction rates for the reactions with the residual solids (which determine the rate of disappearance of the trace element from the solution) would be greater for the radiotracers than for the "cold" trace elements because the radioactive elements were not present in the sediment phases when extraction was started; it could then lead to "apparent" losses. For this reason, we preferred to spike with small but measurable quantities of trace elements. In practice, for a given trace element, additions representing between 50% and 100% of the amounts measured in a given fraction were found to be a good compromise between acceptable precision in the measurement of the adsorption and preservation of the normal conditions of extraction. Thus, unless specified, trace element additions did not exceed 100% of the amounts present in the control subsamples.

In testing a given step of the procedure, the corresponding extraction was performed in parallel on two series of triplicate subsamples (1.6 g of wet weight; equivalent to 1 g of dry weight) of the original sediment: a control series to which no trace element was added, and a series to which trace elements had been added (As, Cd, Cu, Ni, Pb, and Zn). Prior to their spiking, the subsamples of the latter series were extracted up to the step being tested. The trace elements were added as small volumes (30–400 μL) from acidified stock solutions of trace metal nitrates (Cu, Ni, Pb) or chlorides (Cd, Zn), and of arsenic acid (As). For all steps but step a, the trace element spikes were made immediately after the addition of the extraction reagents, i.e., at the beginning of the extractions. For step a, however, the additions of trace elements were made directly to the $MgCl_2$ solution, which was then adjusted to pH 7 and added to the sediments. It was found necessary to use this procedure for step a to avoid recoveries greater than 100%, presumably due to the dissolving action of the acid spikes when added to the unbuffered solution of $MgCl_2$. Centrifugation (12000g; 30 min) was performed within 30 min after completion of an extraction; the supernatants were transferred to polyethylene vials, and their pH was lowered to <1.5 when necessary (fractions F1 and F2) to prevent metal losses during storage. Between each consecutive extraction, the residue was washed with a mini-
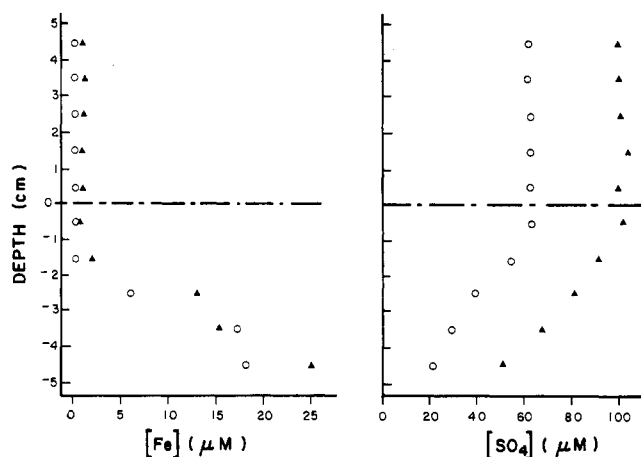
Figure 1. Porewater profiles of total dissolved iron and dissolved sulfate concentrations in the sediments of Lakes Brompton (O) and Joannes (▲). The dashed line indicates the sediment–water interface.

mum volume of demineralized water (8 mL) to remove the excess reagent and centrifuged. The amount of water remaining with the residue after this centrifugation was determined by weighing and was used to correct for the dilution of the concentrations found in the next extract.

Analyses. The sediment samples for measurement of total trace element concentrations were digested with a $HF-HNO_3-HClO_4$ mixture. Concentrations of Fe, Mn, Ti, Cd, Cu, Ni, Pb, and Zn in the sediment extracts and high concentrations of Fe in the interstitial water samples were determined by flame atomic absorption spectrophotometry (Varian Techtron, Model 575 ABQ); arsenic in the sediment extracts and the low concentrations of iron in the porewater samples were determined by flameless atomic absorption spectrophotometry (Varian Techtron, Model SpectrAA30; GTA-96). Quantification was achieved with appropriate calibration curves obtained with the metals added to solutions containing either the reactants used for the extractions (sediment extracts) or the HNO_3 concentration used to acidify the samples (porewater). Concentrations of sulfate in the interstitital water samples were determined by ion chromatography (Dionex AutoIon, System 12). Carbon concentrations in the sediments were measured with a CHN analyzer (Hewlett-Packard, Model 185B). X-ray diffraction measurements were performed on the two sediments with a Rigaku Rotaflex spectrometer.

