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Contrasting two methods for determining trace metal partitioning in oxidized lake sediments

LEAH BENDELL YOUNG[1], MICHELLE DUTTON[2] & F. R. PICK[1]

[1] *Dept. of Biology, University of Ottawa, Ottawa, Ontario, K1N 6N5 and* [2] *Dept. of Biology Dalhousie University, Halifax, Nova Scotia, Canada*

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Abstract. A simultaneous (SIM) sediment extraction procedure for low carbonate sediments, which partitions sediment-bound trace metals (Fe, Mn, Zn, Cu, and Cd) into easily reducible (associated with Mn oxides), reducible (associated with Fe oxides) and alkaline extracted (bound to organic) metal is presented. The SIM method was compared to the sequential (SEQ) extraction procedure of Tessier et al. (1979). Both methods showed good agreement for the partitioning of Zn and Cd among the easily reducible, reducible and organic components of sediment. Both methods also showed the same general distribution of Mn, Fe and Cu among the three sediment components, however concentrations of metals recovered by the two methods differed; less Mn and Fe and more Cu was recovered from sediments by the SEQ vs. the SIM procedure. Less recovery of Mn is in part attributed to the loss of this metal in the 'in between' reagent rinses required in the SEQ procedure. Greater recovery of Cu by the SEQ vs. the SIM method may be due to the pretreatment of sediment with strong reducing agents prior to the step used for liberating organically bound metals. Advantages of a SIM over the SEQ include rapid sample processing time (i.e. the treatment of 40 samples per day vs. 40 samples in three days), plus minimal sample manipulation. Hence, for partitioning metals into easily reducible, reducible and organic sediment components in sediments low in carbonate, we recommend the use of a SIM extraction over that of a SEQ procedure.

Introduction

Aquatic sediments are the ultimate sink for trace metals of both natural and anthropogenic origin (Evans et al. 1983; Wong et al. 1986). Once in the sediments these metals can be accumulated by benthic-dwelling organisms which can then transfer such metals from the sediments to the next trophic level. However, the availability of these metals to benthic organisms depends on a number of factors including the geochemical characteristics of the sediments plus the partitioning of the metal among the different sediment components (Luoma & Jenne 1977).

In oxic lake sediments, the three most important sediment components have been identified as oxides of Mn, Fe and organic matter (Luoma & Bryan 1981; Campbell et al. 1988; Shea 1988). Because metal availability is affected by the metal's association within one or more of these sediment components, total metal concentrations provide little information about potential interactions between the abiotic and biotic environments. Therefore, knowledge of the partitioning of a particular metal among these three sediment components is useful in providing a better estimate of the metals bioavailability. For example, Tessier et al. (1984), and Bendell-Young (1991) found that metal concentrations of a bivalve and a chironomid respectively were more closely related to an easily extractable fraction of sediment rather than total metal sediment concentrations.

One of the most commonly used procedures for estimating the partitioning of metals among various sediments components is a sequential extraction such as that of Tessier et al. (1979, 1989) and variations thereof (see Campbell et al. (1988) for review). The sequential extraction of Tessier et al. (1979, 1989) is designed to partition metals into six sediment components; exchangeable, carbonates, Mn oxides, Fe oxides, organic material and residual or metals incorporated into silicate lattices. However, in oxidized sediments from low alkalinity freshwater systems, the six fractions identified by Tessier et al. (1979) may not be the most appropriate. Specifically, the extraction step for the removal of metals associated with carbonates would not be required as sediments will contain only trace amounts of this ligand. Further, as metals associated within the residual fraction of sediment are essentially unavailable to benthic biota, for studies which are assessing metal availability, it may not be necessary to estimate amounts of metal incorporated into this fraction of sediment. A procedure which simply defines metal associated with Mn oxides or easily reducible metal, Fe oxides or reducible metal and finally, metals bound with organics, would be more geochemically appropriate for studies dealing with the partitioning of metals in sediments from low alkalinity systems.

