

Sequential Extraction Procedure for the Speciation of Particulate Trace Metals

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An analytical procedure involving sequential chemical extractions has been developed for the partitioning of particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. Experimental results obtained on replicate samples of fluvial bottom sediments demonstrate that the relative standard deviation of the sequential extraction procedure is generally better than $\pm 10\%$. The accuracy, evaluated by comparing total trace metal concentrations with the sum of the five individual fractions, proved to be satisfactory. Complementary measurements were performed on the individual leachates, and on the residual sediments following each extraction, to evaluate the selectivity of the various reagents toward specific geochemical phases. An application of the proposed method to river sediments is described, and the resulting trace metal speciation is discussed.

Most studies dealing with particulate metals in natural water systems (i.e., metals associated with suspended matter or bottom sediments) concern total metal concentration. Relatively few attempts have been made to evaluate the speciation of particulate metals, i.e., the partitioning among the various forms in which they might exist. Use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable.

Conceptually, the solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents; considering the similarities between sediments and soils, extraction procedures can be borrowed or adapted from the methods of soil chemical analysis (1). Several experimental procedures, varying in manipulative complexity, have recently been proposed for determining the speciation of particulate trace metals. These procedures can be grouped into (i) methods designed to effect the separation between residual and nonresidual metals only (2-5), and (ii) more elaborate methods making use of sequential extractions (6-14). The former methods normally involve a single extraction and offer a better contrast between anomalous and background samples than does the determination of the total metal concentration. Despite their rapidity and relative simplicity, these techniques suffer from the difficulty of finding a single reagent effective in dissolving quantitatively the nonresidual forms of metal without attacking the detrital forms. The use of sequential extractions, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals.

The purpose of this study was to develop and examine the merits of a method of sequential "selective" extractions for partitioning particulate trace metals into chemical forms likely to be released in solution under various environmental conditions. The trace metals Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn were studied. For convenience, the experiments were

performed with bottom sediments, which are more easily obtained in workable quantities than is suspended matter. Although iron and manganese are not generally referred to as trace metals in the literature, they have been so designated in the following sections in order to simplify the presentation of the results.

SELECTION OF FRACTIONS

In defining the desired partitioning of trace metals, care was taken to choose fractions likely to be affected by various environmental conditions; the following five fractions were selected.

Fraction 1. Exchangeable. Numerous studies (15-23) performed on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect sorption-desorption processes.

Fraction 2. Bound to Carbonates. Several workers (9, 11, 24, 25) have shown that significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.

Fraction 3. Bound to Iron and Manganese Oxides. It is well established (26) that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (i.e., low Eh).

Fraction 4. Bound to Organic Matter. Trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals.

Fraction 5. Residual. Once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

EXPERIMENTAL

Sampling. Sediment samples were collected at two sampling stations, Saint-Marcel and Pierreville, located in the lower reaches of the Yamaska and Saint-Francois rivers (Québec, Canada), respectively. An Ekman dredge was used to collect a large amount of sediment; without emptying the dredge, a sample was taken from the center with a polyethylene spoon to avoid contamination by the metallic parts of the dredge. The samples were stored at 4 °C for ≤ 3 days, then dried at 105 °C in a forced air oven. They were subsequently ground in an agate mortar, homogenized and stored at 4 °C until needed.

Leaching Procedures and Reagents. After a critical evaluation of the available literature, the following chemical extraction methods were retained for further study; the quantities indicated below refer to 1-g sediment samples (dry weight of the original sample used for the initial extraction).

(i) *Exchangeable*. The sediment was extracted at room temperature for 1 h with 8 mL of either magnesium chloride solution (1 M MgCl_2 , pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation.

(ii) *Bound to Carbonates*. The residue from (i) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated.

(iii) *Bound to Fe-Mn Oxides*. The residue from (ii) was extracted with 20 mL of either 0.3 M $\text{Na}_2\text{S}_2\text{O}_4$ + 0.175 M Na-citrate + 0.025 M H-citrate, as prescribed by Anderson and Jenne (27), or 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc . The latter experiments were performed at $96 \pm 3^\circ\text{C}$ with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated.

(iv) *Bound to Organic Matter*. A method described by Gupta and Chen (9) was adopted. To the residue from (iii) were added 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 , and the mixture was heated to $85 \pm 2^\circ\text{C}$ for 2 h with occasional agitation. A second 3-mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to $85 \pm 2^\circ\text{C}$ for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH_4OAc is designed (9) to prevent adsorption of extracted metals onto the oxidized sediment.

(v) *Residual*. The residue from (iv) was digested with a $\text{HF}\text{--}\text{HClO}_4$ mixture according to the procedure described below for total metal analysis.

The "selective" extractions were conducted in centrifuge tubes (polypropylene, 50 mL) to minimize losses of solid material. Between each successive extraction, separation was effected by centrifuging (Sorvall, Model RC2-B) at 10 000 rpm (12 000 g) for 30 min. The supernatant was removed with a pipet and analyzed for trace metals (see below), whereas the residue was washed with 8 mL of deionized water; after centrifugation for 30 min, this second supernatant was discarded. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid material, particularly organic matter.

