

SEDIMENT QUALITY CRITERIA FOR METALS:
II. REVIEW OF METHODS FOR QUANTITATIVE
DETERMINATION OF IMPORTANT ADSORBENTS
AND SORBED METALS IN SEDIMENTS

Work Assignment 56, Task 4

August 1987

Prepared by:

Everett A. Jenne

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Richland, Washington

for:

U.S. Environmental Protection Agency
Criteria and Standards Division
Washington, D.C.

Submitted by:

BATTELLE

Washington Environmental Program Office
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ABSTRACT

This report is one in a series of reports that collectively describe an approach for establishing sediment criteria for metals. The approach uses surface complexation constants in conjunction with estimates of sorbed metals and the quantities of important adsorbents to estimate the equilibrium activity of metals in the pore water of sediments. This estimate of metal activity in pore water will then be used to evaluate the potential toxicity of the sediments to benthic organisms.

Predicting the equilibrium concentrations of metals in pore waters and soil solutions requires reliable estimates of both the total quantities of the important adsorbents and sorbed metals, as well as estimates of appropriate adsorption constants. Various authors have concluded that amorphous Fe, cryptocrystalline Mn, and particulate organic carbon constitute the important adsorbents for metals in a large portion of oxygenated sediments and soils. Many methods have been proposed for determining the quantities of these adsorbents. Recently, a consensus has evolved that acidic hydroxylamine hydrochloride is the preferred chemical extractant for estimating the quantity of cryptocrystalline Mn oxides. Importantly, this extractant also provides an effective means of estimating quantities of amorphous Fe oxides. Alkaline extractants appear to be appropriate for estimating the reactive particulate organic carbon content of sediments.

The extensive literature on the "selective" extraction of trace metals and metalloids from individual adsorbents in sediments indicates that none of the available extraction methods will selectively remove

trace metals from individual adsorbents to the exclusion of other adsorbents. Similarly, it is exceedingly difficult to selectively dissolve individual adsorbents without simultaneously dissolving a significant portion of another adsorbent(s). This nonselectivity of extraction methods is indicated both by the plethora of published extraction methods and the variable importance that different studies ascribe to individual adsorbents. Because the various acid and/or reducing extraction methods are known to attack multiple adsorbents, I conclude that it is physicochemically impossible to distinguish among the quantities of trace metals adsorbed separately by amorphous Fe oxide, poorly crystallized Mn oxide, and reactive particulate organic carbon.

Nevertheless, the total quantity of sorbed metal may be determined simultaneously with the quantities of amorphous Fe and poorly crystallized Mn oxide by using the hot acidic hydroxylamine hydrochloride extraction method. An alkali extractant is recommended to estimate the quantity of reactive particulate organic carbon. An experimental effort is required to select between alternative alkali extractants to be used to estimate the reactive particulate organic carbon, optimize experimental procedures for the selected extraction methods, determine appropriate adsorption constants, and validate the approach detailed in this report for determining sorbed metal concentrations.

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INTRODUCTION

The Criteria and Standards Division of the U.S. Environmental Protection Agency is developing sediment quality criteria for both nonpolar organic contaminants and metals. These criteria will be used in conjunction with water quality criteria to protect aquatic organisms and the 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 and requires only that the quantity of each important adsorbent (sorption "sink") and the quantity of sorbed metals be determined. These data, plus surface adsorption constants for the individual adsorbents, are used along with an appropriate algorithm (model) to estimate the activities of metals in pore water. This approach separates the problems of determining metal availability and evaluating toxicity. Importantly, the approach relates sediment quality criteria to the water quality criteria.

This report is one in a series of five reports that review the overall rationale for the approach (Jenne et al. 1986), the available

sorption data for reactive particulate organic carbon (RPOC)^(a), and the selected adsorption constants for Fe oxides^(b); and both review and present recalculations of selected adsorption data for Mn dioxide^(c). The objectives of this report are to consider the nature and occurrence of the important adsorbents, evaluate the published extraction methods for determining sorbed metals and adsorbents, and select appropriate extraction methods for further evaluation.

