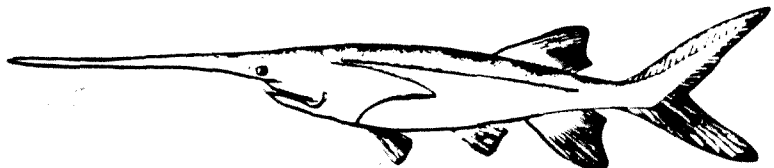
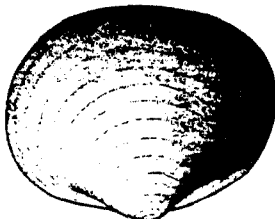
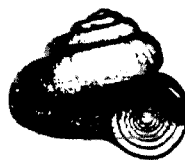
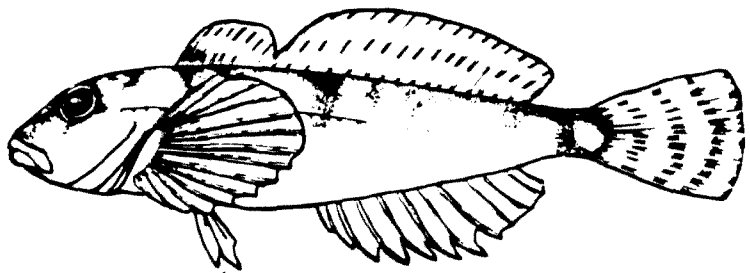




**SEDIMENT QUALITY CRITERIA FOR METALS: V.
OPTIMIZATION OF EXTRACTION METHODS
FOR DETERMINING THE QUANTITY OF SORBENTS
AND ADSORBED METALS IN SEDIMENTS**



SEDIMENT QUALITY CRITERIA FOR METALS:
OPTIMIZATION OF EXTRACTION METHODS FOR DETERMINING THE
QUANTITY OF SORBENTS AND ADSORBED METALS IN SEDIMENTS

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ABSTRACT

The Criteria and Standards Division of the U.S. Environmental Protection Agency (EPA) is developing sediment quality criteria for nonpolar organic and metal contaminants. The approach that EPA is considering for developing sediment criteria for metals requires that the quantities of sorbed metals and major sorbents be estimated. It has been proposed that the quantities of these sorbed metals and sorbents be determined by chemical extraction methods. In this study, a variety of sediments were used to optimize an acidic hydroxylamine hydrochloride extraction method for determining sorbed metals, and amorphous iron oxide and manganese oxide sorbents. The results confirm the usefulness of the procedural aspects of the hydroxylamine hydrochloride method, except that a longer reaction time (60 min rather than 30 min) is indicated.

In addition, the efficiency of two alkali methods, ammonium hydroxide and potassium hydroxide, were compared for determining the quantity of the reactive particulate organic carbon sorbent. The potassium hydroxide method, which was found to have advantages over the ammonium hydroxide method, was optimized. Again, an extraction time of 60 min rather than 30 min is indicated.

ACKNOWLEDGMENTS

We would like to thank Dr. John Moore of the University of Montana for collecting the sediment samples from the Clark Fork River. We also thank Ms. Robin Canterbury of Clemson University for collecting the samples from Lake Issaquenna, South Carolina; Pendleton Swamp, South Carolina; and Lake Burton, Georgia.

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INTRODUCTION

The Criteria and Standards Division of the U.S. Environmental Protection Agency (EPA) is developing sediment quality criteria for nonpolar organic contaminants and metals. These criteria will be used in conjunction with water quality criteria to protect aquatic organisms and man's food chain in both freshwater and saltwater. The approach selected for developing sediment quality criteria for metals involves calculating the thermodynamic activity of the uncomplexed metal in the sediment pore water, and relating this thermodynamic activity to the toxic level of the metal, which is inferred from the water quality criteria for individual metals (Jenne et al. 1986). This approach assumes that the activity of metals in pore water is in equilibrium with the sorbed metals. The data required are the quantity of each important sorbent (sorption "sink"), the quantity of sorbed metals, and surface adsorption constants for the individual sorbents. These data can then be used with an appropriate algorithm (model) to estimate the activities of metals in pore water. The most important advantages of this approach are that sediment quality criteria are related to the water quality criteria and the problems of determining metal availability and evaluating toxicity are separated.

Therefore, the objectives of this study are to provide recommended standard methods for 1) estimating the quantity of sorbed metals and the major oxide sorbents and 2) determining the reactive particulate organic carbon (RPOC) content to estimate the surface adsorption constants. These methods are intended for oxic sediments. Various methods for estimating sorbed metals and the three major sorbents, amorphous iron (Fe) oxide, manganese (Mn) oxide, and RPOC, in oxic sediments were reviewed in an earlier paper (Jenne 1984). To achieve the study's objectives, we 1) evaluated and optimized the hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) method of Chao and Zhou (1983) for determining the quantity of sorbed metals and the oxide sorbents, 2) compared the effectiveness of the potassium hydroxide (KOH) and ammonium hydroxide (NH_4OH) method of Jenne (1984) and Luoma and Bryan (1981), respectively, for extracting RPOC, and 3) optimized the KOH method for determining the quantity of RPOC.

The $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction method was evaluated for 1) its extraction efficiency for Fe and Mn minerals, 2) the possibility for readsorption of desorbed metal during the extraction, 3) the extraction efficiency of various acid concentrations and solid:solution ratios, and 4) the optimum length of extraction time.

In addition, reference materials of Fe and Mn were used to determine if the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction method will dissolve crystalline Fe and Mn oxides. The extensive dissolution of crystalline Fe oxides while the quantity of amorphous Fe sorbent is being determined is undesirable. If crystalline oxides are abundant in the sediments and dissolve during extraction, an overestimation of the amorphous Fe sorbent would result. However, dissolution of the surface layers of the crystalline oxides may be desirable because these surfaces also provide sorption sites. If the contribution of the surface layer of crystalline Fe oxides is included in the estimate of the amorphous Fe adsorbent, a separate determination of the quantity of crystalline Fe oxides may not be necessary to model the sorption of metals onto sediments. Although pyrolusite ($\beta\text{-MnO}_2$) is not a diagenetic mineral, it was included in this experiment to test whether a highly crystalline Mn oxide is dissolved by this method.

This report also presents the results of experimental studies that compared the effectiveness of the KOH and NH_4OH methods for extracting RPOC from sediment, and that optimized the extraction time for the KOH method. These studies involved determining the effects of reagent strength and solid:solution ratio on extraction efficiency.

Certain criteria were used to select appropriate sediment samples for this study. To demonstrate the effectiveness of the extractants over a range of environmental conditions, an effort was made to collect sediments that had a range of concentrations of Fe, Mn, and organic carbon (OC). Because the $\text{NH}_2\text{OH}\cdot\text{HCl}$ method for extracting sorbed metals, Mn oxide, and amorphous Fe oxide is intended to be used for oxic sediments, sediment samples were selected to minimize the content of sulfides and carbonates. Any sediment samples that were black or had an odor of hydrogen sulfide were not used. The sediment samples were characterized for chemical content and particle size distribution. From the 16 samples, three were chosen for use in evaluating the $\text{NH}_2\text{OH}\cdot\text{HCl}$ method because they represented a reasonable range in the concentrations of

metal contaminants and Fe and Mn sorbents. All 16 sediments were used initially for evaluating the KOH and NH_4OH methods for extracting RPOC. Five of the 16 sediments, representing a range in the RPOC and sediment characteristics, were used for the KOH optimization study.

EXPERIMENTAL METHODS

SAMPLES

Sources of Sediments and Minerals

Fine-grained sediments were collected in the spring and summer of 1987 from the Duwamish River in Washington; the Willamette River in Oregon; the Clark Fork River in Idaho; Lake Issaquenna and Pendleton Swamp, South Carolina; and Lake Burton, Georgia. The samples were promptly returned to the laboratory, spread out on clean polyethylene sheets, and allowed to air-dry. The >60-mesh (>0.25-mm) material was removed with a nylon screen and stored in plastic containers.

Standard reference sediments from the National Bureau of Standards [SRM 1645a (a river sediment), and SRM 1646 (an estuarine sediment)], and National Research Council of Canada [MESS-1 (a marine sediment)], were used as received. Magnetite (Fe_3O_4 , sold as "black iron oxide"), lepidocrocite ($\gamma\text{-FeOOH}$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$, sold as "red iron oxide") were obtained from Reade Metals and Minerals Corp., Rumson, New Jersey, in <60-mesh form. $\beta\text{-MnO}_2$ (tetragonal, presumed to be pyrolusite) was obtained from CERAC, Inc., Milwaukee, Wisconsin, in <100-mesh form. Humic acid was used as received from the Aldrich Chemical Company.