Deionized water used in preparing stock solutions and in each step of the leaching procedure was obtained from a Millipore Milli-Q3RO/Milli-Q2 system. All glassware used for the experiments was previously soaked in 14% HNO_3 (v/v) and rinsed with deionized water. All reagents used in this study were of analytical grade or better and were checked for possible trace metal contamination; of all the reagents used, only sodium dithionite showed serious contamination (Zn).

Trace Metal Analysis. Trace metal concentrations were determined by atomic absorption spectrophotometry (Varian Techtron Model AA-5) involving direct aspiration of the aqueous solution into an air-acetylene flame. The following techniques were used for the first four fractions. For the trace metals Cd, Co, Cu, Ni, Pb, and Zn, a standard addition technique was employed because matrix effects, presumably due to material leached from the sediments, were observed; these effects would have contributed in many cases to an error of as much as 15%. For the metals present in high concentrations (Fe and Mn) the supernatant solution was diluted (20 to 50 \times) with deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor.

For total or residual trace metal analysis, the solid was digested with a 5:1 mixture of hydrofluoric and perchloric acids. For a 1-g (dry weight) sample, the sediment was first digested in a platinum crucible with a solution of concentrated HClO_4 (2 mL) and HF (10 mL) to near dryness; subsequently a second addition of HClO_4 (1 mL) and HF (10 mL) was made and again the mixture was evaporated to near dryness. Finally, HClO_4 (1 mL) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12 N HCl and diluted to 25 mL. The resulting solution was then analyzed by flame atomic absorption spectrophotometry for trace metals using the standard addition technique.

Complementary Measurements. To assess the selectivity of each of the extraction steps, complementary measurements were performed on both the leachates (concentrations of Si, Al, Ca,

S, inorganic and organic carbon) and the sediments before and after the various chemical treatments (X-ray diffraction; concentrations of S, inorganic and organic carbon).

Silica, aluminum, and calcium concentrations in the leachates were determined by atomic absorption spectrophotometry using a nitrous oxide-acetylene flame. For Al and Si, the leachate 5 was obtained by fusion with lithium metaborate followed by dissolution of the fused material in 1.2 N HCl. Sulfide concentrations were measured with a selective ion electrode (Orion Model 96-16A) using the sulfide antioxidant buffer solution (SAOB), as prescribed by the manufacturer. The SAOB solution was added to the supernatant immediately after centrifugation and separation from the sediments. Dissolved inorganic and organic carbon concentrations were determined with a Beckman Total Organic Carbon Analyzer (Model 915A).

Particulate sulfur and carbon were determined with a Leco Total Sulfur Analyzer (Model 1R-32) and a Leco Total Carbon Analyzer (Model 1R-12), respectively. Inorganic carbon was assumed to be the difference between total and organic carbon concentrations, the latter being measured after acid treatment (HCl) of the sediment to dissolve the carbonate fraction. X-ray diffraction analyses were performed on the whole sediment as well as on the 2–16 μm and <2- μm fractions; separation of the fractions was effected by differential centrifugation, according to Stoke's law.

RESULTS AND DISCUSSION

Choice of Reagents and Leaching Conditions. In the choice of reagents for the sequential extractions, particular emphasis was placed on the potential selectivity of each leaching solution. Procedures currently used in soil chemical analysis were considered, together with those developed in recent studies of trace metal partitioning in sediments and suspensions.

Many reagents, including ammonium acetate (1, 9, 25, 28–30), sodium acetate (28), and magnesium chloride (8, 13), have been employed to liberate *exchangeable* metals. Of these, NH_4OAc (pH 7.0) has been the most extensively used in soil and sediment analysis. However, according to many workers (1, 28, 30), it may also attack carbonates. According to Chapman (28), the solubility of CaCO_3 is much lower in 1 M sodium acetate at pH 8.2, a reagent currently used in measuring the cation-exchange capacity of soils, than in the neutral ammonium acetate. For this reason, NH_4OAc was not considered in the present study; the merits of 1 M NaOAc (pH 8.2) and MgCl_2 (pH 7.0), as suggested by Gibbs (8, 13), were examined and are discussed below.

Reagents recommended for dissolving selectively the *carbonate* fraction in sediments generally make use of sodium acetate and/or acetic acid at acidic pH values (6, 9, 24, 31, 32). The procedure selected involves 1 M NaOAc and adjustment of the pH to 5.0 with HOAc . Grossman and Millet (33) reported that organic carbon and free iron concentrations in noncalcareous soil samples were unchanged after contact with this buffer for nine weeks; other workers (6, 9, 32) have demonstrated that lower pH values lead to a partial attack of Fe and Mn oxides. The time required for carbonate dissolution will depend upon such factors as particle size, percentage and type of carbonate present, and sample size (31). To evaluate the optimum time for leaching the carbonate fraction, sediment samples were first extracted during 1 h for exchangeable metals with either 1 M NaOAc (pH 8.2) or 1 M MgCl_2 (pH 7.0), and then further leached with 1 M NaOAc (pH 5.0, adjusted with HOAc); the calcium concentration was measured in centrifuged supernatants after different time intervals. Figure 1 indicates that for both sediments dissolution of calcium was complete within 5 h. This extraction time is likely to be sufficient for most samples of finely divided suspended solids. However, for coarse bottom sediments with high carbonate content, longer leaching times and frequent pH adjustment might be necessary.