Results

Sediment Characterization. Total trace element concentrations, total iron, titanium, and manganese concentrations, and organic carbon content of the two sediments used for the experiments are presented in Table I. The results show different levels of trace elements, as expected from land use. The results of X-ray diffraction analyses performed on samples of the two sediments indicate that the mineralogy of both samples is quite similar (Table I). The porewater profiles of total dissolved iron show that the oxidation of the upward migrating Fe(II) (and its precipitation as iron oxyhydroxides) occurs in both sediments at 1–2 cm below the sediment–water interface (Figure 1). This indicates that the sediments retained for the experiments originated from the oxic (or suboxic) layer and not from the anoxic zone. This observation is confirmed by the dissolved sulfate profiles that show no SO_4 reduction (resulting in sulfide production) at least in the first centimeter below the interface. It is essential to characterize the redox state of the sediment, as careless use of a mixture of sediments from both the oxic and

anoxic zones could lead to complications in the interpretation; such samples would contain solid phases such as freshly precipitated iron oxyhydroxides and iron sulfides that do not naturally coexist in the same sediment stratum and would thus be inherently unstable. Oxic sediments were chosen in this study because they contain the components (organic matter, various oxides, clays) that were suspected to be responsible for postextraction readsorption of trace elements (5, 6, 20–22).

Recovery of Standard Additions. Results for the recovery of small amounts (<100% of the control subsamples) of As, Cd, Cu, Ni, Pb, and Zn spiked during the various extraction steps of the sequential extraction procedure are given in Figure 2. In this figure are shown the values of the trace element spikes (S) and the concentrations of these elements measured in the unspiked (C) and spiked (T) subsamples. From these results it is apparent that, if T is lower than the sum of C and S, there has been some loss of the added trace element that can presumably be attributed to adsorption; the degree of readsorption can be estimated by the ratio $(C + S - T)/S$. The term adsorption is taken here in a broad sense. It should be noted that, for a given fraction, spikes were not made for those trace elements for which the concentrations in the control subsamples (C) were below the analytical detection limit; this was a consequence of our decision to avoid adding trace elements at concentrations greater than 100% of the concentration found in the control subsamples, i.e., to preserve as much as possible the normal conditions of extraction. The accuracy of the extraction technique itself has already been tested (4) by comparing the sum of the five sequential extractions (F1–F5) and the total digest on the complete sediment.

Examination of Figure 2 indicates that the mean value of T is slightly lower than that of $(C + S)$ for most trace elements in fractions F1 and F2, but not in the other fractions. The losses are, however, much lower than expected from the predictions of the previous studies (6, 20, 22). None of the differences was found to be statistically significant (t test; level of significance, $P < 0.05$), with the exception of that for lead extracted with the acetate buffer; for this case, a 90% Pb loss is calculated. For all the other cases, the spikes were recovered within the limits given by the experimental errors.

Low recoveries have been reported (6) when trace elements were spiked during extraction of natural sediments with $NH_2OH \cdot HCl$; the spikes, however, largely exceeded the trace element concentrations found in the natural sediments. In a separate experiment designed to test the effect of the size of trace element spikes on their loss during extraction, we added various amounts of trace elements to Lake Joannes sediment during extraction step d (fraction F3B), which uses $NH_2OH \cdot HCl$. Except for Cd, statistical significant differences (t test; $P < 0.05$) were found for all trace elements between mean values calculated for $(C + S)$ and for T when trace element spikes were much larger than C (6–22 fold) (Table II). However, no such differences were found when the spikes did not exceed 100% of C. The results clearly show that large statistically significant losses (up to 70% in this study) can be experienced for extraction step d when the spikes greatly exceed the amounts present in the control subsamples.