Sediment Characterization

The total metal concentrations of Al, Fe, Mn, Cu, Zn, and Pb in the sediment samples was determined by energy dispersive X-ray fluorescence (XRF) (Nielson and Sanders 1983). The cadmium concentration was determined by Zeeman graphite furnace atomic absorption, after total digestion of the sediment in a Teflon bomb using a mixture of nitric, perchloric, and hydrofluoric acids.

The concentration of total organic carbon (TOC) in sediments was determined by combustion, using a Leco carbon analyzer after the sediment had been treated with HCl to remove inorganic carbon (IC) (such as carbonates). The

IC concentration in sediments was calculated by subtracting the TOC concentration from the carbon concentration of sediment that had not been treated with HCl.

EXTRACTION METHODS

The following extraction methods were used over a range of conditions to optimize the methods. The recommended standard methods are presented in Appendixes A and B. All containers and filters that came in contact with the extracting solutions were carefully cleaned. For metals, a 24-h soak in 5% HCl was used. For organic carbon, a 24-h soak at 95°C in 1M KOH was used.

Hydroxylamine Hydrochloride

All extractions contained 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and either 0.1M, 0.25M, or 0.5M HCl. The solution (100 mL) was brought to 50°C in a 250-mL polyethylene bottle and 0.2, 0.4, or 1.0 g of air-dried sediment was added. The bottle was placed in a 50°C shaking water bath for times ranging from 1 min to 12 h. The sample bottles were removed from the hot water bath and an aliquot was filtered (for evaluation of extraction variables) through an 0.2- μm Gelman polysulfone Acrodisic (product No. 4192) membrane filter into a 30-mL polyethylene vial. Filtrates and procedural blanks were analyzed by inductively coupled plasma (ICP) for Fe, Mn, Cu, Zn, and Pb, and by atomic adsorption spectroscopy for Cd.

KOH

A 250-mL glass bottle containing 100 mL of 0.25N or 0.5N KOH was heated to 95°C. Either 0.25, 0.5, or 1.0 g of air-dried sediment was added to the glass bottle and put into a 95°C shaking hot water bath for times ranging from 1 min to 8 h. The bottle was removed and placed in cold water bath (approximately 15°C) for 10 min, and swirled at intervals of 3 to 4 min. Then 30 mL of suspension was filtered through a 0.2- μm Gelman membrane. Filtrates and procedural blanks were analyzed for dissolved organic carbon (DOC) in a Dohrmann Model DC-80 carbon analyzer.

NH₄OH

One of the air-dried sediments was placed in a 250-mL glass bottle, 100 mL of 1N NH₄OH was added, and the solution held at 20°C. The solution was swirled daily for 1 week, then filtered and analyzed for DOC as in the KOH method.

RECOVERY OF METALS

The spike recovery experiment determined if sorbed metals released by dissolution of amorphous Fe and/or Mn oxides may be adsorbed by another sorbent, such as OC, thereby underestimating the quantity of sorbed metal. To allow the maximum opportunity for sorption onto other sorbents, metal spikes were added at the beginning of the 30-min extraction period. Standard conditions were used (0.4 g sediment/100 mL solution, 0.25M NH₂OH•HCl, 50°C, and 30 min) on three sediments and a procedural blank. Each bottle was spiked with quantities of individual metals equivalent to those expected to be extracted from the sediment. The metal spikes were added within 1 min after the sediment was placed into the preheated extraction solution. Spike recovery was calculated as the difference between the quantity of the metal in the extract solution of the recovery experiment and the quantity in the standard 30-min extract solution.

OPTIMIZATION OF EXTRACTION TIMES

Extraction times were evaluated to optimize the efficiency of the NH₂OH•HCl method in determining the quantity of sorbed metals and sorbents. The concentrations of metals extracted from sediments versus the extraction times were determined for six sediments. The extractant was 0.25M NH₂OH•HCl, 0.25M HCl, with a solid:solution ratio of 0.4 g/100 mL, and a temperature of 50°C. Ten extraction times of 1, 3, 7, 10, 20, and 30 min, and 1, 3, 6, and 12 h were used.

To optimize the KOH method for estimating the quantity of RPOC, the concentration of dissolved organic carbon extracted from the sediments versus the extraction time was determined for five sediments. The extractant used

was 0.5M KOH, with a solid:solution ratio of 0.4 g/100 mL, at 95°C, and with time intervals of 1, 3, 7, 10, and 30 min, and 1, 4, and 8 h.

RESULTS

CHARACTERIZATION OF SEDIMENTS

The sediment samples were first characterized for total metal concentrations, TOC, IC (carbonates), and particle-size (<63- μ m fraction) to verify that a range of concentrations of Fe, Mn, and TOC were present in these samples and that the IC concentrations were relatively low. The concentration of total metals and other constituents of interest in the 16 sediments varied considerably, ranging over approximately one order of magnitude (Table 1). Sediments RS-1 to RS-6, which were collected below urban areas, had heavy metal concentrations typical of sediments from moderately contaminated water bodies (Salomons and Förstner 1984). The sediments from the Clark Fork River (CF-1 to CF-4), which were contaminated by earlier mining activities, contained relatively high metal concentrations, as did standard reference material SRM 1645, which was from an industrially contaminated river. The concentrations of metals in the sediments collected from the southeastern United States (RS-7 to RS-9), and the estuarine and marine reference standard materials (SRM 1646 and SRM MESS-1) were typical of relatively uncontaminated sediments.

The total organic carbon (TOC) concentrations ranged from 0.2% to 5.1%. The relatively low inorganic carbon (IC) concentrations, which ranged from 0.03% to 0.87%, were in accord with the selection criteria of a low carbonate content.

EXTRACTIONS OF Fe AND Mn OXIDE MINERALS

Reference oxide minerals were extracted to determine if the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction method would dissolve crystalline Fe and Mn oxides. Because the dissolution of minerals after grinding (the samples were received ground) is initially high (because of the disordering of the surface layers and the presence of small particles that adhere to the surfaces of larger particles), two sequential extractions were carried out on replicate samples. The effects of disorganized surface layers and fine-sized particles were presumed to be much less in the second extraction of Fe oxides than in the first.

TABLE 1. Composition of Sediments^(a)

	<u>TOC</u>	<u>IC</u>	<u>Cd</u> <u>µg</u> g	<u>Al</u>	<u>Fe</u>	<u>Mn</u>	<u>Cu</u>	<u>Zn</u> g/g	<u>Pb</u>	<u>Cd</u>
<u>Duwamish River</u>										
RS-1 Lat. 47 32.4'	2.1	0.24	73	8.1	4.7	587	60	144	48	0.68
2 Lat. 47 33.4'	1.7	0.33	85	8.8	4.8	688	91	174	79	0.58
3 Lat. 47 33.6'	1.1	0.13	58	8.6	4.8	674	39	87	19	0.38
<u>Willamette River</u>										
RS-4 River mile 0.8	1.8	0.13	43	7.9	4.4	758	37	156	22	0.88
5 River mile 4.3	2.1	0.38	85	8.9	5.5	1819	57	165	31	0.52
6 River mile 6.8	2.7	0.36	88	8.9	5.4	1225	67	148	28	0.38
<u>Clark Fork River^(b)</u>										
CF-1 38 km	1.8	0.42	43	8.3	3.2	1817	2718	1958	1231	5.28
2 52 km	0.7	0.23	41	6.9	3.1	1293	1388	1185	498	2.48
3 47 km	0.2	0.08	46	6.5	1.4	267	223	283	432	0.67
4 69 km	0.8	0.32	32	7.1	2.4	2118	539	1333	117	5.78
<u>Lake Issaquena^(c)</u>										
RS-7	3.9	0.14	49	14.7	3.1	383	24	68	29	0.28
<u>Pendleton Swamp^(c)</u>										
RS-8	5.1	0.83	45	11.5	12.2	1583	22	98	29	0.15
<u>Lake Burton^(c)</u>										
RS-9	1.5	0.83	48	17.3	6.8	595	51	115	49	0.18
<u>Estuarine Sediment^(d)</u>										
SRM 1846	1.5	0.88	NA ^(e)	6.3	3.4	375	18	138	28	0.36
<u>Marine Sediment^(d)</u>										
SRM MESS-1	2.5	0.88	NA	5.8	3.1	513	25	191	34	0.59
<u>River Sediment^(d)</u>										
SRM 1845a	3.5	0.87	NA	2.4	8.5	758	185	1648	728	18.88

- (a) Metal analysis by XRF, except for Cd, which was analyzed by graphite furnace atomic absorption spectroscopy; data reported on a dry weight basis.
 (b) Distance downstream from Warm Springs Ponds, collected by Dr. John Moore, University of Montana.
 (c) Collected by Robin Canterbury, Clemson University
 (d) Concentration of metals taken from the certification sheets provided with the samples.
 (e) NA = Not analyzed

This lack of dissolution was confirmed by the results (Table 2), which indicate that less than 0.5% Fe was dissolved from hematite or magnetite after two extractions. However, nearly 30% the lepidochrocite (γ -FeOOH) was dissolved, with about as much dissolved in the second extraction as the first. The almost total dissolution of the pyrolusite by the first extraction (Table 2) supports the premise that the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction solubilizes this Mn oxide.