In addition to the geological relevance of a particular sequential extraction scheme, there are several analytical pitfalls of a sequential scheme which could be overcome through the use of a simultaneous extraction (i.e. the use of a single aliquot of sediment for all geochemical phases and obtaining the concentrations of metal in the three sediment fractions by differences vs. the use of a single aliquot of sediment for each phase). Sequential extraction schemes such as that of Tessier et al. (1979) require a 'wash' between each extraction step which is discarded. Kheboian & Bauer (1987) have suggested that metals can ultimately be lost in these rinses. The use of individual sediment aliquots would avoid the necessity of between reagent rinses. Etcheber et al. (1983) reported losses of up to 20% of organic matter from estuarine sediments during the first three steps of a five-step extraction procedure which included dissolution of oxides. Exposing sediments to only one reagent would minimize such methodological artifacts. Finally, whereas the sequential procedure can take up to 3 days to complete all 5 steps for one sample, a simultaneous extraction would require less than one day thereby avoiding possible alteration of the sediment associations during the 3 day storage period.

The objective of the following study is first to present a simultaneous sediment extraction scheme designed to estimate concentrations of metals partitioned into an easily reducible, reducible and organic component of sediments sampled from a low alkalinity wetland located on the Canadian shield, and second, to compare this method with a well known sequential scheme (i.e. Tessier et al. 1979) to evaluate the strengths of a simultaneous extraction over that of a sequential extraction.

Methods

Sediment collection

Sediments were sampled in late July from a small, acidic (pH = 5.2), low alkalinity (25 μeq/l) wetland in the Muskoka-Haliburton region of Ontario (Lat 45°11′, Long 78°50′). Ten sediment cores (i.e. 5 cores for each method) were taken at two locations within the wetland using a modified gravity corer with a 6.6 cm diameter Plexiglas core tube. Cores were carefully extruded in the field and the upper-most oxidized portion of sediment (i.e. 0.5–2 cm) retained for analyses. Only this portion was sampled for analysis as this region is directly involved in the exchange of trace elements between sediment and overlying water plus provides the layer of sediment to which benthic organisms are most exposed. As well, by remaining in the oxidized region of sediment, potential artifacts, such as the introduction of reduced species (e.g. sulphides) can be avoided. Extruded sediments were placed in acid-washed 50 mL polypropylene centrifuged tubes and kept at 4 °C for transport to the laboratory prior to wet extraction. All samples were analyzed within 48 hrs of sampling to minimize microbial alteration of the sediment. Prior to extraction, wet sediments were centrifuged to removed pore water.

Sediment extraction

For both procedures all glassware was acid-washed and rinsed 7 times with distilled deionized water (DDW) prior to the chemical extraction of the sediment components. Reagents used were 'AnalaR grade' or better.

Simultaneous extraction

Sediments were divided into 4 subsamples, 3 of which were exposed to a simultaneous extraction scheme (with a 15:1 solution:solid extractant ratio) designed to partition metals into (1) easily reducible metal (Mn oxides) (Chao 1972), (2) reducible metal (Fe oxides) (Tessier et al. 1979) and (3) alkaline extracted metal (organically bound) (Luoma 1986). A final aliquot was used for a wet weight/dry weight sediment conversion factor (Fig. 1). Sediment fractions were continuously shaken during the various extraction times and centrifuged to separate the supernatant from the host sediment. Supernatants were submitted to the University of