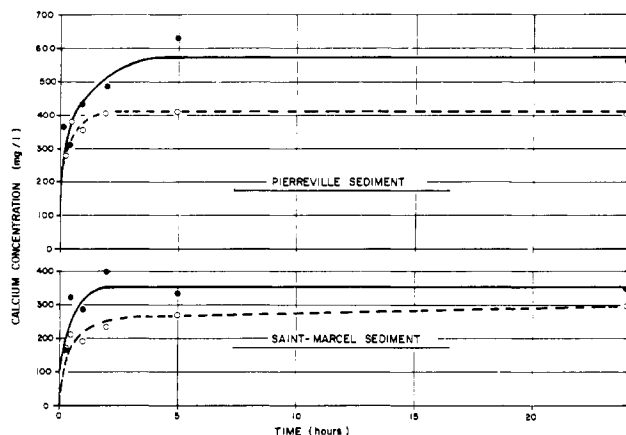


Figure 1. Effect of leaching time on calcium concentrations in the NaOAc-HOAc (pH 5.0) extracting solution for sediments previously leached for exchangeable metals with 1 M MgCl_2 at pH 7.0 (●—●) or with 1 M NaOAc at pH 8.2 (O---O)

Figure 1 shows that for both sediments a lesser amount of calcium is found in fraction 2 when NaOAc rather than MgCl_2 is used in the preliminary extraction to leach exchangeable metals. This effect can probably be ascribed to the complexing ability of acetate, i.e., $\text{Ca}^{2+} + \text{OAc}^- = \text{CaOAc}^+$; $\log K = 1.24$ (34); thermodynamic calculations, taking into account the acetate complex formation, predict even more pronounced differences than those observed in Figure 1. For this reason, and also because it has recently been found (35) to be an effective reagent for desorbing specifically adsorbed trace metals, MgCl_2 was finally selected as the initial reagent in the sequential extraction procedure.

The most successful methods for leaching *iron and manganese oxides* involve the combined action of reagents reducing these metals to their ferrous and manganous forms, respectively, and of agents capable of keeping in solution the relatively large amounts of metals liberated; the two couples most often used are hydroxylamine hydrochloride-acetic acid (2, 4, 7, 9, 24, 36) and sodium dithionite-citrate (8, 9, 13, 31, 37, 38). With the latter combination, using concentrations prescribed by Anderson and Jenne (27), we observed substantial precipitation of trace metals, presumably due to the formation of sulfide as result of the disproportionation of dithionite. Examination of the results of Gupta and Chen (9), who employed both combinations in parallel experiments, reveals that trace metal concentrations were consistently lower in the leachates obtained with dithionite-citrate than in those obtained with hydroxylamine hydrochloride-acetic acid; the differences were greatest for those trace metals which form the most insoluble sulfide salts. Furthermore, several additional problems are raised by the utilization of the dithionite-citrate couple: (i) dithionite is highly contaminated with zinc and its purification by a chelation-extraction procedure proves difficult (12); (ii) frequent clogging of the burner is observed upon analysis of the aqueous extracts by flame atomic absorption spectrophotometry, due to the high salt content of the extraction solution; to minimize this problem, a chelation-extraction step is required before analysis (38). Consideration of these problems led us to eliminate the dithionite-citrate couple from further study.

To evaluate the optimum time for reducing and dissolving the Fe and Mn oxides, sediment samples, previously extracted for exchangeable metals (MgCl_2) and carbonates (NaOAc + HOAc, pH 5.0), were leached with the $\text{NH}_2\text{OH}\cdot\text{HCl}$ + HOAc solution, and the iron concentration was measured in the centrifuged supernatants after different time intervals. The results (Figure 2) indicate that for both sediments extraction of reducible iron was essentially complete after 6 h. In

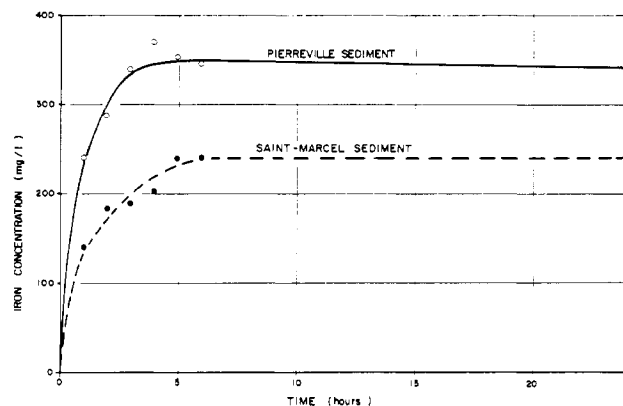


Figure 2. Effect of leaching time on iron concentrations in the 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -25% (v/v) HOAc extracting solution for sediments previously leached for exchangeable metals with 1 M MgCl_2 and for the carbonate fraction with NaOAc-HOAc (pH 5.0)

subsequent experiments, a leaching time of 6 h was adopted, as longer times would have increased the possibility of attacking fractions 4 and 5.