PRECISION OF EXTRACTIONS

The precision of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction procedure was determined by extracting subsamples of three sediments in duplicate on two days, giving a total of four data points for each sediment. The coefficients of variation for Fe, Mn, Cu, and Zn in the three sediments, based on the four data points, did not exceed 12.1%, and were generally below 10% (Table 3).

TABLE 2. $\text{NH}_2\text{OH}\cdot\text{HCl}$ Extraction^(a) of Fe and Mn from Minerals by Two Sequential Extractions of the Same Sample

Mineral	Replicate	Fe Extracted			Mn Extracted		
		1st	2nd	Total	1st	2nd	Total
		-----*(b)-----					
Hematite (α -Fe ₂ O ₃)	1	0.24	0.18	0.42	0.0034	0.0005	0.0039
	2	0.30	0.24	0.54	0.0030	0.0005	0.0035
	avg.	0.27	0.21	0.48	0.0032	0.0005	0.0037
Magnetite (Fe ₃ O ₄)	1	0.074	0.054	0.128	0.0004	0.0002	0.0006
	2	0.102	0.070	0.172	0.0004	0.0004	0.0008
	avg.	0.088	0.062	0.150	0.0004	0.0003	0.0007
Lepidochrocite (γ -FeOOH)	1	3.5	12.0	15.5	<0.001	<0.001	<0.002
	2	18.7	14.0	32.7	<0.001	<0.001	<0.002
	avg.	16.1	13.0	29.1	--	--	--
Pyrolusite (β -MnO ₂)	1	<0.010	<0.010	<0.010	62.0	8.0	70.0
	2	0.015	0.013	0.028	63.0	4.1	67.1
	avg.	--	--	--	63.0	6.0	69.0

(a) Conditions are 0.4 g sediment/100 mL solution, 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 0.25M HCl, 50°C, and 30 min.

(b) Percentage of initial oven-dry weight of mineral.

TABLE 3. Average Precision of Four Replicate Extractions of Each Sediment^(a)

Sediment	Fe		Mn		Cu		Zn	
	Mean ^(b) %	CV ^(c) %	Mean $\mu\text{g/g}$	CV %	Mean $\mu\text{g/g}$	CV %	Mean $\mu\text{g/g}$	CV %
RS-2	1.06	5.5	186	11.0	62	7.0	87	9.9
RS-6	1.15	6.9	812	5.5	38	6.3	131	12.1
CF-1	1.06	9.8	377	9.6	2690	12.0	493	3.6

(a) Standard conditions are 0.4 g sediment/100 ml solution, 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$

(b) Dry weight basis

(c) CV is the coefficient of variation (i.e., mean \div standard deviation).

RECOVERY OF METALS

The recoveries of metals added during the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction procedure were evaluated to determine if metals extracted from one sorbent (i.e., Fe and Mn oxides) were resorbed on other sorbents (i.e., organic carbon). Iron and Mn spikes were used to determine if these metals were sorbed by the organic carbon, resulting in an underestimation of the quantity of these sorbents. Spike recoveries for six metals (Cd, Cu, Zn, Fe, Pb, and Mn), averaged across the three sediments, ranged between 98% and 109% (Table 4). Thus, the extraction conditions resulted in 100% recovery of the five metals, within experimental error. Unexplainably, Fe was slightly anomalous with only an 88% recovery.

OPTIMIZATION OF $\text{NH}_2\text{OH}\cdot\text{HCl}$ EXTRACTION

The extraction efficiency, using 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$, was examined for three concentrations of HCl (0.1M, 0.25M, and 0.5M) and three solid:solution ratios (0.2, 0.4, and 1.0 g/100 mL) of extractant at 50°C for 30 min. The results of metal extractions from three sediment samples (RS-2, RS-6, and CF-1) at the three acid concentrations and three solid:solution ratios are presented in Table 5. Slightly more Fe (expressed as %) was extracted from the 0.1- and 0.4-g samples than from the 1.0-g samples. Also, slightly higher solution concentrations of Cd, Cu, Fe, and Mn occurred in some samples when the higher HCl concentrations were used. However, the differences in the metal

TABLE 4. Recovery of Metals Simultaneously Spiked into Suspension at the Beginning of Extraction Period^(a)

	<u>RS-2</u>	<u>RS-6</u>	<u>CF-1</u>	<u>Average</u>	<u>Blank Spike</u>
<u>Metal</u>	-----%				
Fe	90	89	86	88	90
Mn	115	107	106	109	114
Cu	108	102	94	101	100
Zn	107	104	94	102	110
Pb	100	108	NA ^(b)	104	104
Cd	100	100	94	98	90

(a) Standard conditions are 0.4 g sediment/100mL solution, 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$

(b) NA = Not analyzed

concentrations for the different samples were insufficient to indicate that sample sizes less than 1.0 g or HCl concentrations greater than 0.25M should be used. This lack of dependence on the sample size permits a desirable flexibility in the quantity of sediment used for the sorbed metal determinations, which facilitates analyses of metal concentrations well above the analytical detection limits.

OPTIMIZATION OF EXTRACTION TIME

There is appreciable variation among samples in the slope of the extraction curve over the 30-to 360-min period (Figures 1 to 5). For most samples (RS-2, RS-6, RS-7, CF-1, and SRM 1646), the slope of the Fe extraction curve is relatively steep over the 30- to 60-min interval. For the SRM 1645a sediment sample, the 30-min point is anomalously high for most metals when compared to the other time points. These results indicate that 60 min rather than 30 min be used to estimate the quantity of amorphous Fe oxide. In some instances, the 60-min extraction period also appears preferable to a 30-min period for estimating the quantity of other metals [i.e., for Mn (RS-2, RS-7, CF-1, and SRM 1646), Cu (CF-1), Zn (RS-2, RS-6, and CR-1) and Pb (CF-1)]. If the CF-1 sample (which contains sulfide and thus is not be oxic) is disregarded, there are only three instances in which a 60-min extraction period

TABLE 5. Extraction of Metals at Three Solid:Solution Ratios and Three HCl Molar Concentrations

Metal (a)	Weight (g) of Sample per 100 mL Solution								
	0.2			0.4			1.0		
	Molarity of HCl								
	0.1	0.25	0.5	0.1	0.25	0.5	0.1	0.25	0.5
SEDIMENT RS-2									
Fe (%)	1.17	1.16	1.32	1.07	1.17	1.32	1.01	1.04	1.15
Mn (µg/g)	196	185	203	182	194	206	181	179	186
Cu (µg/g)	60	58	68	60	66	66	59	61	62
Zn (µg/g)	120	105	122	100	114	113	101	102	106
SEDIMENT RS-6									
Fe (%)	1.09	1.22	1.29	1.00	1.21	1.33	0.93	1.09	1.22
Mn (µg/g)	830	810	790	770	815	820	771	761	779
Cu (µg/g)	34	39	40	33	39	43	33	36	40
SEDIMENT CF-1									
Fe (%)	0.96	1.20	1.32	1.02	1.11	1.38	0.82	1.03	1.06
Mn (µg/g)	324	400	474	348	373	525	283	366	396
Cd (µg/g)	19	24	24	21	22	24	15	21	21
Cu (µg/g)	2625	2900	2845	2775	2675	3000	2500	2490	2530
Pb (µg/g)	389	700	970	375	695	1020	186	630	610
Zn (µg/g)	580	540	710	588	510	743	436	491	502

(a) Metal concentration in percent or µg/g dry weight of sediment. Parameters were 100 mL of 0.25M Hydroxylamine Hydrochloride for 30 min at 50°C.