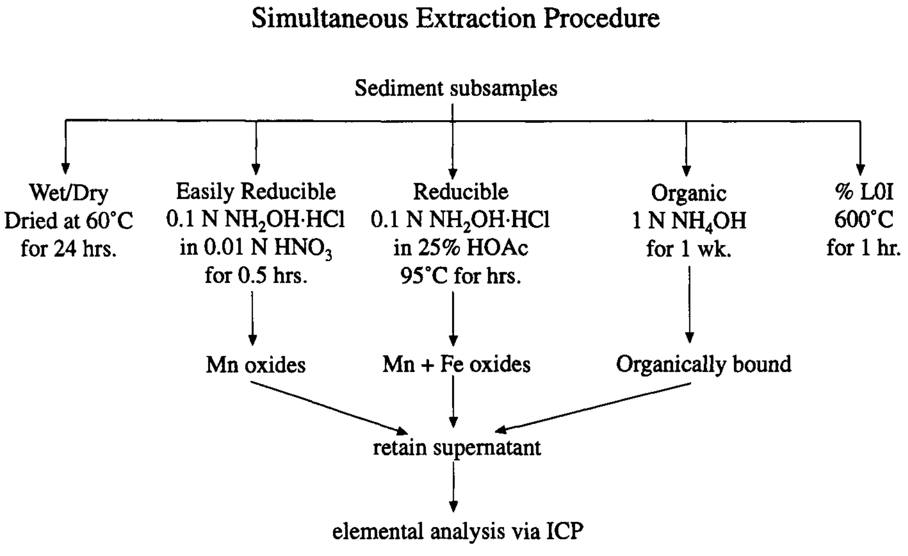
Simultaneous Extraction Procedure

Fig. 1. Simultaneous extraction scheme for the partitioning of trace metals into three major sediment components, easily reducible metal (associated with oxides of Mn), easily reducible + reducible metal (associated with both oxides of Mn and Fe) and organic matter. To determine amounts of metal associated with only the reducible portion of sediment, the concentrations of metal recovered by the easily reducible reagent (ER) is subtracted from the concentrations of metal recovered by the stronger reducing procedure (ER + R) (i.e. (ER + R) − ER = R).

Ottawa, Analytical services, Department of Geology for multi-elemental analysis via inductively coupled plasma emission spectroscopy (Thermo Jarell Ash atomscan 25). If the reagent designed to remove oxides of Mn and metals associated with these oxides is ER and the reagent used to remove oxides of both Mn and Fe and metals associated with both these oxides is ER + R then those metals that are associated with just Fe oxides (R) can be estimated by: ER + R fraction − ER fraction = R fraction. The easily reducible (ER) fraction will also include those metals which have been previously described as being readily exchangeable or leachable (e.g. Tessier et al. 1985, 1989). It is recognized that this fraction will also contain the most reactive portion of the amorphous Fe in the surficial sediments. However, it is assumed that the majority of metal recovered from this fraction is primarily exchangeable and/or associated primarily with the oxides of Mn. Metals bound to organics (ORG) are simply the concentrations of metals in the alkaline extract.

Sequential extraction

Individual steps of the sequential procedure are outlined in Fig. 2. Further

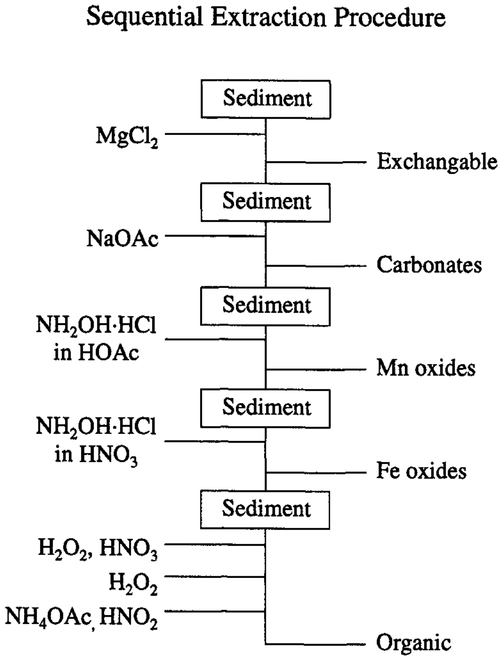

Fig. 2. Sequential extraction scheme of Tessier et al. (1979).

details can be found in Tessier et al. (1979, 1989). For the purposes of comparison, the metal concentrations recovered from the first three fractions of the SEQ extraction procedure were summed and defined as easily reducible metal (ER fraction = exchangeable + carbonates + Mn oxides). Hence, the sum of the first three fractions determined by the SEQ method were compared to the easily reducible fraction as determined by the SIM method. It is important to note that sediments treated sequentially will have been exposed to two reagents, 1N MgCl and NaOAC, prior to the same reagent used in the SIM for removal of metals associated with Mn oxides.

Acid extractable metal

To ensure that sediments for the SEQ and SIM procedure were geochemically similar and to determine percent recovery of metal by the two extraction procedures, concentrations of acid extractable (AE) metal were determined on a separate aliquot of sediment by aqua regia digests; sediments were digested overnight at 70 °C in a 2:1 mixture of HCl and HNO_3. AE metal was not significantly different between the samples of sediment used for the SIM and SEQ extraction procedures (*t*-test, $P \geqslant 0.05$) (Table 1).