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- (a) Allen, H. E., and J. M. Mazzacone. 1987. Sediment Quality Criteria for Metals: III. Review of Data on the Complexation of Trace Metals by Particulate Organic Carbon. Drexel University. Submitted by Battelle, Washington Environmental Program Office, Washington, D.C. to the U.S. Environmental Protection Agency, Criteria and Standards Division.
 - (b) Jenne, E. A. 1987. Sediment Quality Criteria for Metals: IV. Surface Complexation and Acidity Constants for Modeling Cadmium and Zinc onto Iron Oxides. Submitted by Battelle, Washington Environmental Program Office, Washington, D.C. to the Environmental Protection Agency, Criteria and Standards Division.
 - (c) Di Toro, D. M., and B. Wu. 1987. Sediment Quality Criteria for Metals: V. Review of Data for Determining the Intrinsic Adsorption Constants for Manganese Dioxide. HydroQual Co., Inc. Submitted by Battelle, Washington Environmental Program Office, Washington, D.C. to the U.S. Environmental Protection Agency, Criteria and Standards Division.

BACKGROUND

Various approaches are used to identify sediments possessing anomalous (i.e., geochemically interesting and potentially biologically dangerous) trace metal contents. These approaches involve size and/or density separations, various normalization techniques, and/or selective extraction methods. Metal analyses of sediment size fractions provide information on the distribution of metals as a function of particle size; however, such analyses are labor intensive (Jenne et al. 1980; Salomons and Förstner 1984). Total metal concentrations may be normalized to remove the dilution effect of various primary minerals (e.g., quartz). This normalization technique assumes that all of the trace metals are contained in the smaller diameter particles (e.g., $<16\ \mu\text{m}$) and requires that grain-size analyses be performed on separate samples (De Groot 1964). Alternatively, trace metal analyses may be normalized to a primary mineral-free basis by using chemical analysis to determine a suite of primary minerals and computing the trace metal concentrations by assuming that the primary minerals contain none of the trace metals of interest (Thomas and Jaquet 1976). A related normalization technique assumes that particular solid phases such as Si oxides and/or carbonates contain low trace metal concentrations and serve as dilutents. This technique may be applied, for example, by normalizing the trace metal concentrations to unit Al concentration (see references cited by Salomons and Förstner 1984).

Chemical extraction has been the most general approach used to identify anomalous trace metal concentrations and to estimate the

quantities of particular geochemical adsorbents. Chemical extraction methods are used specifically to 1) quantify solid phases important in soil classification (McKeague and Day 1966), 2) estimate the quantity of major adsorbents present in soils (Blume and Schwertmann 1969), 3) locate potential ore deposits by identifying geochemical halos in soils and locally anomalous trace metal concentrations in stream sediments (Chao 1984), 4) investigate the partitioning of trace metals among various adsorbents in sediments, 5) investigate the cycling of metals (Gibbs 1977) and radionuclides (Spalding 1985), 6) estimate soil fertilization requirements and interpret responses to trace metal fertilization (Miller, Martens and Lelalny 1986), and 7) evaluate the potential toxicity of sediment-bound metals to aquatic organisms (Diks and Allen 1983).

Extensive literature exists on the "selective" extraction of trace metals and metalloids from individual adsorbents. This literature indicates that even the most selective extraction methods do not remove trace metals from one particular adsorbent to the exclusion of other adsorbents. Similarly, selective extraction methods intended to dissolve an individual adsorbent frequently dissolve a significant portion of other important adsorbents. This nonselectivity is indicated by the plethora of published extraction methods (Appendix 1) and the variable importance ascribed to individual adsorbents in various studies. Because the various methods containing acid and/or reducing agents are known to attack multiple adsorbents, it is probably impossible to reliably distinguish between trace metals sorbed by the major adsorbents. For example, the carbonates of surficial sediments may contain significant amounts of metals (Jenne 1977; Tessier, Campbell and Bisson 1980). Thus, the