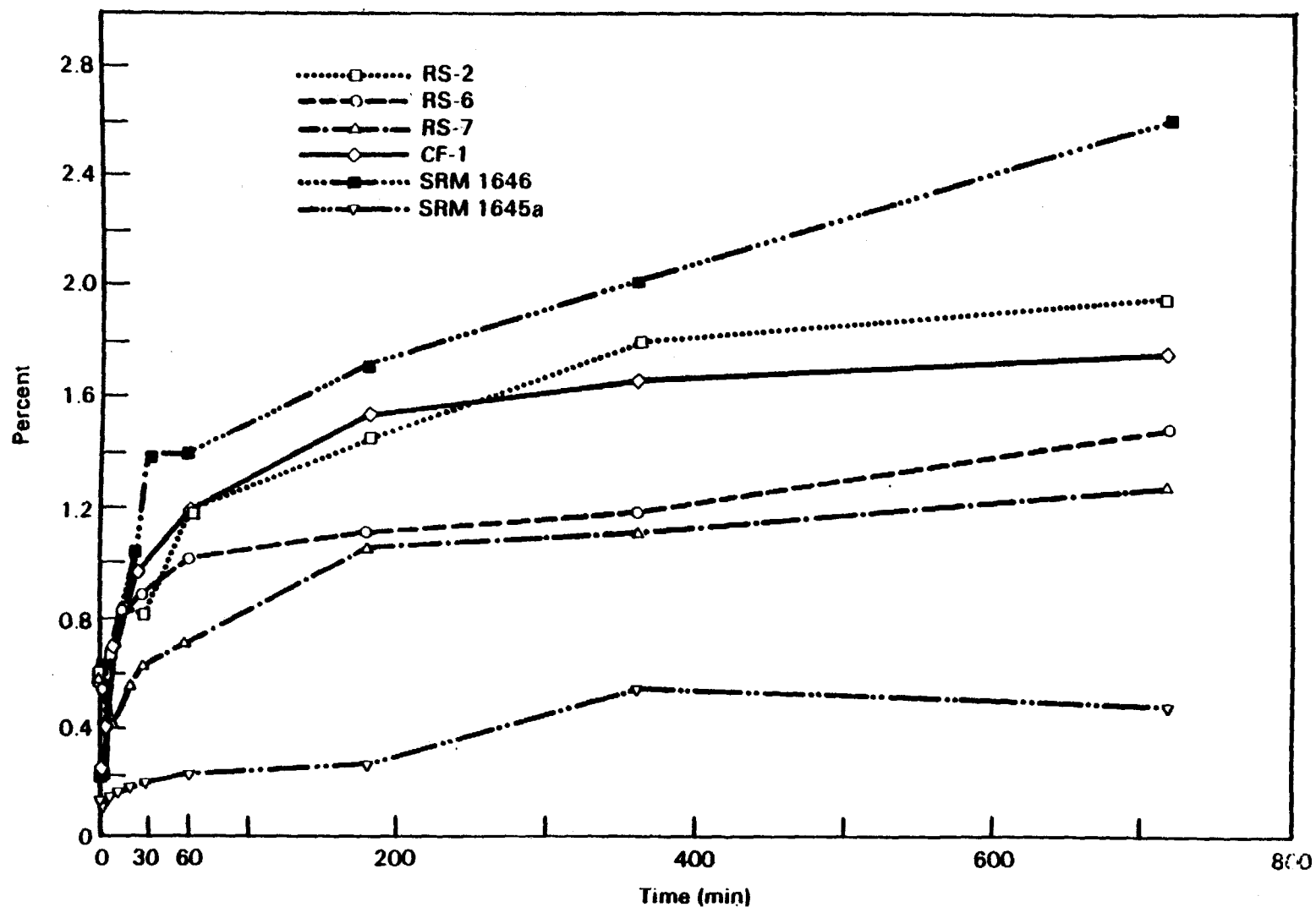


FIGURE 1. Time Dependent Dissolution of Amorphous Fe Oxides from Six Sediments, Using the Hydroxylamine Hydrochloride Method

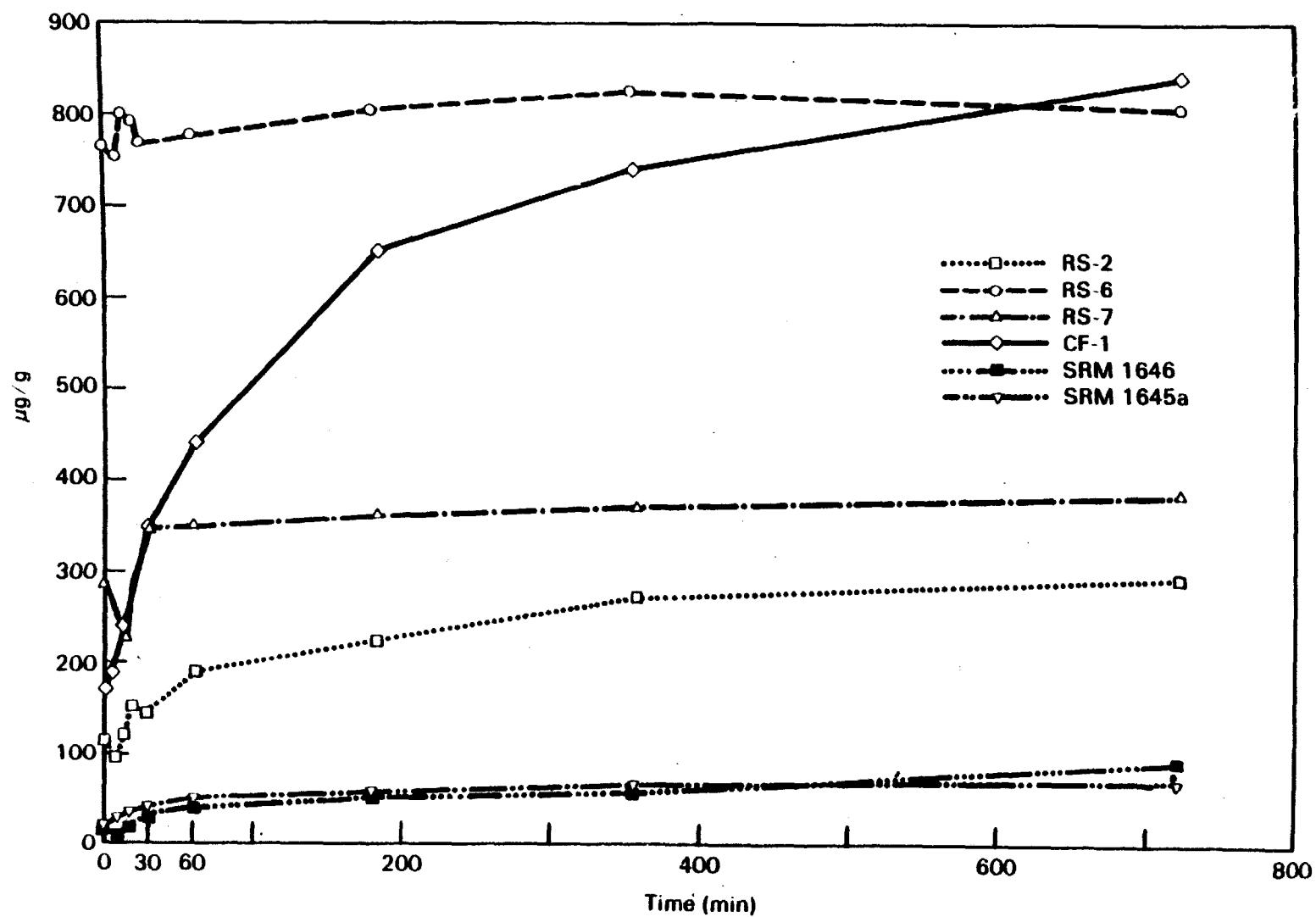


FIGURE 2. Time Dependent Dissolution of Mn Oxides from Six Sediments, Using the Hydroxylamine Hydrochloride Method