Concentrations of metal recovered from the SIM, SEQ and AE sediment extractions were converted to μg metal/g dry weight of sediment for

Table 1. Concentrations (μg/g) of acid extractable metal recovered from sediments sampled from the low alkalinity wetland.

Metal	SIM	SEQ	*t*	*P*
Site 1				
Cd	2.5 ± 0.1	2.1 ± 0.1	2.76	N.S.
Mn	76.1 ± 34	61.6 ± 17	0.65	N.S.
Fe	12919.0 ± 3371	10689.0 ± 2572	0.92	N.S.
Zn	206.0 ± 48	208.7 ± 86	2.75	N.S.
Cu	15.6 ± 6.6	22.4 ± 3.6	0.05	N.S.
Site 2				
Cd	—	—		
Mn	82.7 ± 34	121.0 ± 54	1.05	N.S.
Fe	13924.0 ± 4813	21225.0 ± 12792	0.93	N.S.
Zn	260.0 ± 20	211.0 ± 24	0.05	N.S.
Cu	22.4 ± 6.6	20.4 ± 7.5	0.41	N.S.

comparison of the two methods. Results expressed as a % of AE metal are also presented. Significant differences ($P < 0.05$) between concentrations of ER, R and ORG metal recovered by the two methods were determined by student's *t*-test (Zar 1974).

Results and discussion

Several researchers (e.g. Luoma & Bryan 1981, Robinson 1984, Kheboian & Bauer 1987) have questioned the validity of extraction procedures for obtaining information about the association of trace metals in sediments because of the potential problems of post-extraction trace metal resorption. However, recently, Belzile et al. (1989) have demonstrated that post-extraction re-absorption of Cd, Cu, and Zn is minimal in naturally occurring oxidized freshwater lake sediments.

Unlike previous studies which determine the distribution of trace metals among various geochemical substrates through sequential extractions (e.g. Tessier et al. 1979; Tessier et al. 1984; Campbell et al. 1985; Hakansson et al. 1989), the simultaneous extraction determines where the metal is located using individual aliquots of sediments and arriving at metals associated with the different sediment components by difference. A comparison of the SIM and SEQ procedures indicated that the two methods were in agreement for both Zn and Cd, however, differences occurred for Fe, Mn and Cu.

Zn and Cd

Both methods recovered the same concentrations of Zn ($P > 0.05$, *t*-test) from the reducible fraction of sediment, with small amounts being associated with the easily reducible and organic components of sediment (Fig. 3a and b). Cadmium also showed good agreement with both methods recovering all the Cd from the reducible fraction of sediment ($P > 0.05$, *t*-test) (Fig. 4a and b).

Fe and Mn

Both methods indicated the same distribution of Fe among the three sediment components. On an individual sediment component basis, however, there was a significant difference ($P < 0.05$, *t*-test) in the concentrations of Fe recovered by the two methods. The SEQ method over-recovered Fe from the organic component of sediment and under-recovered Fe from the reducible portion of sediment as compared to the SIM method (Fig. 5a