Discussion

The only statistically significant loss of a spiked trace element when the additions were kept at low levels was that observed for lead during step b of the sequential extraction procedure, i.e., with the acetate buffer. Previous measurements on stream sediments low in carbonates have
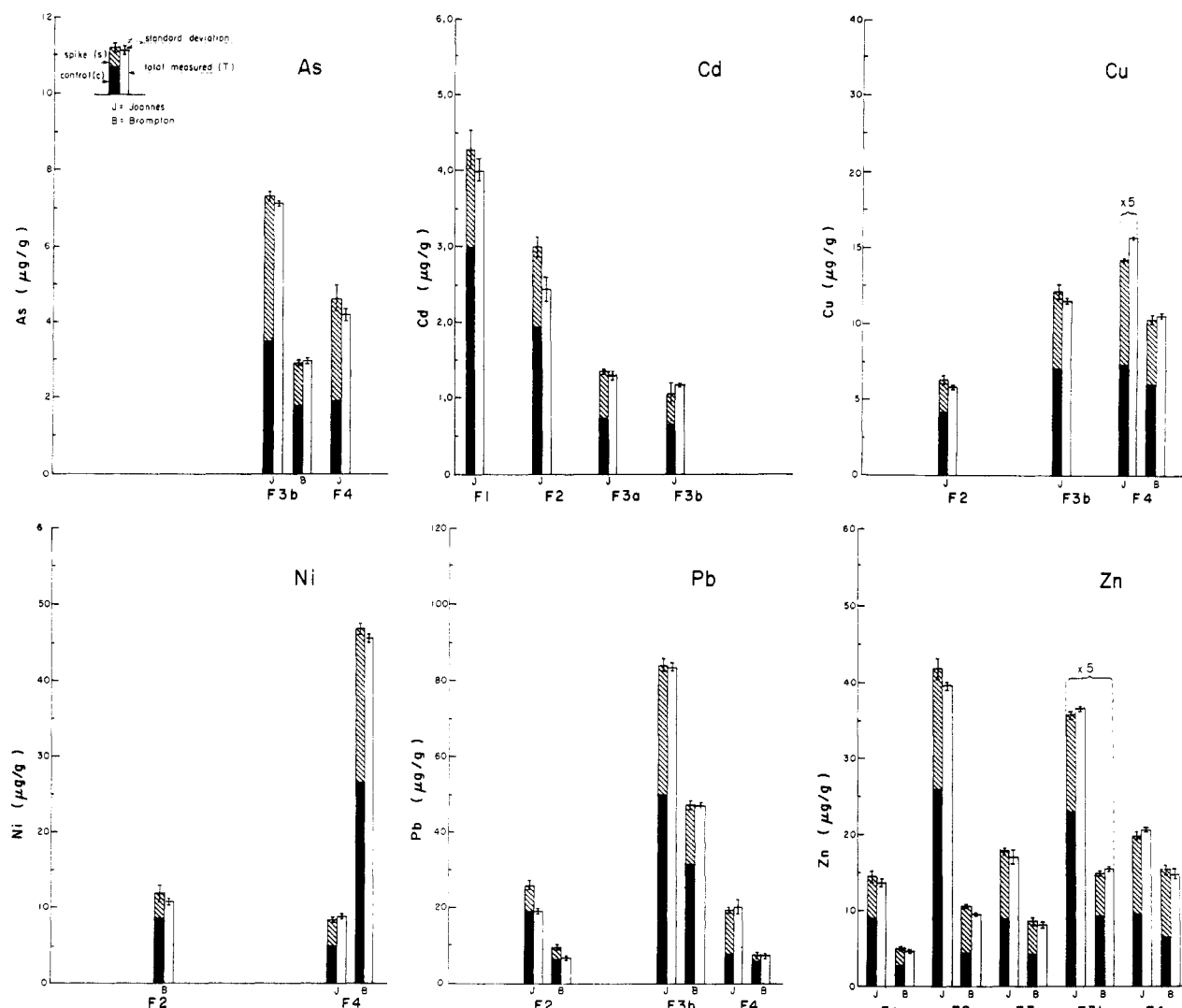
Figure 2. Recovery of As, Cd, Cu, Ni, Pb, Zn added in the presence of the various reagents used to extract the sediments of Lakes Brompton and Joannes. On the horizontal axis, B and J represent sediments of Lakes Brompton and Joannes, respectively. Fractions F1, F2, F3A, F3B, and F4 are described in the text. For each fraction, control (C), spike (S), and total measured (T) shown in the inset represent, respectively, the concentrations of the trace elements extracted in the control subsamples, in the spike, and in the subsamples having received the spike. The scale should be multiplied by 5 when $\times$5 is indicated.