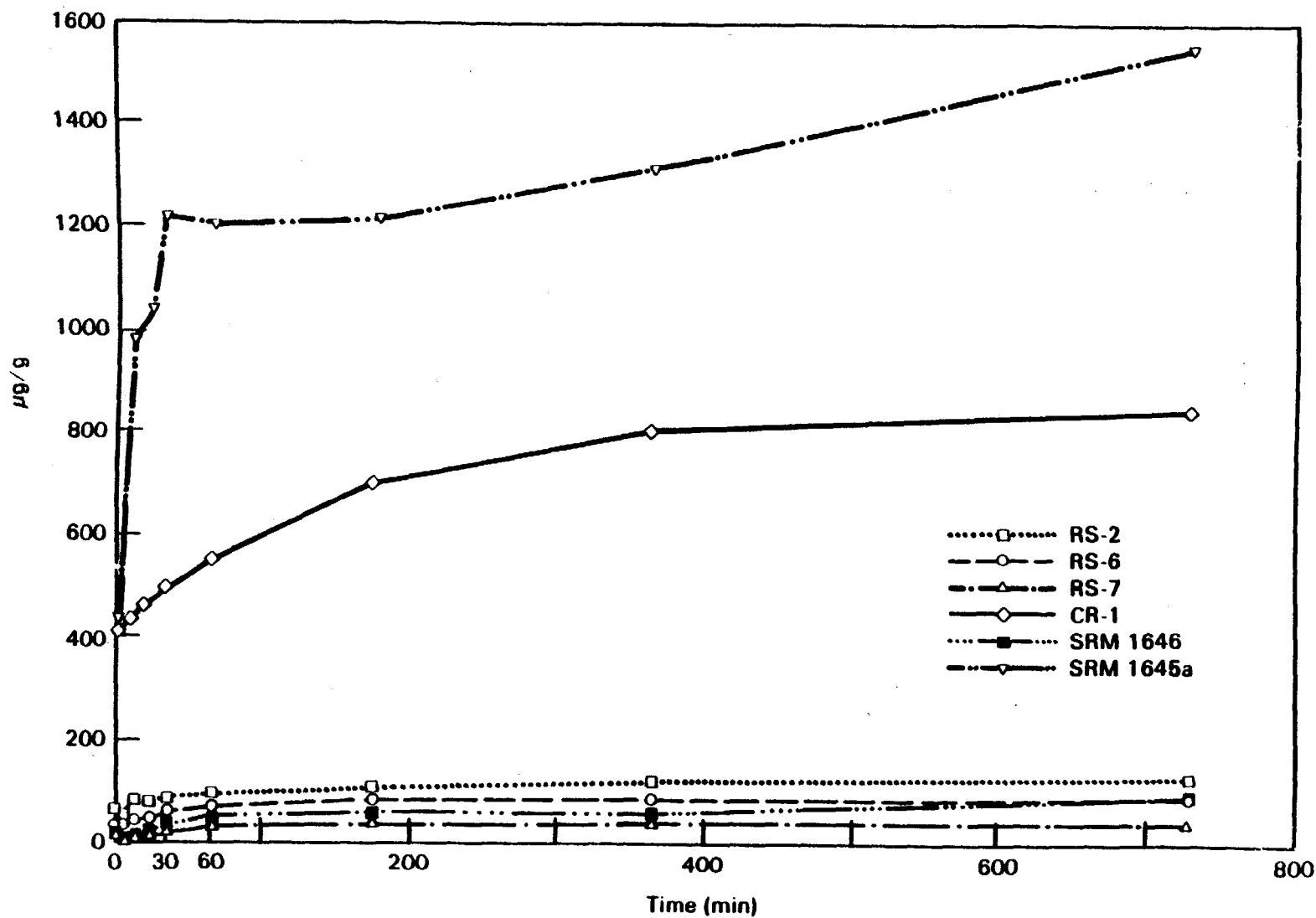


FIGURE 3. Time Dependent Desorption of Zn Oxides from Six Sediments, Using the Hydroxylamine Hydrochloride Method

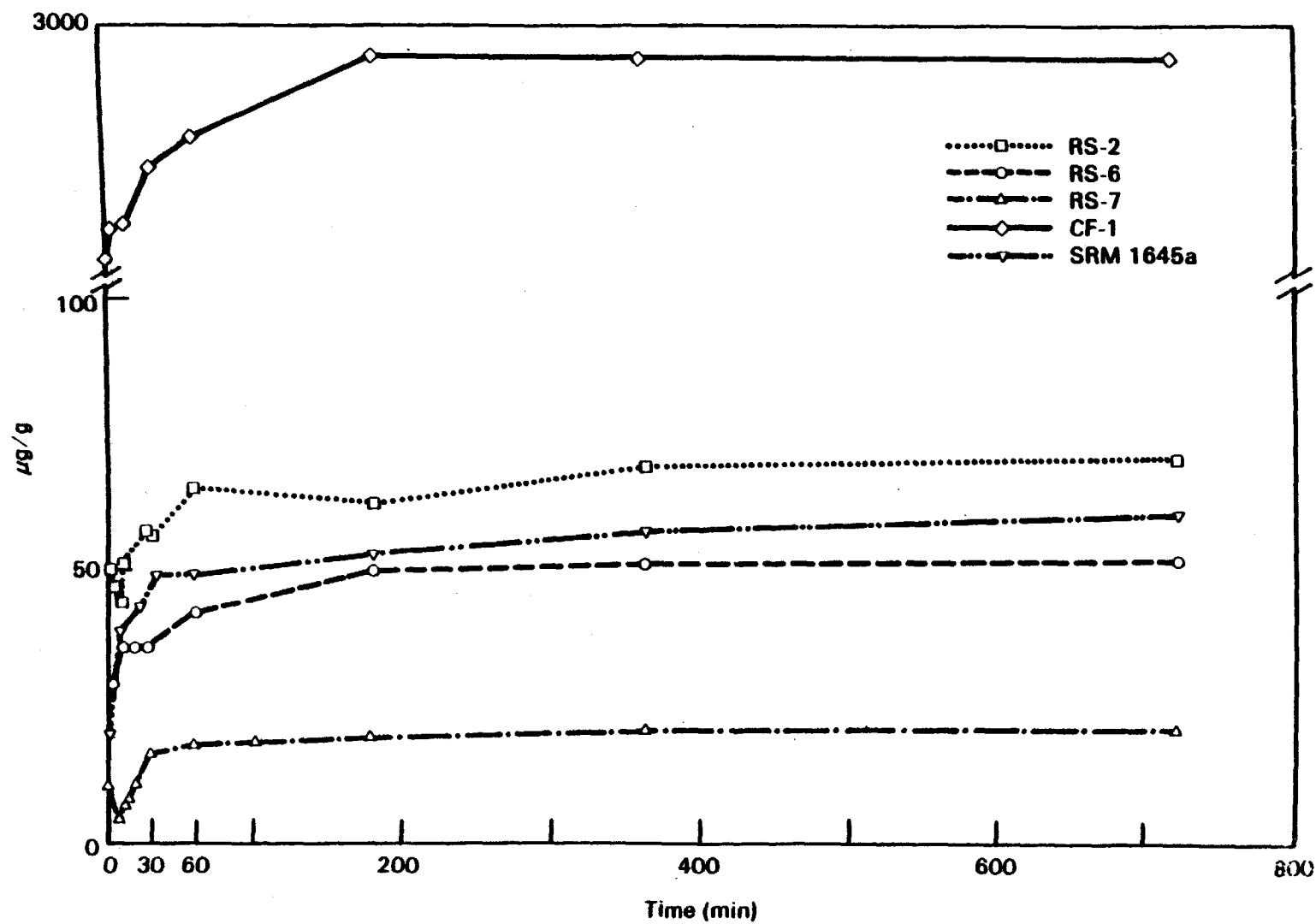


FIGURE 4. Time Dependent Desorption of Cu Oxides from Five Sediments, Using the Hydroxylamine Hydrochloride Method