acidification commonly used to decrease readsorption during reductive dissolution of Mn and/or Fe oxides may dissolve significant quantities of carbonates and released occluded metals. Using competitive exchange to quantify the total amount of sorbed metals present in sediments (as opposed to a readily exchangeable fraction) is conceptually simple but quantitatively difficult because of the extended time that may be required to reach equilibrium (Cutshall et al. 1973). Extended equilibration times have the disadvantage of allowing precipitation and/or dissolution reactions to proceed. As discussed in the following section, the precipitation of oxides (e.g., Fe or Si), carbonates, or organic carbon on the surfaces of soil particles tends to armor the interior of the particle from pore water. Differing degrees of aggregation and armoring of sediment particles are expected to yield widely variable times for a given fraction of the sorbed metals to desorb from different sediments. These factors probably preclude an accurate estimate of the total quantity of sorbed metals via partial desorption.

The following sections identify the major adsorbents and their mode of occurrence, review the available methods for determining the amounts of the major adsorbents, select a provisional set of extraction methodologies, and provide a rationale for the selected methodology.

MAJOR ADSORBENTS

In oxygenated sediments that are not composed primarily of carbonates, the major adsorbents for metals are the oxides of Fe and Mn, as well as particulate organic carbon (POC) (Jenne 1968, 1977). Because the sediment-water interface is frequently oxidized, the Fe and Mn oxides may also be important adsorbents for metals that are present in the water column, even when the sediments are largely anoxic. These three adsorbents are considered to be major adsorbents because of their 1) large surface areas that result from their general occurrence as coatings on minerals and aggregated particles, although they also occur as discrete particles or aggregates (Niehof and Loeb 1972; Johnson 1974; Suarez and Langmuir 1976; Jenne 1968, 1977; Hunter and Liss 1979; Hunter 1980); 2) high reactivity, as indicated by the extent that other elements are coprecipitated with and adsorbed onto amorphous Fe and cryptocrystalline Mn oxides; and 3) comparatively large surface complexation constants for metals as compared to major cations. The Mn oxides that form in soils and sediments are referred to as cryptocrystalline because of their great structural disorder that results from extensive substitution by many other cations (Jenne 1977).

The relative proportions of amorphous and crystalline Fe oxides (e.g., goethite and hematite) occurring in soils varies considerably (McKeague 1967). The same is probably true for sediments. Amorphous Fe oxide will crystallize to goethite or hematite within weeks to years in the absence of crystal growth inhibitors (Schwertmann, Fischer and Papendorf 1968; Avotins 1975). However, the crystallization of amorphous Fe is inhibited

by the following: 1) excess salts as compared to dialyzed preparations (Gastuche, Bruggenwert and Mortland 1964); 2) low concentrations of anionic ligands that form complexes or compounds with Fe, such as phosphate (Scheffer, Weite and Ludwig 1957; Krause and Borkowska 1963) and Si (Schellmann 1959; Anderson and Benjamin 1985; Aggett and Roberts 1986); and 3) coprecipitation with fulvic acid (Schwertmann, Fischer and Papendorf 1968; Kodama and Schnitzer 1977) and dissolved organic substances in general (Kuntze 1966; Schwertmann 1966). A marked decrease in the dissolution rate of amorphous Fe oxide in ethylene diaminetetraacetic acid (EDTA) occurred after the oxide aged for 4 weeks (Aggett and Roberts 1986). These authors also found that the dissolution rate decreased only slightly upon aging when the amorphous Fe oxide was precipitated in the presence of and onto chromatographic Si gel. These results suggest that dissolved Si inhibits crystallization of the amorphous Fe precipitate.