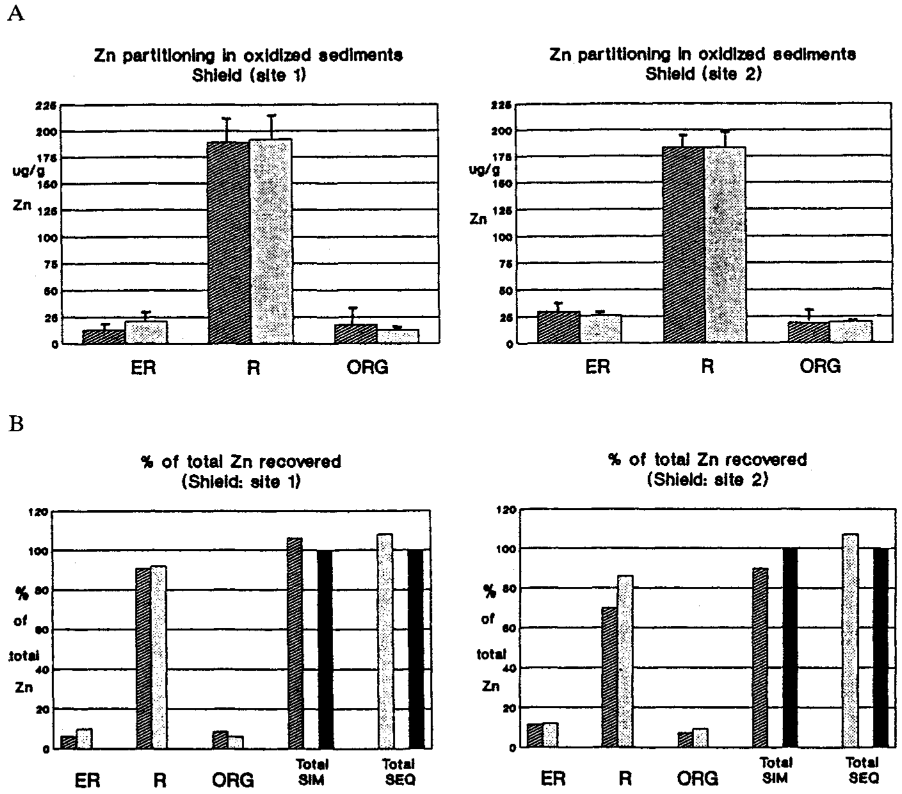

Fig. 3. a: Concentration of Zn ± 1 S.E. (μg/g dry weight) recovered from the easily reducible, reducible and organic portions of sediment by the SIM (hatched bar) and SEQ (stippled bar) methods. * indicates where concentrations are significantly different (t-test, $P < 0.05$). b: Percent recovery of Zn (normalized to concentrations of metal recovered by an aqua regia digest) from the three sediment components by the SIM (hatched bar) and SEQ (stippled bar) methods. Solid bar represents 100% of metal recovered.

and 5b). Luoma & Bryan (1981) found that pretreatment of sediments with strong reducing agents resulted in greater extraction of organically bound Fe (and Cu). Further, Jenne & Luoma (1977) noted that treatment of sediment with strong oxidizing agents such as those used by the SEQ method for the destruction of organic material may also cause the oxidation of Fe within the silicates, thereby liberating some of the residual metal. Both of these problems could explain the greater amount of organically bound Fe extracted by the SEQ procedure vs. the SIM procedure. Under-recovery of Fe from the reducible portion of sediment may be in part a result of the aging of the sediment over the time required to complete the various stages in the sequential extraction. For the SEQ

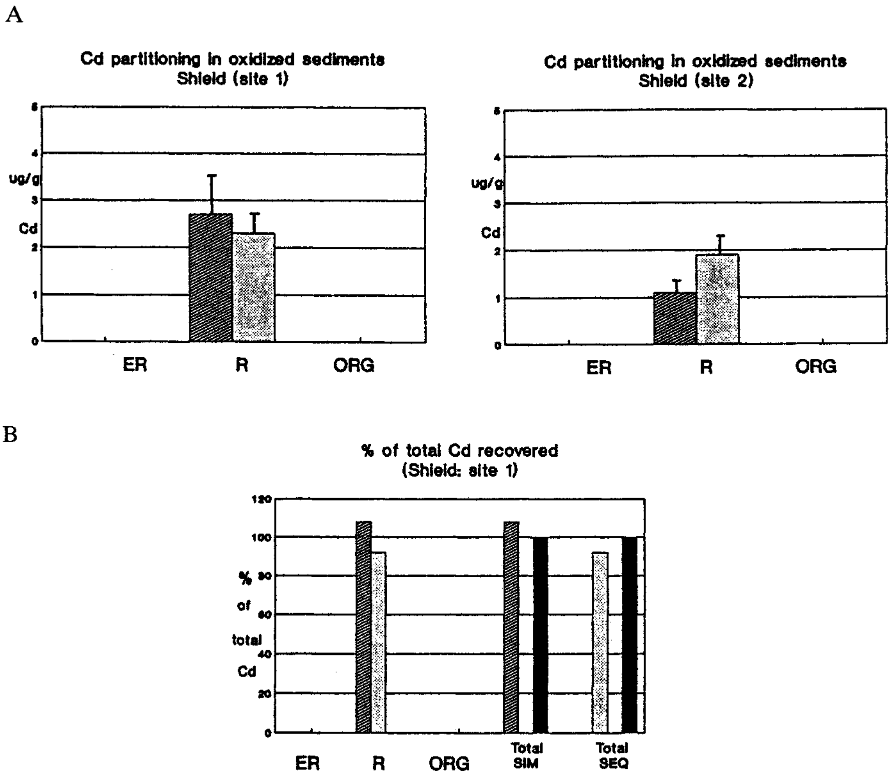

Fig. 4a and b. As in Fig. 3a and 3b except for Cd.

extraction procedure, sediments are not extracted for the reducible sediment components until 24 hrs after sample collection. Slavek & Pickering (1986) showed that aging of Fe oxides even over a period of hours was sufficient to prevent their total dissolution by reducing agents. Hence, the time required to perform the SEQ extraction vs. that of the SIM may be sufficient to prevent total recovering of reducible Fe.