Table II. Effect of the Amount of Spiked Trace Element on Its Recovery during Extraction Step d

trace element	control (C)	spike (S)	total measd (T)	loss,[b] %
	concn,[a] $\mu g/g$ of dry weight			
As	3.4 ± 0.1	3.8	7.1 ± 0.1	NS
		38.2	19.4 ± 0.8	58
		79.8	42.3 ± 0.4	49
Cd	0.7 ± 0.1	0.4	1.17 ± 0.01	NS
		5.7	6.2 ± 0.4	NS
		11.5	11.5 ± 0.8	NS
Cu	7.1 ± 0.4	5.1	11.5 ± 0.1	NS
		45.9	30.1 ± 0.9	50
		91.7	54.6 ± 1.0	48
Pb	49.5 ± 1.1	34.4	83 ± 1	NS
		357	358 ± 8	14
		713	618 ± 7	20
Zn	114 ± 2	64	182 ± 1	NS
		637	423 ± 16	51
		1274	452 ± 10	73

[a] Mean value and standard deviation for three replicate determinations. [b] The percentage of loss [$100(C + S - T)/S$] was calculated only in the cases where statistically significant differences (t test; $P < 0.05$) were found between mean values of ($C + S$) and T; NS indicates nonsignificant differences.

suggested that Pb leached by this reagent was not derived from the dissolution of some host phase of the sediments, such as carbonates, but rather was mostly desorbed from the surface of the iron oxyhydroxides (15). As our lake sediments are low in carbonates (Table I), lead leached by this reagent also probably originated from the surface of iron oxyhydroxides. Since lead has a strong affinity for iron oxyhydroxides, a pH of 5, as used in step b, is probably not low enough to prevent some readsorption by this substrate (31), particularly under the circumstances where the lead concentration was increased in the extract by 50–100%. Such readsorption is not observed for Cd, Cu, Ni, and Zn, which have a lower affinity for iron oxyhydroxides (32). It should be noted, however, that in the absence of any spike (as in normal extractions), there would not be any readsorption in these low-carbonate sediments, as the reagent should not destroy any phase. The extractant should act rather as a more or less efficient desorbent. The same comment should apply also to the MgCl$_2$ solutions, which in principle should not attack geochemical phases.

The minimal losses of low-level spikes of trace elements observed in the present study contrast with the pessimistic predictions of high percentages of postextraction read-

sorption reported recently as being a severe limitation to the use of partial extractants with natural sediments (6, 20–22). Possible reasons for these differences in behavior must be examined carefully.

Two approaches have been used to date to evaluate postextraction readsorption of trace elements during partial extractions of natural sediments. One of the approaches uses model sediments built up from solid phases prepared in the laboratory, only one of the phases having previously been doped with one or more trace elements (20–22). Application of partial extractants to these model sediments often leads to a lower recovery than expected in the extract corresponding to the doped phase; the observed loss of trace elements is often attributed to readsorption of the trace elements released during destruction of a phase onto the remaining phases. With this approach, low recoveries of trace elements in the expected fractions have been observed for many reagents including H_2O_2 (21), NH_4Cl (21), acetate buffer (20), and $NH_2OH \cdot HCl$ (20, 22).

For example, the following high percentages of readsorption during extraction of model sediments with $NH_2OH \cdot HCl$ have been reported: >90% readsorption of copper (ref 20; model sediment P); 99.8% readsorption of As onto goethite (22); 83–99.6% readsorption of As on anatase (22). The results obtained in the present study for extraction of real sediments with the same reducing reagent (Figure 2; fractions F3A and F3B) do not, however, show any statistically significant readsorption ($P < 0.05$). Several explanations can be offered for these great differences. First, the mixtures of sediment phases used in such model sediments are probably not always representative of natural sediments, such as were used in the present study. For example, Kheboian and Bauer (20) combined in equal proportions large quantities of freshly prepared amorphous iron oxides and iron sulfide; these two phases are mutually exclusive in natural sediments, and a sample of natural sediment properly collected should not contain large quantities of both. As discussed previously, our sediment samples were collected in the oxic sediment stratum and should not contain appreciable amounts of fresh iron sulfide. Gruebel et al. (22), for their part, used proportions of anatase (TiO_2) that varied between 10% and 100% of the amount of iron oxyhydroxides in their binary mixtures; readsorption increased as a function of TiO_2 concentration. The highest proportion used by these researchers is much greater than the proportion of Ti present in our lake sediments (~10% of iron; Table I). Based on total concentrations of Ti and Fe measured in Lake Brompton and Lake Joannes sediments (Table I), the lowest proportion of anatase (10% of Fe oxyhydroxides) used by Gruebel et al. seems more reasonable; however, the exact nature of the Ti phases in our natural sediments is unknown. Second, the driving force for metal redistribution should be greater in model than in natural sediments. Indeed, mixing a phase doped with a trace element with other phases not doped with that trace element creates an unstable system. The trace element added will have a natural tendency to redistribute among the various phases of the model sediments even in the absence of any extractant; if equilibrium is attained, the distribution of the trace element among the various solid phases that compose the model sediment will depend on the relative binding strengths of each component for the trace element and the number of available binding sites for each component (33, 34). Hence, the incomplete recoveries experienced with model sediments are in part intrinsic to the approach and cannot be attributed solely to artifacts in the extractions. A natural sediment properly collected