Although the quantity of crystalline Fe and Mn oxides may exceed the quantity of amorphous Fe and Mn oxides in sediments, other factors tend to increase the relative importance of the amorphous oxides as adsorbents. Although the surface complexation constants for Cd and Zn do not appear to be systematically larger for amorphous Fe oxide than for goethite^(a) (Leckie 1986), the quantity of trace metal sorbed per mole of Fe is larger for the amorphous oxide because the number of sites per unit mass of amorphous Fe is large compared to that of well-crystallized Fe oxides

(a) Jenne, E. A. and J. M. Zachara. "Factors Influencing the Sorption of Metals." In Fate and Effects of Sediment Bound Chemicals in Aquatic Systems, eds. K. L. Dickson, A. W. Maki and W. Brungs. Pergamon Press (in press).

(Anderson and Benjamin 1985). The relative adsorption capacities for cryptocrystalline and crystalline Mn oxides indicate that the number of sorption sites is considerably larger for the cryptocrystalline Mn oxides than for the well-crystallized Mn oxides (Anderson, Jenne and Chao 1973). The large number of sorption sites associated with poorly crystallized Fe and Mn oxides, in conjunction with the general occurrence of amorphous Fe coatings and cryptocrystalline Mn oxide particles on the surfaces of sediment particles (Jenne 1968), suggests that the poorly crystallized oxide fractions of these two metals are more important as adsorbents for trace metals and metalloids than their corresponding crystalline fraction.

The Fe, Si, and Al oxides and POC "coatings" that form on the surfaces of soil and sediment particles may occur in partially alternating layers. These coatings tend to isolate portions of individual adsorbents located in the interior portion of particles, preventing them from reacting with dissolved metals in the pore water. Thus, Jenne (1960) found that days to weeks were required to rehydrate air-dried coastal Oregon soils that were high in amorphous alumino-silicates. The ability of Fe coatings to limit equilibration of particle interiors with pore water is strongly suggested by the significantly smaller amounts of Al, and particularly Si, that were dissolved by hot sodium hydroxide if the alkali extraction was performed prior to extracting the soils with dithionite-citrate (to remove Fe coatings), as compared to the amount removed if the dithionite-citrate treatment is carried out first (Jenne 1960). Similarly, alternating dithionite and hydrogen peroxide treatments increased the amount of total dithionite-extractable Fe. These results suggest that only a portion of each of these adsorbents are available for

equilibration with dissolved metals. This reactive portion of a major adsorbent is, therefore, the parameter that should be measured to model the extent of sorption and desorption of trace metals in sediments. The amorphous nature of the major Fe adsorbent, the cryptocrystalline nature of Mn oxides, and the need to estimate the reactive portion of these oxides and of the particulate organic carbon (i.e., RPOC) largely precludes using any physical method for quantifying the reactive portions. Therefore, chemical extraction techniques must be used. Estimating adsorbent mass by chemical extraction involves the dissolution of these oxides by a major alteration in pH, reduction in valence, complexation, or a combination of these processes.

QUANTIFICATION OF AMORPHIC IRON AND CRYPTOCRYSTALLINE MANGANESE

The chemistry of Fe and Mn are sufficiently similar that any chemical extractant used to dissolve amorphous Fe or cryptocrystalline Mn also dissolves at least part of the other adsorbent. Thus, the partitioning of sorbed trace metals between these two adsorbents cannot be determined by extraction techniques. One objective of this review is to evaluate the possibility that a single extraction method can be used to estimate the quantity of both adsorbents. After considering two of the more promising extraction methods, the advantages and limitations of certain other extractants are presented.

ACIDIC AMMONIUM OXALATE

Acidic ammonium oxalate is the classical extractant used to estimate the amorphous Fe oxide content of soils and sediments in the presence of crystalline Fe oxides (Lundblad 1934; Schwertmann 1959, 1964; McKeague and Day 1966; McKeague, Brydon and Miles 1971). A decrease in Fe oxide crystallinity is generally accompanied by an increase in surface area and in the rate of dissolution in acidic ammonium oxalate (Karim 1984). Although the crystallinity of precipitated Fe oxides commonly increases with time, the crystallinity of naturally occurring oxides is principally determined by the amount of extraneous coprecipitated elements that are present in the oxides. For example, the amount of Fe extracted increased from 47% to 82% of the total amount present in a single 2-h acidic ammonium oxalate extraction, paralleling an increase in the Si content of ferrihydrite from 1.19% to 1.85% (Karim 1984).