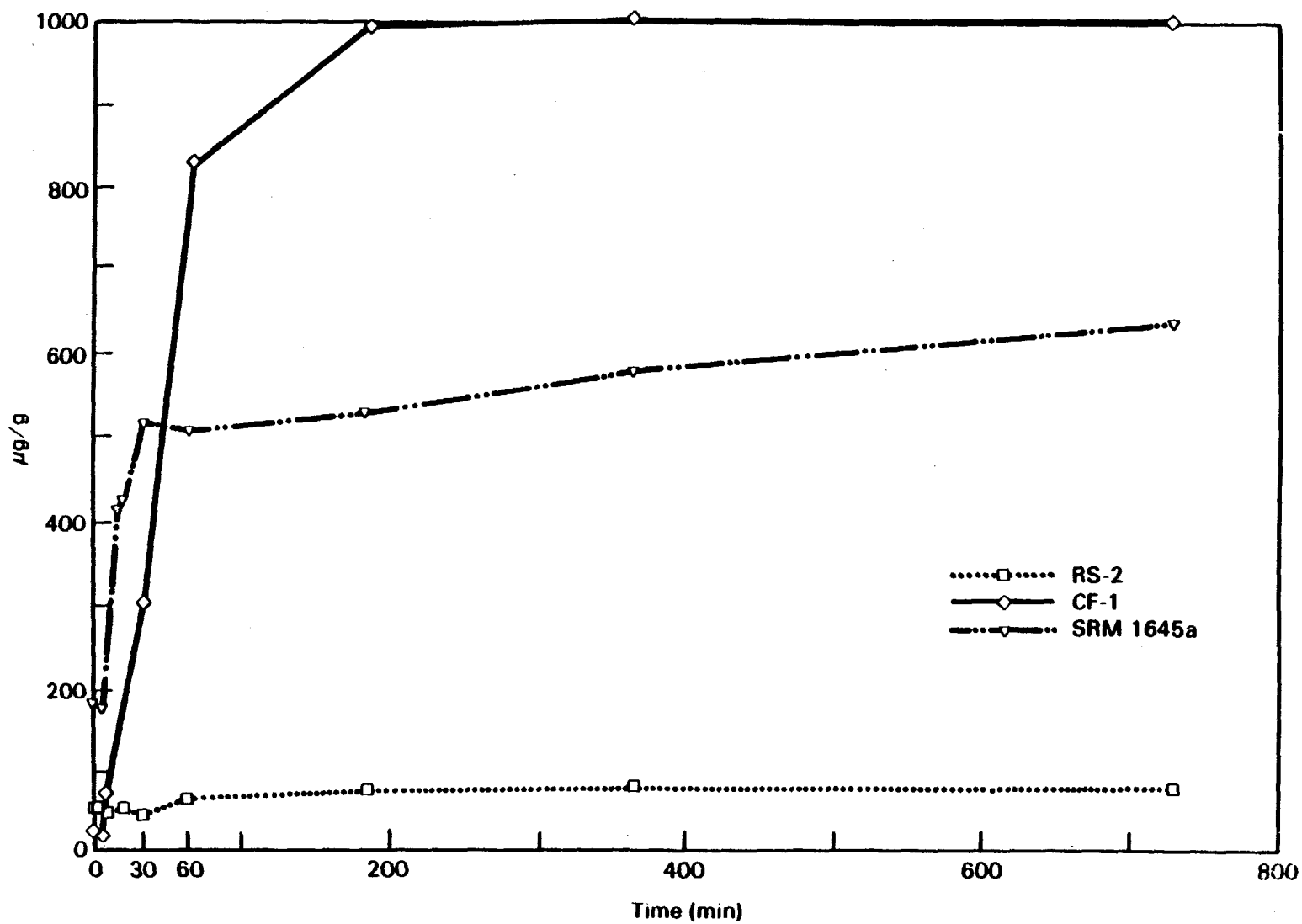


FIGURE 5. Time Dependent Desorption of Pb Oxides from Three Sediments, Using the Hydroxylamine Hydrochloride Method

appears preferable to a 30-min period for metals other than Fe. Although Fe continued to be extracted after 60 min for the RS-2 and CF-1 samples, the extractions were at a much lower rate than before.

OPTIMIZATION OF KOH EXTRACTION

Two extraction methods for determining the quantity of reactive particulate organic carbon (RPOC) were compared, then one method was optimized. Initially, duplicate samples of all 16 sediments were extracted, with both 0.5M KOH at 95°C for 30 min and 1M NH₄OH at 20°C for 1 week. The concentration of carbon extracted by each method was plotted versus TOC concentration in the sediment (Figure 6). The TOC concentrations in the sediments were determined on unextracted sediment samples and compared to RPOC, which was determined on extracts of sediment samples. The KOH procedure extracted approximately 41% of the TOC, with a range of 7% to 54%. The NH₄OH procedure extracted about 23% of the TOC, with a range of 2% to 36%. Linear regression analysis between RPOC and TOC yielded R² values of 0.71 for KOH and 0.56 for NH₄OH (Figure 6). Because KOH extracted more RPOC and provided a regression against TOC with much less scatter than the NH₄OH regression, further experiments were conducted only with KOH.

To optimize RPOC extraction with the KOH method, solution strengths and solid:solution ratios were varied in a series of experiments (data not shown). The amounts of RPOC extracted from sediment and humic acid (humic acid represents a solid phase with 100% TOC) were compared for two concentrations of KOH (0.25M and 0.5M) and three solid solution ratios (0.25, 0.5 and 1.0 g/100 mL) at 95°C for 30 min. No significant effect of the solid:solution ratio in the range of 0.25 to 1.0 g sediment/100 mL KOH (95°C) was noticed. Neither was there any apparent difference in extraction efficiency between 0.25M and 0.5M KOH.

To optimize the KOH method, extraction of RPOC as a function of time for five sediment samples was determined (Figure 7). The quantity of RPOC extracted increased significantly with time up to 30 min. For two samples, RS-2 and RS-6, there was approximately a 10% increase in RPOC extracted in the interval between 30 and 60 min. The 30-min values for RS-7, SRM MESS-1, and SRM 1645a

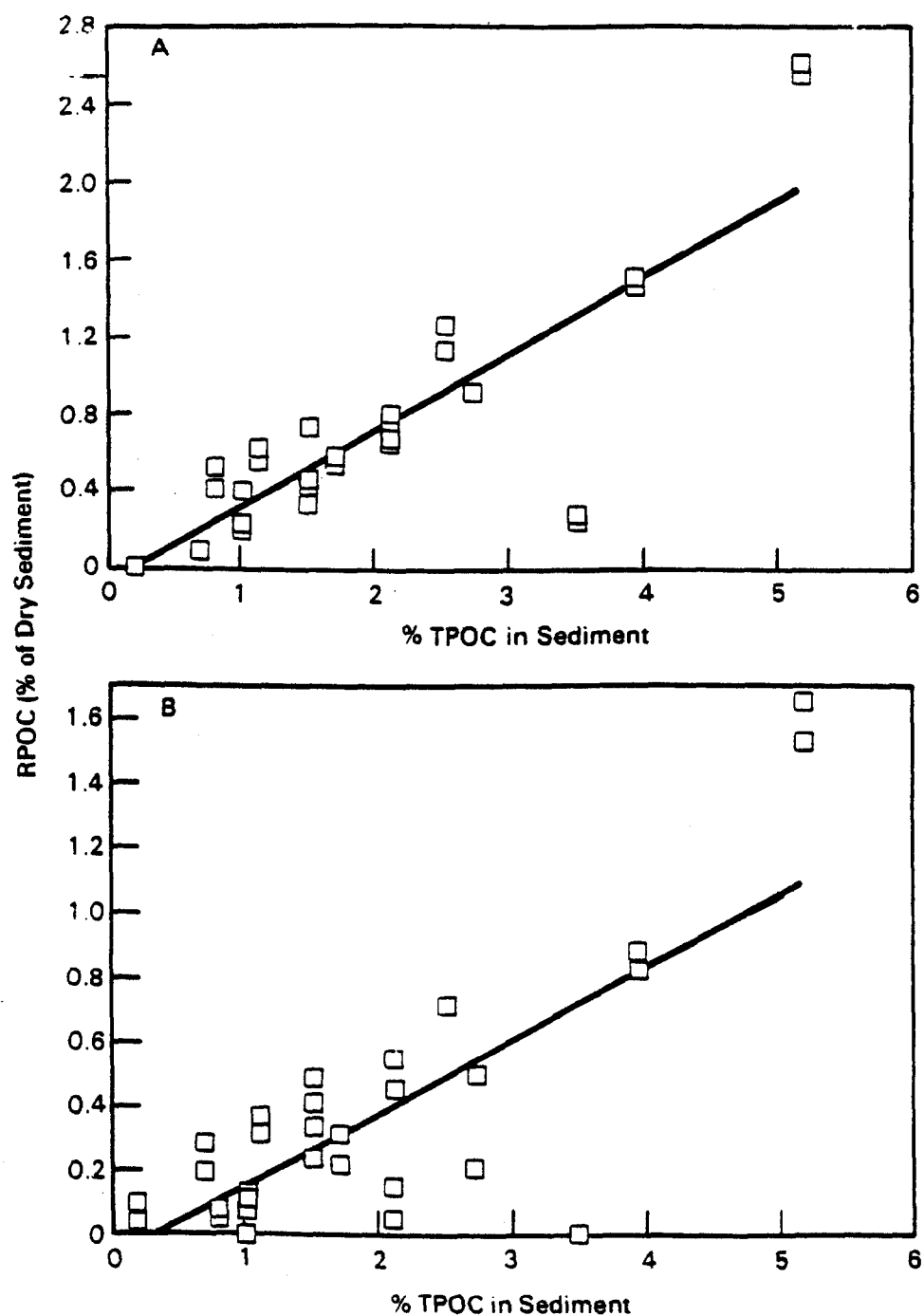


FIGURE 6. Reactive Particulate Organic Carbon, as Determined by Potassium Hydroxide (A) and Ammonium Hydroxide (B), Plotted Versus the Total Particulate Organic Content of the Sediments Studied