The SEQ method also significantly ($P < 0.05$, *t*-test) under-recovered Mn from all three sediment components as compared to the SIM method (Fig. 6a and b). The poorer recovery of Mn from the sediments treated by the SEQ method vs. the SIM method is in part a result of the loss of this metal in the between reagent rinses that are required by the SEQ method. Analysis of these rinses indicated that this was indeed a source of metal loss for Mn but not for any of the other metals (Table 2). In addition, as with Fe, the longer processing time required by the SEQ method may be sufficient to allow for the reduction of previously oxidized Mn (i.e. greater than 24 hrs.) hence preventing its dissolution by the reducing reagents.

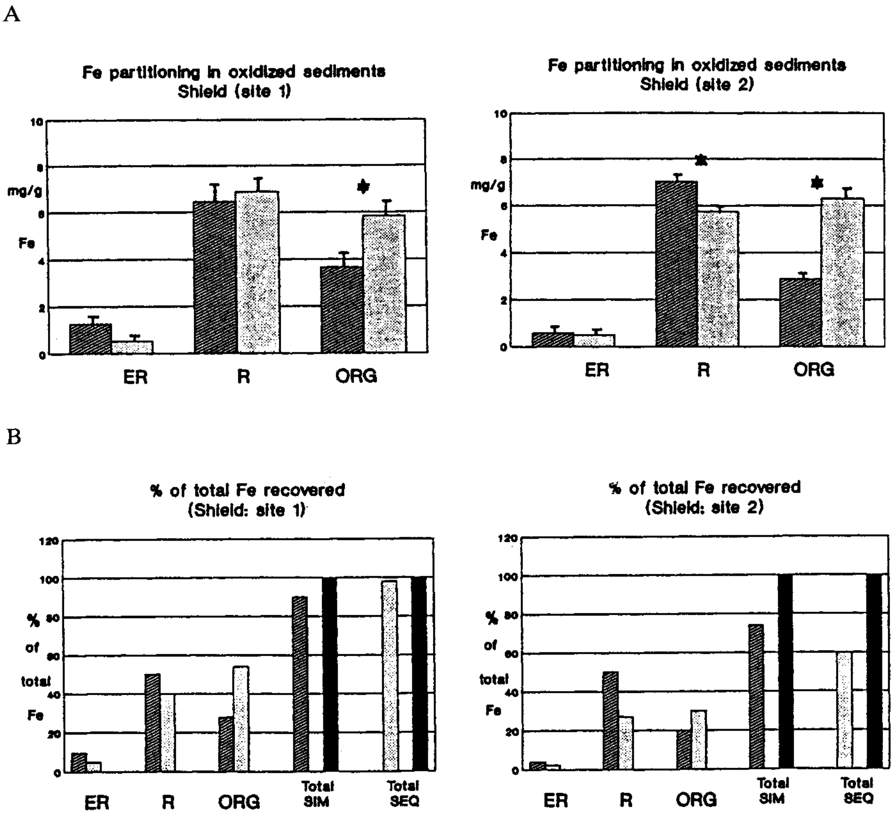

Fig. 5a and b. As in Fig. 3a and 3b except for Fe.