There are some limitations to using the acidic ammonium oxalate method for dissolving amorphous oxides of Fe. This extraction method may only partially remove poorly crystallized Fe oxides, as some ferrihydrite remained even after three oxalate extractions (Carlson and Schwertmann 1981). Another disadvantage of this method is that crystalline Fe oxides are partially dissolved. For example, magnetite (Fe_3O_4) is quite susceptible to dissolution during an acid oxalate extraction (Baril and Bitton 1967; McKeague, Brydon and Miles 1971; Rhoton et al. 1981; Borggaard 1982; Chao and Zhou 1983; Walker 1983). Some maghemite ($\alpha\text{-Fe}_2\text{O}_3$) (Borggaard 1982), and to a lesser degree lepidocrocite ($\alpha\text{-FeOOH}$) (Pawluk 1972; Schwertmann and Taylor 1972; Schwertmann 1973), is also dissolved. Schwertmann (1973) reported that oxalate extracted a major part of organic Fe and presumably dissolves Mn oxides. Another analytical disadvantage of the acidic ammonium oxalate method is the need to carry out the procedure in darkness (Schwertmann 1973).

ACIDIC HYDROXYLAMINE HYDROCHLORIDE

The common extractant for cryptocrystalline Mn oxides is hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), which is a relatively mild reducing agent that has been used at various concentrations and acidities (Appendix 1). Chao and Zhou (1983) and Chao (1984) have modified the hydroxylamine method, originally developed by Chester and Hughes (1967) for the dissolution of Mn oxides, to include the dissolution of amorphous Fe oxides. The modified method dissolved less than 1% of the crystalline Fe oxides that were present and provided estimates of amorphous Fe that are similar to those obtained using the acidic ammonium oxalate method. Thus,

this method appears preferable for simultaneously determining poorly crystallized Fe and Mn oxides.

The necessity of acidic conditions is a limitation of both the acidic ammonium oxalate and hydroxylamine methods because of the increased analytical effort required to adjust the pH during the extraction and the possible dissolution of additional absorbents. Luoma and Bryan (1981), using the 0.1N $\text{NH}_2\text{OH}\cdot\text{HCl}$ plus 0.01N HNO_3 method of Chao (1972), noted that carbonates in the sediment caused the pH to increase. The partial dissolution of carbonates is undesirable for two reasons. A pH increase may allow sorbed metals that are released from oxide and RPOC absorbents to be partially readsorbed onto other solids (Rendell, Batley and Cameron 1980). To avoid this problem, Thompson-Becker and Luoma (1985) titrated the hydroxylamine hydrochloride-sediment suspension back to pH 2 after adding sediment to eliminate the effects of variable pH among samples. The second reason that the attack on carbonate minerals is undesirable is that the carbonates may be important adsorbents in some sediments. However, there are no satisfactory means to avoid acidic conditions in the hydroxylamine method.

OTHER EXTRACTANTS

Numerous other extractants are sometimes used to remove poorly crystallized Fe and/or Mn oxides from earth materials. Sodium acetate at pH 5 (Jackson 1956) has been used to remove Mn oxides from soils and sediments (e.g., Lion, Altmann and Leckie 1982). The advantage of this extraction method is that it is rather mild. However, the lack of specificity of acidic sodium acetate for poorly crystallized Mn oxides is

indicated by its frequent use to remove carbonates from earth materials (Appendix 1). Thus, the use of sodium acetate does not appear to have merit in comparison with hydroxylamine hydrochloride.