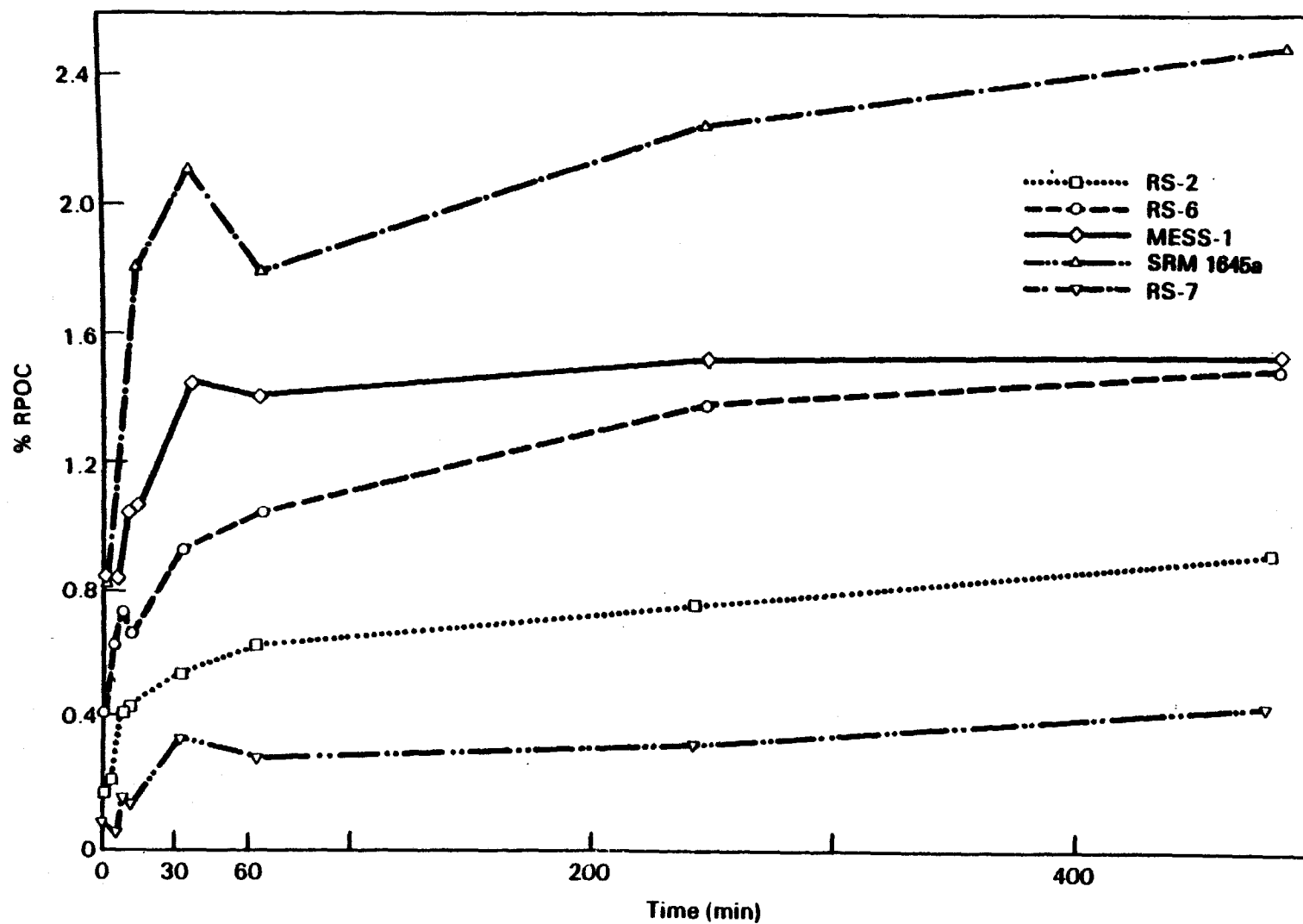


FIGURE 7. Time Dependent Dissolution of Reaction Particulate Organic Carbon Determined with Potassium Hydroxide for Five Sediments

are anomalously high in comparison to the 60-min value; hence, they cannot be used to determine the optimum extraction time. For consistency with the hydroxylamine-Hydrochloride extraction method, we tentatively selected a 60-min extraction period.

DISCUSSION

The approach that EPA is considering to develop sediment quality criteria for metals requires that the quantities of sorbed metals and the quantities of the major sorbent phases in the sediments be estimated. The estimation methods must be usable by federal agencies and private companies. Therefore, the methods for estimating the quantity of sorbed metals and sorbent phases should be easily applied and relatively insensitive to variations in extraction parameters, such as the solid:solution ratio, concentration of extractants, and time. For ease of application, a single extraction time that yields the maximum quantity of the target sorbent (e.g., amorphous Fe oxide) and the minimum amount of other phases with different absorptive properties (e.g., crystalline Fe oxides) should be selected.

The effects on the extraction efficiency of varying the extraction parameters have been used to prepare a recommended method for using $\text{NH}_2\text{OH}\cdot\text{HCl}$ extractant to estimate the quantity of sorbed metals, amorphous Fe oxide, and Mn oxide (Appendix A). The $\text{NH}_2\text{OH}\cdot\text{HCl}$ method was effective in extracting amorphous Fe oxide but not crystalline Fe oxides. The metal recovery experiments indicated that readsorption of soluble metals to other sorbents was not a problem with this procedure for the sediments studied. These results are in contrast with the results obtained by Rendell et al. (1980), who used a series of "selective" extractants. Although the reason for this difference is not known, it is possible that their use of a dithionate extractant, which is more of a reducer than the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extractant, may have affected the resorption of the metals. The precision studies with the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction method suggest that the coefficient of variation between estimates on the same sediment samples will be 12% or less.

Based on the time curves of Chao and Zhou (1983) and Jenne (1984), it was expected that there would be little increase in Mn and amorphous Fe oxides extracted per unit time after about 30 to 60 min. Our results indicated that this hypothesis is generally true, and that a 60-min extraction time is desirable. However, the fraction of the total Mn and Fe dissolved by the $\text{NH}_2\text{OH}\cdot\text{HCl}$ method after 60 min for the RS-7 and CF-1 sediment sample is significant.

The increase in the amount of Mn and Fe dissolved from the RS-7 sample after 60 min suggests that an Fe-containing mineral is in the sample. This mineral is considerably less soluble than the amorphous Fe oxide, but still dissolves at a significant rate in the acidified $\text{NH}_2\text{OH}\cdot\text{HCl}$. Based on the results of the extraction of crystalline Fe oxides (Table 2), this Fe-containing mineral may be lepidochroite. The possible error introduced into the estimate of the amorphous Fe oxide sorbent by the presence and dissolution of lepidochroite merits further investigation.

As mentioned above, the Clark Fork River sample (CF-1) also showed an increase in the amount of Mn and Fe dissolved after 60 min. The results do not indicate whether many or most of these trace metals were released from Mn and amorphous Fe oxides, or from the oxidation of detrital sulfides. Although the $\text{NH}_2\text{OH}\cdot\text{HCl}$ method is clearly valid with oxic sediments, the extent to which detrital sulfides confound the estimation of amorphous Fe oxide and sorbed metals also merits careful further investigation.

Comparison of two methods for estimating the quantity of RPOC indicated KOH is superior to NH_4OH and that the method, in the range investigated, is not sensitive to the solid:solution ratio and extractant concentration. Under the test conditions used, KOH extracted twice as much organic carbon as NH_4OH and produced a higher correlation between RPOC and TOC in sediments than NH_4OH . There also may be occasions when timeliness is important, making extraction in 1 h instead of 1 week an advantage. Appendix B gives the recommended standard method for the KOH extraction method.

While the methodology evaluations reported here are important, they are only a first step in evaluating the effectiveness of the extractions. In this study, our analysis was restricted to oxic sediments that have a specific range in characteristics. As these methods are applied to additional sediments, a better evaluation of the strengths and limitations of the extraction methods will result. One issue that will need to be addressed in using the extracted quantity of Fe, Mn, and RPOC in sorption models is the correlation between these quantities and the density of sorption sites. If there is no correlation, then the extracted quantities may be used in empirical models. If there is a correlation, then classical models (e.g., the triple-layer adsorption model) can be used. The next step in the sediment criteria development effort will

be to evaluate alternative algorithms for estimating the interstitial water activity of the metal contaminants and then choose the most appropriate procedure. —

CONCLUSIONS

The methods tested are suitable for estimating the quantities of sorbed metals and the major sorbent phases in sediments. Recommended standard methods for estimating the quantities of sorbed metals and major oxide sorbents, and for determining the RPOC content of sediments, are given in Appendixes A and B, respectively. Other conclusions are:

- Recoveries of the metal spikes were 90% or better, indicating that the metals were not readsorbed by other sorbents.
- Extractions of Fe and Mn minerals indicate amorphous Fe and Mn oxides are dissolved while the dissolution of crystalline Fe oxides is minimal.
- Variation in the solid:solution ratio (0.25 to 1.0 g/100 ml) did not significantly affect the estimation of sorbed metals, oxide-sorbents, or RPOC on the sediments investigated.
- Variation in the HCl or KOH concentrations did not significantly affect the $\text{NH}_2\text{OH}\cdot\text{HCl}$ or KOH extraction methods. The use of 0.25M HCl rather than a more dilute 0.10M HCl will permit sample sizes to range from 0.2 to 1.0 g with only minor changes in metal extraction efficiencies. This insensitivity facilitates obtaining metal concentrations in an appropriate concentration range for analysis by varying the sample size.
- No benefits were found for the use of NH_4OH (20°C for 1 week) instead of KOH for determining RPOC.
- There is merit in extending the extraction time for both the metals and RPOC extractions from 30 to 60 min.