Cu

Both methods showed the same distribution for copper, with 80–90% of the copper being recovered from the organic fraction of sediment. However, the SEQ method significantly over-recovered amounts of organically-bound copper ($P < 0.05$, *t*-test) (Fig. 7a and b). Similar to Fe, treatment of sediments with a strong reducing agent, prior to the oxidation of organic matter may result with the over-extraction of this metal from the organic phase. As well, the procedural blanks that were run in parallel with the sediment extraction indicated that although reagents were 'Analar R' grade or better, they still contained significant amounts of Cu (Table 3). It is possible that as a result of the strong affinity of sediment organic matter for copper, any copper in the reagents used prior to the step for oxidizing organic matter was complexed by the sediment (i.e. concentrations of copper were lower in the extracts which contained the sediments

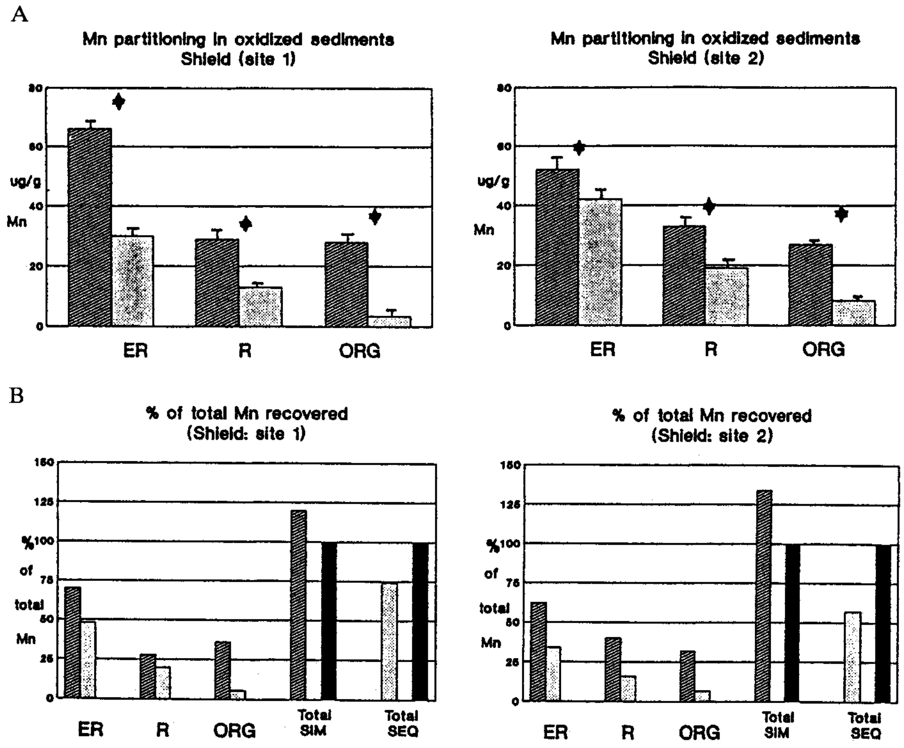

Fig. 6a and b. As in Fig. 3a and 3b except for Mn.

Table 2. Concentrations (μg/g) and % (of the total metal extracted by the sequential extraction) of metal found in the wash supernatant of the sequential extraction performed on sediments sampled from the low alkalinity wetland.

Metal	Mean total extracted	Mean total in wash	% of total
Site 1			
Fe	12442.72	193.2	1.55
Mn	46.3	5.4	11.46
Zn	225.9	5.9	2.6
Cu	25.6	0.02	0.07
Cd	2.3	0	0
Site 2			
Fe	12546.70	187.4	1.5
Mn	69.7	6.12	9.0
Zn	228.4	7.04	3.0
Cu	28.6	0.41	1.4
Cd	1.9	0	0