differs markedly from such model sediments in that the trace element have already been distributed at least partially among the various sediment phases. Third, postextraction readsorption could be more rapid for model than for natural sediments. Indeed, the latter, contrary to model sediments, are composed of aggregates, and it would be expected that some sites are not readily available for reaction, being for example armored by relatively inert compounds. These points suggest that results obtained with model sediments cannot be extended with ease to natural sediments.

In a different and more appropriate approach to studying postextraction readsorption, Rendell et al. (6) verified the recovery of trace metals added to various partial extractants during extractions of natural sediments; they found low recoveries of trace elements during extraction of five river sediments with dilute HCl, $NH_2OH \cdot HCl$, acetic acid, sodium citrate, ammonium acetate, and H_2O_2. For example, these authors reported the following degrees of readsorption during extraction with $NH_2OH \cdot HCl$: 35–93% Cu readsorbed (samples 1–5); 37% Pb readsorbed (sample 1). Again, these results contrast with the absence of statistically significant losses noted in the present study during extraction with the same reducing reagent (Figure 2). Apart from the differences in sediment composition between their river sediments and our lake sediments, several reasons could explain this difference in behavior. First, the amounts of spiked trace elements relative to the amounts already present in their control (C) samples were certainly much larger than in the present study. Indeed, the amounts of trace elements added by Rendell et al. were even much higher (factors of 3–14 for Cu, 1–6 for Pb) than the total trace element concentrations present in their original sediments (these ratios represent minimum figures for a given extraction, as only a fraction of total trace element would have been extracted). Adding large amounts of metal relative to that already present in the extract alters the conditions of normal extraction. Table II clearly indicates that large trace element additions during extraction with $NH_2OH \cdot HCl$, similar in scale to those used by Rendell et al., lead to significant redistribution of the spiked trace elements; the extent of redistribution of trace elements in our sediments is, in these cases, similar to that reported by Rendell et al. for the same extractant. An explanation for the increased trace metal redistribution with increased spike size might be related to the small amounts of organic matter released upon dissolution of iron and manganese oxyhydroxides (35). This organic matter could complex small spikes of trace metals, thus preventing their readsorption, but would be overloaded by large spikes. Whatever the mechanism, this result suggests that attention should be paid to preserving the experimental conditions of extractions if meaningful results are to be obtained. Second, the experimental conditions during the extraction by $NH_2OH \cdot HCl$ were slightly different in the two studies. The contact time between the added trace elements and the sediments was longer in the experiments of Rendell et al. (16 h) than in the present study (5 h); if there were kinetic effects, i.e., sites not readily available for reaction, increasing time would have led to increasing readsorption. In addition, these researchers used single partial extractants, not in sequence as in the present study. Use of the reactants in a sequence can make some difference as some components that would otherwise adsorb trace elements or alter the solution chemistry (e.g., increase of pH) during a given extraction could have been removed in earlier steps. For example, Rendell et al. reported a pH increase during the

extraction with $NH_2OH \cdot HCl$, and their highest percentages of readsorption were in fact observed for the highest pH increase; a preceding step, using a well-buffered solution that can dissolve phases that consume H^+ (like carbonates), would probably have prevented such a pH increase. We did not experience any pH increase during extractions with $NH_2OH \cdot HCl$ that followed a step involving an acetate buffer.

Conclusions

The present study, performed with natural sediments and under experimental conditions similar to those found during normal extractions, contradicts previous predictions of an important postextraction readsorption. It must however be realized that the sediments used do not cover the whole range of natural sediments; more studies performed on various natural sediment types are therefore required before definitive conclusions can be drawn.

Acknowledgments

Registry No. As, 7440-38-2; Cd, 7440-43-9; Cu, 7440-50-8; Ni, 7440-02-0; Pb, 7439-92-1; Zn, 7440-66-6; C, 7440-44-0; Fe, 7439-89-6; Ti, 7440-32-6; Mn, 7439-96-5.

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