REFERENCES

- Chao, T. T., and L. Zhou. 1983. "Extraction Techniques for Selective Dissolution of Amorphous Iron Oxides from Soil and Sediments." Soil Sci. Soc. Amer. J. 47:225-232.
- Jenne, E. A. 1984. "Quantitative Determination of Sorption Sinks." In Radionuclide Migration in Groundwater, pp. 43-54. NUREG/CR-3712 (PNL-5040), U.S. Nuclear Regulatory Commission, Washington, D.C.
- Jenne, E. A., D. M. DiToro, H. E. Allen, and C. S. Zarba. 1986. "An Activity-Based Model for Developing Sediment Criteria for Metals: I. A New Approach." In Proceedings of the Chemicals in the Environment: International Conference, eds. J. N. Lester, A. Perry, and R. M. Sterritt. pp. 560-562. Selper Ltd., London.
- Luoma, S. N., and G. W. Bryan. 1981. "A Statistical Assessment of the Form of Trace Metals in Oxidized Estuarine Sediments Employing Chemical Extractants." Sci. Total Environ. 17:165-196.
- Nielson, K.K., and R.W. Sanders. 1983. "Multielement Analysis of Unweighed Biological and Geological Samples Using Backscatter and Fundamental Parameters." Adv. X-ray Anal. 26:385-390.
- Rendell, P. S., G. E. Batley and A. J. Cameron. 1980. "Adsorption as a Control on Metal Concentrations in Sediment Extracts." Environ. Sci. Tech. 14:314-318.
- Salomons, W., and U. Förstner. 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin.

APPENDIX A

NH₂OH•HCl METHOD FOR EXTRACTING SORBED METALS AND
AMORPHIC Fe AND Mn OXIDES FROM A SEDIMENT SAMPLE

APPENDIX A

NH₂OH•HCl METHOD FOR EXTRACTING SORBED METALS AND AMORPHIC Fe AND Mn OXIDES FROM A SEDIMENT SAMPLE

SUMMARY OF METHOD

Air-dry, sieve, and homogenize the sediment sample. Add a portion of the sample (0.40 g) to 100 mL of hot (50°C) extraction solution (0.25M NH₂OH•HCl and 0.25M HCl) and shake for 60 min. Filter approximately 25 mL of the suspension through a 0.2- μ m membrane filter. Store the filtrate in a polyethylene bottle. Analyze the filtrate for metals by inductively coupled plasma (ICP), atomic adsorption spectroscopy (AA) or equivalent method.

EQUIPMENT

- shaker hot water bath
- analytical balance with 0.1-mg accuracy
- reagent grade hydroxylamine hydrochloride
- reagent grade hydrochloric acid
- 250-mL and 30-mL polyethylene bottles
- 1-L wide-mouth polyethylene bottles
- 100-mL graduated cylinder
- 30-mL plastic syringes
- 0.2- μ m in-line membrane filters (Gelman polysulfone Acrodisic, product no. 4191)
- 60-mesh (0.25-mm) sieve with nylon screen
- inductively coupled plasma, atomic adsorption spectrometry or equivalent equipment

EQUIPMENT PREPARATION

- To clean polyethylene bottles, graduated cylinder, and syringes, soak in 5% HCl for 24 h and rinse five times with double-deionized water. Air-dry in laminar flow hood.
- To clean in-line filters, force 30 mL of 5% HNO₃ through the filters and rinse with 90 mL of double-deionized water.

SAMPLE PREPARATION

To avoid developing anoxic conditions, promptly return sediment samples to the laboratory and spread out on clean polyethylene sheets to air-dry. In drying, the sediment can form a hard pancake, which should be broken up using a mortar and pestle. Sieve the sediment to remove material >0.25 mm (>60 mesh) using a nylon screen, and store the sieved samples in wide-mouth polyethylene containers.

ANALYTICAL PROCEDURE

- Prepare an aqueous extraction solution of 0.25M hydroxylamine hydrochloride (NH₂OH•HCl) and 0.25M hydrochloric acid (HCl).
- Place 100 mL of extraction solution in a 250-mL polyethylene bottle.
- Warm solution to 50°C in a hot water bath.
- Add 0.40 g of sieved sediment to warm solution. (Up to 1.0 g/100 ml of sieved sediment may be used to increase the soluble concentration of metal, if necessary.)
- Return sample bottle to hot water bath (50°C) and shake for 60 min.
- Remove sample bottle from the hot water bath.
- Withdraw 25 mL of solution from sample bottle using a 30-mL plastic syringe and filter through a 0.2 µm in-line filter (Gelman polysulfone Acrodisic, product no. 4192).
- Collect filtrate in a 30-mL polyethylene bottle.

- Cap filtrate bottles tightly.
- Analyze ~~filtrate~~ for metals by ICP, AA or equivalent method.

QUALITY CONTROL

- Analytical balances should be inspected and calibrated on a preassigned schedule.
- The equipment used for analysis of the filtrates for metal concentrations should be calibrated on a preassigned schedule following the manufacturers specifications.
- 10% of samples should be analyzed in duplicate.
- Prepare procedural blanks by following the procedure, but without adding sieved sediment. One procedural blank for each ten samples should be included.
- Spike replicates of three sediment samples with quantities of individual metals equivalent to that expected to be extracted from the sediment should be analyzed. Add spikes immediately after placing the sediment into the preheated extraction solution. Calculate spike recovery as the excess in the recovery experiment compared to that in the standard extraction.

APPENDIX B

KOH METHOD FOR EXTRACTING THE REACTIVE PARTICULATE ORGANIC CARBON FROM A SEDIMENT SAMPLE

APPENDIX B

KOH METHOD FOR EXTRACTING THE REACTIVE PARTICULATE ORGANIC CARBON FROM A SEDIMENT SAMPLE

SUMMARY OF METHOD

Air-dry, sieve, and homogenize the sediment sample. Add a portion of the sample (0.50 g) to 100 mL of hot 0.5M KOH solution and shake for 60 min. Filter approximately 25 mL of the suspension through a 0.2- μ m membrane filter. Store the filtrate in a polyethylene bottle. Analyze filtrate for dissolved organic carbon.

EQUIPMENT

- reagent grade potassium hydroxide
- shaker hot water bath
- analytical balance with 0.1-mg accuracy
- 250-mL and 30-mL polyethylene bottles
- 1-L wide-mouth polyethylene bottles
- 100-mL graduated cylinder
- 30-mL plastic syringe
- 60-mesh (0.25-mm) sieve with nylon screen
- 0.2- μ m in-line polycarbonate membrane filters (Gelman)
- deionized, distilled water
- carbon analyzer (e.g., Dohrmann Model DC-80)

EQUIPMENT PREPARATION

Clean all labware to be used in this extraction by filling with 1.0M KOH and heating to 95°C overnight. Rinse three times with distilled, deionized water and dry in a laminar flow hood.

SAMPLE PREPARATION

To avoid developing anoxic conditions, promptly return sediment samples to the laboratory and spread out on clean polyethylene sheets to air-dry. In drying, the sediment can form a hard pancake, which should be broken up using a mortar and pestle. Sieve the sediment to remove material >0.25 mm (>60 mesh) using a nylon screen, and store sieved samples in polyethylene containers.

ANALYTICAL PROCEDURE

- Prepare an aqueous solution of 0.5M potassium hydroxide (KOH).
- Place 100 mL of KOH solution into a 250-mL polyethylene bottle.
- Warm solution to 95°C in a hot water bath.
- Add 0.50 g of sieved sediment to sample bottle. (Up to 1.0 g/100 ml of sieved sediment may be used to increase the concentration of DOC, if necessary.)
- Return sample bottle to hot water bath (95°C) and shake for 60 min.
- Transfer sample bottles to cold water bath for 10 min. Swirl solutions at 3- to 4-min intervals.
- Withdraw 25 mL of solution from sample bottle using a 30-mL plastic syringe and filter through a 0.2- μ m in-line filter (Gelman polycarbonate membrane).
- Collect filtrate in a 30-mL polyethylene bottle.
- Cap bottle tightly and store in refrigerator.
- Analyze for dissolved organic carbon using carbon analyzer.
- Rinse the syringe three times with deionized, distilled water between uses.

QUALITY CONTROL

- Prepare procedural blanks by following the procedure, but without adding sieved sediment. One procedural blank for each 10 samples should be included.
- Calibrate the carbon analyzer on a preassigned schedule following manufacturers specifications.
- 10% of samples should be analyzed in duplicate.
- All analytical balances should be inspected and calibrated on a preassigned schedule.