Hydrogen peroxide in an acidic medium is generally used to oxidize *organic matter* in soil (1, 31) and sediment (6, 7, 9, 12, 14) analysis, even though oxidation of all forms of organic matter may not be complete (1). More efficient methods for destroying organic matter do exist (e.g., concentrated nitric acid used separately or in combination with hydrochloric or perchloric acids), but they usually suffer from a lack of specificity in the sense that they may also effect a partial attack of silicate lattices. In the present study, a method involving treatment with hot hydrogen peroxide in a nitric acid medium was adopted (9).

Procedures for dissolving primary and secondary minerals (*residual fraction*) usually involve either alkaline fusion (1, 6, 8, 13, 39) or dissolution with mixtures of hydrofluoric acid (1, 7, 9, 11, 12, 25, 32) and some other strong acid (e.g., nitric or perchloric acid). To ensure complete decomposition of the silicates, a large excess of fusing salt must be used, leading to high salt concentrations in the solution to be analyzed for trace metals; this can cause instability and high background readings in atomic absorption spectrophotometry. For these reasons, we selected the $\text{HF}\text{-HClO}_4$ digestion procedure described previously.

The overall procedure finally adopted thus involves five successive extractions with: (i) MgCl_2 (pH 7.0); (ii) NaOAc/HOAc (pH 5.0); (iii) $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc (pH ~2); (iv) $\text{H}_2\text{O}_2/\text{HNO}_3$ (pH ~2) and subsequently NH_4OAc ; (v) HF and HClO_4 .

Precision and Accuracy. The analytical precision for each of the extraction steps, and for the overall procedure, was tested by subjecting six sub-samples of each of the Saint-Marcel and Pierreville sediments to the sequential procedure described above; the results obtained, together with the detection limit (expressed in micrograms metal per gram of dry sediment), are shown in Table I. Note that the detection limit, defined as twice the base-line noise, could be lowered by using higher sediment/solution ratios. As anticipated, the precision is generally low when the concentration approaches the detection limit but improves for higher concentrations; coefficients of variation of 10% or lower are typically observed for metal concentrations amounting to five times or more the detection limit. Precision, while acceptable in most cases for the whole sediment, is expected to improve when the sequential procedure is applied to suspensions or to the fine fraction of bottom sediments (e.g., $<20\ \mu\text{m}$).

Low reproducibility of the results is observed for lead in the Pierreville sediment. Leaching and analytical procedures are probably less responsible for this result than is the

Table I. Detection Limit, Precision, and Accuracy of the Sequential Extraction Procedure as Determined on Two Sediment Samples^a

	mean and standard deviation ^b				mean and standard deviation ^b			
	fraction ^c	detection limit	sediment No. 1 (Saint-Marcel)	sediment No. 2 (Pierreville)	fraction ^c	detection limit	sediment No. 1 (Saint-Marcel)	sediment No. 2 (Pierreville)
Cd	1	0.1	<0.1	<0.1	1	0.6	<0.6	<0.6
	2	0.3	<0.3	<0.3	2	0.5	2.6 ± 0.4	9.4 ± 5.5 ^d
	3	0.1	<0.1	0.15 ± 0.05	3	1.0	3.8 ± 0.6	10.3 ± 2.9 ^d
	4	0.2	<0.2	<0.2	4	1.2	2.7 ± 0.6	7.8 ± 1.7 ^d
	5	0.1	<0.1	<0.1	5	1.4	7.8 ± 1.2	10.1 ± 2.0 ^d
	Σ				Σ		16.9 ± 1.4	37.7 ± 11.1 ^d
	M _T	0.1	<0.1	<0.1	M _T	1.4	18.2 ± 2.9	42.5 ± 6.6 ^d
Co	1	0.5	<0.5	<0.5	1	0.1	<0.1	<0.1
	2	2.0	<2.0	<2.0	2	0.5	11.2 ± 0.6	7.9 ± 2.0
	3	0.5	3.6 ± 0.5	6.4 ± 0.7	3	0.1	22.2 ± 0.5	33.5 ± 0.6
	4	1.4	<1.4	<1.4	4	0.1	3.9 ± 0.2	9.0 ± 1.3
	5	1	5.4 ± 0.4	9.2 ± 0.8	5	1	49.9 ± 7.8	71.7 ± 4.8
	Σ		12.9 > X̄ > 9.4	19.6 > X̄ > 16.3	Σ		87.2 ± 7.2	122.1 ± 5.4
	M _T	1	13.2 ± 1.9	19.5 ± 1.8	M _T	1	88 ± 2	127 ± 5
Cu	1	0.1	0.15 ± 0.05	0.2 ± 0	1	0.4	0.4 ± 0.1	0.4 ± 0.1
	2	0.5	3.2 ± 0.3	8.2 ± 0.5	2	0.4	732 ± 33	476 ± 21
	3	0.4	4.0 ± 0.3	9.1 ± 0.8	3	50	4630 ± 100	6910 ± 120
	4	0.5	5.0 ± 0.7	11.3 ± 1.5	4	80	620 ± 60	1150 ± 30
	5	1	7.9 ± 0.5	16.4 ± 1.0	5	10	30300 ± 1000	39500 ± 2400
	Σ		20.2 ± 1.0	45.2 ± 1.1	Σ		36300 ± 1100	48000 ± 2500
	M _T	1	25.0 ± 4.9	48.6 ± 4.0 ^d	M _T	10	36100 ± 260	50400 ± 360
Ni	1	0.2	<0.2	<0.2	1	2.5	99 ± 2	38 ± 0
	2	1.1	1.1 ± 0.3	1.9 ± 0.5	2	9	90 ± 21	314 ± 20
	3	0.5	6.9 ± 0.8	13.2 ± 0.7	3	10	106 ± 5	265 ± 10
	4	0.6	1.4 ± 0.5	2.7 ± 0.3	4	1.2	10.9 ± 0.8	30 ± 1
	5	1	17.3 ± 2.6	38.4 ± 3.7	5	2	413 ± 21	456 ± 29
	Σ		26.5 ± 2.4	56.2 ± 4.0	Σ		720 ± 30	1103 ± 37
	M _T	1	28.8 ± 1.5	60.2 ± 1.5	M _T ^e	2	768 ± 17	1090 ± 30