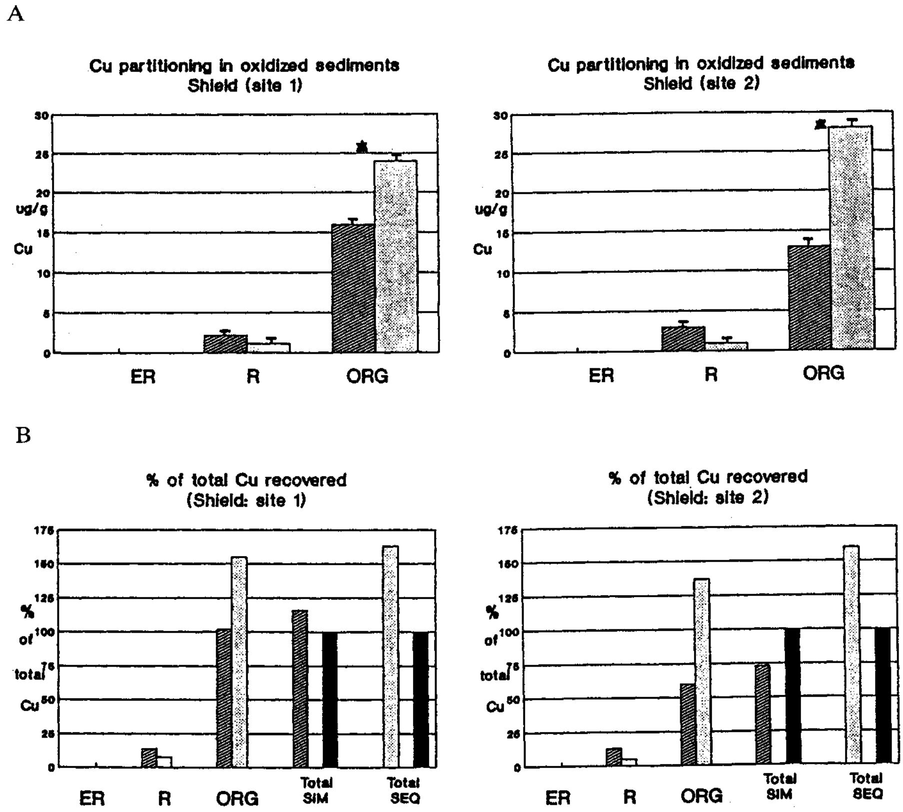

Fig. 7a and b. As in Fig. 3a and 3b except for Cu.

samples as compared to the reagent blanks). Once the organic matter is decomposed by the hydrogen peroxide digestion, copper from the sediments plus that removed from the reagents would be recovered in this step. Use of a single aliquot of sediment minimizes such contamination carry-over. In the current study, contamination of sediment samples by reagents used for the SEQ procedure added an additional 0.17 mg/L of Cu to the sediment, which resulted in an over-extraction of 6.3 μg/g Cu from the organic component of sediment. This amount subtracted from the amount of Cu recovered from the organic component of sediment by the SEQ procedure results in values which are comparable to those determined by the SIM procedure.

Table 3. Trace metal concentrations (mg/L ± 1. S.D. (n = 3)) in the reagents used for the SIM and SEQ extraction of sediments.

Reagent	Fe	Mn	Zn	Cd	Cu
SIM					
NH_2OH HCl/HNO_3	N.D.	0.003 ±0.002	N.D.	N.D.	0.007 ±0.002
NH_2OH HCl/HOAc	0.041 ±0.022	N.D.	0.009 ±0.012	N.D.	0.001 ±0.002
NH_2OH	0.008 ±0.012	0.002 ±0.001	N.D. N.D.	N.D. N.D.	0.009 ±0.006
SEQ					
MgCl	N.D.	N.D.	N.D.	0.01 ±0.01	0.025 ±0.01
NaOAc	0.041	N.D.	N.D.	N.D.	0.016 ±0.007
NH_2OH HCl/HOAc	0.013 ±0.005	N.D.	0.004 ±0.002	N.D.	0.009 ±0.004
NH_2OH HCl/HOAC	0.128 ±0.105	N.D.	0.097 ±0.022	0.002 ±0.002	0.006 ±0.008
HNO_3, H_2O_2/ NH_2OAC/HNO_3	0.068 ±0.005	N.D.	N.D.	N.D.	0.117 ±0.148

Summary and conclusions

For oxidized sediments from low alkalinity wetlands and lakes, the simultaneous scheme described here may be more appropriate for partitioning trace metals into three major sediment components (i.e. oxides of Fe, Mn and organics), vs. a SEQ extraction which includes steps for partitioning metals into carbonate and residual fractions. Additional advantages of the SIM method over SEQ methods include rapid sample processing plus minimal sample manipulation such as the 'in-between' reagent rinses. Rapid sample processing minimizes the ageing of the sediments, ensuring a more complete recovery of redox sensitive species such as Fe and Mn. Minimal sample manipulation i.e. the omission of the 'in between' reagent rinses' minimizes the loss of metals such as Mn from the sediments. Finally, as individual aliquots of sediments are exposed to only one reagent vs. the SEQ method where the sediment is exposed to several reagents, contamination of the sediment is minimized. For Cu, contamination of the sediment by the reagents used in this study was significant.

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