Sodium dithionite, plus citrate to complex dissolved metals, is the method generally used to estimate the total oxidic Fe and Mn content of earth materials. The disadvantages of extracting with dithionite to quantify poorly crystallized Fe and Mn are that 1) the dissolution rate is so rapid that time variations in mixing and during phase separation could result in significant differences in the amount of crystalline Fe oxides dissolved; 2) the very low redox potential results in the dissolution of crystalline Fe and Mn oxides; 3) the extractant contains relatively high levels of metal impurities, although the metal impurities can be removed (Jenne, Ball and Simpson 1973); and 4) sulfides may form during the extraction process and result in the precipitation of a portion of the trace metals as sulfides (Tessier, Campbell and Bisson 1979). Interestingly, the dithionite plus citrate extraction method is ineffective in dissolving magnetite (McKeague, Brydon and Miles 1971; Walker 1983).

Complexing agents are occasionally used to estimate the quantity of amorphous Fe oxide in sediments and soils. For example, EDTA was used at an alkaline pH (9 to 10.5) to determine amorphous Fe (Borggaard 1981). Less Fe was removed over a 3- to 8-month period using this method than in a 2-h extraction, in darkness, with 0.2M ammonium oxalate solution at pH 3.0. Another complexing agent, 0.1M tiron (di-sodium salt of catecholdisulphonic acid), was recommended by Biermans and Baert (1977) for the simultaneous dissolution of amorphous Fe, Al, and Si (pH 10.5 at

80°C for 1 h). The tiron method dissolved up to 13% of the gibbsite ($\text{Al}(\text{OH})_3$) present but little of the crystalline Fe oxides. Thus, the combination of the 1) extended reaction periods required by the EDTA method, 2) use of EDTA for carbonate and calcium sulfate removal (Bodine and Fernald 1973; Chao 1984), and 3) high pH conditions with probable extraction of other adsorbents (e.g., RPOC and amorphous aluminosilicate) suggest that these complexing agents have no advantages over hydroxylamine hydrochloride for estimating the quantity of amorphous Fe and cryptocrystalline Mn adsorbents in sediments.

QUANTIFICATION OF REACTIVE PARTICULATE ORGANIC CARBON ADSORBENT

Luoma and Bryan (1981) obtained similar estimates of RPOC using NH_4OH and 0.1N NaOH extractants in their study of a sediment from a British estuary. These authors simultaneously maximized the extraction of both Cu and POC from one of their sediment samples. They estimated the quantity of extracted organic carbon by using absorbance measurements at 640-nm. The 640-nm absorbance measurement was calibrated by repeatedly precipitating the organic substances at a low pH and then weighing the residue. The amount of RPOC in their estuarine sediments was estimated to range from approximately 1% to 23% of the POC.

Jenne (1984) and Zachara et al. (1986) used hot 0.5N KOH and 1N KOH, respectively, with 30-min extraction periods to estimate RPOC in sediments and soils (Table 1). Using 0.5N KOH on four river sediments, Jenne (1984) found total POC contents ranging from 0.015% to 0.034% and RPOC contents ranging from 60% to 76% of the POC. For subsoils developed on parent materials ranging from Colorado oil shale (bituminous dolomite) to alluvium, Zachara et al. (1986) found that the estimated RPOC ranged from 23% to 79% of the total POC. Potassium hydroxide was used in both of these studies to minimize dissolution of layer alumino-silicates (Dudas and Harward 1971). Strong alkali is the extractant of choice because other extractants, such as acids (Schnitzner and Skinner 1968) or phosphates (Luoma and Bryan 1981), generally extract relatively small quantities of POC. Thus, any extractants other than strong alkalis are expected to underestimate the RPOC component of sediments. There is one potential limitation to the alkali extraction method for estimating RPOC.

In sediments with significant silica armoring, the dissolution of silica may release additional POC, resulting in an overestimation of the RPOC.