^a Detection limit, mean value, and standard deviation are all expressed in μg/g of sediment, dry weight.^b Unless otherwise indicated, results for six replicate determinations.^c Following the sequence described in the text: 1, exchangeable, 2, carbonate . . . , Σ represents the sum of the five fractions and M_T represents the total metal concentration.^d A value differing from the mean by more than three times the standard deviation was excluded.^e Results for three replicate determinations.

Table II. Percentages of Total Si, Al, Ca, S, Inorganic Carbon, and Organic Carbon Concentrations Found in the Successive Leachates

parameter	fraction	leached from sediment, %	
		sediment No. 1 (Saint-Marcel)	sediment No. 2 (Pierreville)
Si	exchangeable	0.02	0.01
	bound to carbonates	0.03	0.06
	bound to Fe-Mn oxides	0.45	0.73
	bound to organic matter	0.31	0.47
	residual	99.2	98.7
Al	exchangeable	0.03	0.03
	bound to carbonates	0.06	0.14
	bound to Fe-Mn oxides	1.6	2.2
	bound to organic matter	1.5	2.9
	residual	96.8	94.7
Ca	exchangeable	2.4	4.9
	bound to carbonates	17.9	26.3
	bound to Fe-Mn oxides	3.4	5.4
	bound to organic matter	3.6	4.6
	residual	72.7	58.8
S	exchangeable	<2	<2
	bound to carbonates	<2	<2
inorganic carbon	exchangeable	2.4	2.8
organic carbon	exchangeable	1.3	1.7

heterogeneity of this sediment with respect to Pb, as only one of the two sediments shows a high variability. The high variability reported here for Pb in the Pierreville sediment was also observed during preliminary experiments, despite repeated grinding of the sediment in an effort to improve its homogeneity. Similar problems of low reproducibility for "acid leachable" (pH 1.5) lead in suspended sediments have been reported (40) and were attributed to the presence of relatively large ($>8\ \mu\text{m}$) lead-rich particles originating from aerosols produced by the combustion of leaded gasolines; such particles are observed close to highways (41). Wagemann et al. (30) also reported scattered lead results following leaching of sediments and suspensions with saturated EDTA or 0.1 M HCl solutions.

Comparison of the sum of the metal concentrations in the individual fractions with the total metal concentration $[M]_T$ (Table I) shows good agreement for all trace metals. Note that the variability discussed previously for specific fractions of Pb in the Pierreville sediment is also found in the $[Pb]_T$ determinations for this sediment.

Selectivity. Selectivity of the extraction reagents toward specific geochemical phases is an important performance criterion for a sequential extraction procedure designed to determine the speciation of trace metals. In the following discussion we shall attempt to evaluate the degree to which the desired sediment phases are solubilized, and also the degree to which the remaining phases resist attack. Two types of evidence are considered: (i) the sediment components that are solubilized during each successive extraction and thus are found in the various leachates along with the trace metals, and (ii) the changes in overall sediment composition after treatment with each successive reagent. A knowledge of the principal characteristics of the two sediment samples is a prerequisite to this type of approach. The results of X-ray diffraction on the whole sediments indicate that quartz, plagioclase, and K-feldspar are the major phases whereas chlorite, amphibole, and mica are minor constituents; two other minor phases were identified in the $2\text{--}16\ \mu\text{m}$ fraction (dolomite) and in the $<2\text{-}\mu\text{m}$ fraction (smectites). Inorganic carbon (0.2–0.4% C), organic carbon (0.5–0.7% C), and sulfide (0.04–0.05% S) all represent small percentages of the total sediment composition.

Fraction 1. Exchangeable Metals. The low levels of Si, Al, S, and organic carbon found in leachate 1 (Table II) imply that MgCl_2 treatment does not affect silicates, sulfides, or organic matter. Thermodynamic calculations indicate that Fe and Mn oxides should not be significantly solubilized at pH 7.0, and concentrations of Fe in leachate 1 are indeed very low. The slight dissolution of carbonates (2–3%) could be reduced by shortening the leaching time.

Fraction 2. Metals Bound to Carbonates. Dissolution of the sediment carbonate fraction is essentially complete as evidenced by the disappearance of the dolomite X-ray diffraction peak following treatment with the acetate buffer (pH 5.0). Further evidence is provided by the kinetics of the leaching step (Figure 1); increasing the leaching time from 5 to 24 h does not result in higher calcium concentrations in the leachate.

The low levels of Si, Al, and S found in leachate 2 (Table II) indicate that attack of silicate and sulfide minerals by the $\text{NaOAc}\text{--HOAc}$ reagent is minimal. Furthermore, the organic carbon content of the sediments is undiminished after treatment with the acetate buffer (Table III), suggesting that the organic fraction is also unaffected (cf. 31). The appreciable iron and manganese concentrations found in leachate 2 probably result from the dissolution of divalent salts. Ferrous and manganous carbonate are the logical candidates (42, 43), given the pH values and inorganic carbon concentrations prevalent in natural environments.

Assuming that the trace metals found in fraction 2 originate solely from dissolution of dolomite, the only carbonate phase identified, one can calculate the following concentrations for these metals in $\text{CaMg}(\text{CO}_3)_2$: 190 and 300 ppm Cu, 65 and 70 ppm Ni, 150 and 350 ppm Pb, and 660 and 290 ppm Zn, where the two values refer to Saint-Marcel and Pierreville sediments respectively. These concentrations are far in excess of those reported for carbonate sedimentary rock (44), for deep sea sediments (44), or for calcium carbonate of biogenic origin (45). This raises the possibility that in the preceding extraction the neutral 1 M MgCl_2 did not completely desorb the specifically adsorbed trace metals, the adsorption-desorption processes being strongly pH dependent; lowering the pH to 5.0 in the subsequent extraction would then release the remaining specifically adsorbed trace metals as well as the

Table III. Sulfide and Organic Carbon Concentrations Remaining in Sediments after Successive Leachings

treatment	[sulfide] % S		[organic carbon] % C	
	sediment No. 1 (Saint-Marcel)	sediment No. 2 (Pierreville)	sediment No. 1 (Saint-Marcel)	sediment No. 2 (Pierreville)
none	0.043	0.040	0.5	0.6
NaOAc-HOAc (pH = 5.0)	^a	^a	0.5	0.7
NH ₂ OH·HCl-HOAc (pH ≈ 2)	0.047	0.045	0.5	0.7
H ₂ O ₂ -HNO ₃ (pH ≈ 2)	0.018	0.017	0.1	0.1

^a Not measured.

carbonate-bound fraction. Examination of curves of trace metal adsorption as a function of pH (22, 35) suggests that lowering the pH from 7.0 to 5.0 might release in solution a large fraction of specifically adsorbed trace metals from various solid substrates.

Fraction 3. Metals Bound to Fe-Mn Oxides. Increasing the leaching time from 6 to 24 h did not result in higher iron concentrations in leachate 3 (Figure 2), indicating that the extraction of reducible iron oxide phases is complete; as manganese oxides are known to be more easily leached than iron oxides (46), it is probable that their extraction is also complete. The low levels of Fe and Mn found in the subsequent leachate (fraction 4, Table I) are an additional indication of the completeness of the extraction.

Thermodynamic calculations suggest that metal sulfides should be solubilized to a large extent at the pH of the extracting solution; however, as shown in Table III, sulfur levels are unchanged in the sediments after extraction with NH₂OH·HCl-HOAc. These results imply that the reduced sulfur present in the sediments studied does not exist as amorphous metal sulfides, but rather as well-crystallized phases (e.g., pyrite) or as organosulfur compounds. The organic carbon content of the sediments is also undiminished after treatment with the hydroxylamine hydrochloride-acetic acid reagent, indicating that organic matter is not significantly leached. The possible liberation of some metals from labile organic complexes cannot however be excluded.

The low levels of Si and Al found in leachate 3 indicate that only slight attack of the major silicate components occurs during treatment with NH₂OH·HCl-HOAc. A relative decrease of the smectites X-ray diffraction peak is noted, suggesting partial attack of these minerals. Contrary to the results of Chester and Hughes (24), however, no evidence of chlorite transformation can be observed from X-ray diffraction analysis.

Fraction 4. Metals Bound to Organic Matter. Oxidation of organic matter by acidified hydrogen peroxide, although extensive, is incomplete; sulfide minerals are also extracted to a large extent, as shown in Table III. According to Jackson (1), the remaining organic matter should consist of paraffin-like material and resistant structural (nonhumified) organic matter residues. Stronger oxidizing solutions usually rely upon the use of strong acids, which may seriously attack silicate material. Thus the choice of H₂O₂ represents a compromise between complete oxidation and alteration of silicate material.

The low levels of Si and Al found in leachate 4 suggest that attack of the major silicate phases is indeed minimal. However, a relative decrease in the smectites and chlorite X-ray diffraction peaks is observed, suggesting a partial alteration of these minerals (Figure 3); mica is also subject to partial transformation, as evidenced by the appearance of a small shoulder on the X-ray diffraction peak.

Fraction 5. Residual Metals. The residue remaining after the four preceding extractions consists essentially of detrital silicate minerals, resistant sulfides, and a small quantity of refractory organic material. Treatment with the HF-HClO₄

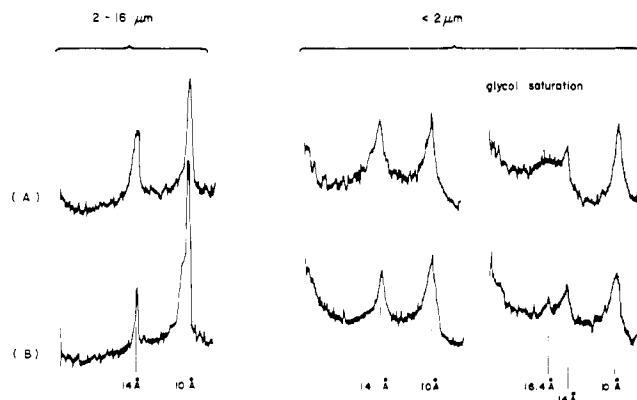


Figure 3. X-ray diffraction spectra for the Saint-Marcel sediment: (A) without any treatment; (B) after the first four extractions. Peaks represent mica (10 Å) chlorite (14 Å) and smectites (16.4 Å)

reagent results in complete dissolution.

Speciation. Having considered in some detail the analytical performance of the proposed sequential extraction procedure, we shall now briefly comment on the trace metal partitioning observed in the sediment samples studied (Table I). Each successive fraction is discussed below: where two concentration values are given, the first refers to the Saint-Marcel sediment and the second to the Pierreville sample.

Fraction 1. Exchangeable Metals. Concentrations found for exchangeable cadmium, cobalt, nickel, lead, and zinc are lower than their respective detection limits; low concentrations of copper (0.15 and 0.2 ppm) and iron (0.4 ppm) are observed, as are relatively high concentrations of manganese (99 and 38 ppm). For the latter element, fraction 1 accounts for 14–3% of the total metal concentration. From available evidence on the extraction of exchangeable metals from bottom sediments or suspended solids (8, 9, 12, 13, 25, 30), these results are to be expected; exchangeable Cd, Co, Cu, Ni, Pb, Zn, and Fe are generally found to represent a minor fraction of the total metal concentration of the solid. The relatively high concentrations of exchangeable manganese suggest that the metal exists in a reduced form; it is recognized (42) that in most natural waters Mn(II) oxidation is a much slower process than Fe(II) oxidation. Our results for exchangeable Mn differ significantly from the findings of Gupta and Chen (9) who reported undetectable concentrations on coastal marine sediments. Possible explanations for this difference include the high ionic strength of seawater, which should favor desorption of Mn, and the higher pH, which should increase the rate of Mn(II) oxidation (42).

Fraction 2. Metals Bound to Carbonates. Concentrations found for cadmium and cobalt in fraction 2 are lower than their respective detection limits; the levels of nickel and iron, though detectable, remain low (<4%) compared to the total metal concentrations. For copper, zinc, and manganese, however, the observed concentrations represent an appreciable proportion of the total metal: 16–18% Cu; 13–16% Zn;

Table IV. Trace Metal Concentrations in Fraction 3 Expressed as Percent of Fe-Mn Oxides^a

sediment	Cd	Co	Cu	Ni	Pb	Zn
Saint-Marcel	<0.0022	0.040	0.044	0.073	0.042	0.247
Pierreville	0.0011	0.048	0.068	0.098	0.094	0.249

^a For the calculation, Fe(OH)₃ and MnO₂ were taken as representative empirical formulas for the Fe and Mn oxides.

13–28% Mn. These results are essentially similar to those reported by Gupta and Chen (9) for marine sediments using a 1 M HOAc extraction.

Fraction 3. Metals Bound to Fe-Mn Oxides. With the exception of cadmium, the trace metal levels in fraction 3 are relatively high and represent a large fraction of the total metal concentrations: ~40% Co; >20% for Cu, Ni, and Pb; 13–14% Fe; 15–24% Mn. Assuming that Fe(OH)₃ and MnO₂ are representative empirical formulas for the Fe and Mn oxides, respectively, and that the observed trace metals originate only from Fe-Mn oxides, one can calculate the trace metal concentrations in the Fe-Mn oxide phases (Table IV); the results illustrate the strong scavenging efficiency of Fe-Mn oxides for trace metals (26).

Fraction 4. Metals Bound to Organic Matter. Levels of cadmium and cobalt found in fraction 4 are once again lower than their respective detection limits. The remaining metals are present in detectable quantities, but only in the case of copper and lead does fraction 4 represent a significant proportion of the total metal concentration: ~25% Cu; 16–21% Pb. The absolute concentrations follow the order Fe > Mn > Cu > Zn > Pb > Ni for each sediment (Table I).

Fraction 5. Residual Metals. Without exception, trace metal concentrations found in fraction 5 are higher than those observed in any of the preceding extractions. In the case of cobalt, nickel, zinc, iron, and manganese, the residual fraction accounts for more than 50% of the total metal concentration. This overwhelming importance of fraction 5, amply borne out by the results of others (7–9, 12, 13, 32), illustrates clearly the difficulty of distinguishing between background and anomalous levels of trace metal contamination when only total metal analyses are performed.

CONCLUSIONS

The precision and accuracy of the sequential extraction procedure are generally good, the limiting factor being the inherent heterogeneity of the sediment; analytical performance should thus improve when the procedure is applied to suspensions or to sized fractions of bottom sediment.

The results obtained for fractions 3 and 4 (Fe-Mn oxides and organic matter) indicate that these phases have a scavenging action for trace metals that is far out of proportion to their own concentration. As these fractions constitute important sources of potentially available trace metals (47), they should be considered explicitly when estimating the bio-availability of a particular metal.

For the moment, it is obvious that the distribution of a given metal between various fractions does not necessarily reflect the relative scavenging action of discrete sediment phases, but rather should be considered as operationally defined by the method of extraction. Before metal concentrations measured in a particular fraction can be ascribed with reasonable certainty to well defined geochemical forms or phases, it will be necessary to develop more selective extraction reagents, notably for sulfide bound trace metals. Spiking experiments, involving the addition of known geochemical phases to sediment matrices, would provide valuable information concerning the selectivity of the proposed sequential extraction procedure. Application of the procedure to a wide range of

bottom and suspended sediments would also be desirable.

Sequential extraction procedures do, however, offer the major advantage that they simulate to a certain extent various environmental conditions to which the sediment may be subjected; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment. Possible applications include the evaluation of the effects of dredging operations and the prediction of trace metal behavior in estuarine waters or in anoxic lacustrine systems.

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Correlation of Electron Capture Response Enhancements Caused by Oxygen with Chemical Structure for Chlorinated Hydrocarbons

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The enhancement of response to 32 simple chlorinated molecules of a constant-current electron capture detector (ECD) caused by the addition of oxygen to its carrier gas has been determined. The effects of size and isomeric differences for alkyl, vinyl, allyl, and phenyl chlorides are examined. Also, the oxygen-induced enhancements of several chlorofluoromethanes are reported. From these data, general trends of structural differences emerge which facilitate the prediction of where oxygen-doping in ECD analyses might be gainfully applied. These data are discussed in terms of a mechanism which was previously proposed and is further developed here into a detailed model of the instrument's response. Response enhancements are attributed to assistance provided by O_2^- in the overall electron capture process. It appears that relative rates of the reaction of O_2^- with halocarbons can be derived from ECD data obtained in the manner described here.

The electron capture detector (ECD) in its usual configuration responds exceedingly sensitively to polychlorinated molecules, but relatively poorly to hydrocarbons having only one or a few chlorine atoms (1). We have recently shown (2, 3), however, that the intentional addition of oxygen to the carrier gas of a gas chromatograph with electron capture detection (GC-ECD) can cause large increases in its response especially to monochlorinated hydrocarbons, thereby increasing the utility of the ECD to this class of compounds. We have shown, for example, that the addition of oxygen to the carrier gas of a constant-current, pulsed ECD leads directly to an improved analysis of methyl chloride in ambient air (3). Another potentially valuable use of oxygen doping may be as an aid in the qualitative identification of all ECD-active compounds, since the magnitude of an oxygen-induced response enhancement has appeared to be quite reproducible for a given compound and varies greatly from one compound type to another. A recent report (4) of an improved analysis of CO_2 in the atmosphere using an ECD and intentionally O_2 -doped carrier gas suggests the applicability of this method to measurement problems beyond those of the halocarbons.

In this article, we report additional measurements of oxygen-induced response enhancements where a systematic

variation of the chlorinated substrate molecules from C_1 to C_6 chlorocarbons has been made. The effect of the position of a chlorine atom or atoms on saturated, olefinic, and phenyl hydrocarbon skeletons is examined. The mechanism previously proposed (2) to account for response enhancements will be further developed here to provide a quantitative description of the response of a constant-current, oxygen-doped ECD to sample molecules. It will also be suggested that the gas-phase, relative rates of the reactions of O_2^- with ECD-active compounds can be determined from the measurement of oxygen response enhancements with an electron capture detector.

EXPERIMENTAL

Standards. All halocarbons studied were reagent grade obtained from commercial suppliers. Further purification was unnecessary because the method of introduction to the ECD is gas chromatography which provides the necessary separation from impurities. Standards were prepared by the successive dilution of the compounds of interest into either nitrogen gas or into hexane or benzene. Standards of compounds having boiling points less than 100 °C were prepared as gases and those above 100 °C, as liquids. The concentrations of standards were adjusted to produce small, but easily quantified peaks in their analysis by GC-ECD. The procedure for gaseous standard preparation has been described in detail previously (3).

Instruments. The gas chromatograph is a Varian 3700 Aerograph with constant-current, pulse-modulated operation of a ^{63}Ni detector. The detector activity is 7.5 mCi and its volume is 0.3 mL. A 10-ft by $1/8$ -in. stainless steel column packed with 10% SF-96 on chromosorb W was generally used at oven temperatures of from 30 to 60 °C depending on the compound studied. For a few of the least volatile compounds examined, a 1.5-ft by $1/8$ -in. column packed with 3% OV-17 was used at temperatures up to 110 °C. Where peak areas were desired for the determination of relative molar ECD responses, an Autolab minigrator was used. All chromatograms were recorded on a strip chart recorder.

The normal carrier gas flow was modified as previously described (3) to allow the controlled addition of oxygen to the carrier gas. This was accomplished by incorporating a 5-L stainless exponential dilution sphere in the carrier gas stream into which aliquots of purified air were added. The carrier gas was ultra high purity nitrogen (Matheson) specified to be greater than 99.999% pure and the air was breathing quality (Chemetron), both of which were passed through traps containing activated charcoal and 13X