Table 1. Total and Reactive Particulate Organic Carbon Determined by Combustion and Extraction with Potassium Hydroxide, Respectively

Extractant	POC (%)	RPOC (%)	RPOC/POC	Material
Jenne (1984) ^(a)				
0.5N KOH	0.034	0.024	0.71	25-46 ft
0.5N KOH	0.025	0.019	0.76	75-85 ft
0.5N KOH	0.015	0.009	0.60	30-41 ft
0.5N KOH	0.016	0.012	0.75	85-95 ft
Zachara et al. (1986) ^(b)				
1.0N KOH	0.24	0.19	0.79	Loring, Typic Fragiudalf, Bx2 horizon
1.0N KOH	0.22	0.16	0.73	Elk, Ultic Hapludalf, C horizon
1.0N KOH	0.26	0.19	0.73	Doront, Ultic Hapludalf, C horizon/residium
1.0N KOH	0.20	0.13	0.65	Westmorland, Ultic Hapludalf, B2t horizon
1.0N KOH	0.35	0.15	0.43	Vebar, Typic Haploboroll, C2 horizon and below
1.0N KOH	1.21 ^(c)	0.41	0.34	Zahl, Typic Argiboroll, C2 horizon and below
1.0N KOH	0.58 ^(d)	0.16	0.28	Anvil Points, unconsolidated material overlying aquifer
1.0N KOH	0.74 ^(e)	0.17	0.23	Ft. Martin, unconsolidated material overlying aquifer
1.0N KOH	0.02	0.04	(f)	Vernita, wind-sorted sand

(a) Columbia River flood plain samples collected at the specified depth and dry sieved to <425 μ m.

(b) The <2-mm fraction of various subsoils.

(c) Contains undecayed roots.

(d) Soil formed from oil shale.

(e) Contains coal fragments.

(f) Calculation not meaningful.

DETERMINATION OF ADSORBED METALS

Three chemical processes are used to estimate the quantity of sorbed metals: 1) competitive exchange by dissolved ions, 2) complexation by dissolved ligands, and 3) selective dissolution of adsorbents.

Many sets of extraction methods have been proposed for partitioning trace metals between the "exchangeable" fraction (i.e., metals adsorbed onto external surfaces) and the fraction absorbed (i.e., metals in the interior of particles) by various adsorbents (Appendix 1). Two of the classical sets of extraction methods are those of Chester and Hughes (1967) and Gibbs (1977). Chester and Hughes (1967) used acidic hydroxylamine to release absorbed trace metals plus associated Fe from cryptocrystalline Mn oxides, and acetic acid to dissolve Fe oxides and release absorbed trace metals. Gibbs (1977) used magnesium chloride to extract sorbed metals, dithionite to release absorbed metals from Mn and Fe oxides, and hypochlorite to release metals associated with RPOC.

Exchangeable metals were historically considered to represent the sorbed metal compartment and were determined by competitive exchange with salts, such as ammonium acetate (Appendix 1). However, ammonium acetate partially dissolves poorly crystallized carbonates and cryptocrystalline Mn oxides (Chapman 1965; Jackson 1965) and solubilizes some RPOC, thereby releasing sorbed metals from these solid phases. More recently, magnesium chloride has been used to displace exchangeable metals (e.g., Gibbs 1977; Campbell et al. 1985). However, Mg is a relatively weak competitor for Cd and Zn on goethite, α -FeOOH (Balistieri and Murray 1982). Thus, alkaline earth and alkali cations may not displace all the metals adsorbed

onto external sites. Because first-transition metals are specifically adsorbed (at least when the fraction of sites occupied is small) onto sites that may differ in adsorption energetics (Benjamin and Leckie 1981), any two competitive adsorption methods will desorb different amounts of a given metal, even in the absence of the partial dissolution of particular adsorbents.

Complexing agents are another class of extractants used to estimate the quantity of sorbed metals. The quantity of a metal removed from individual adsorbents by a complexing agent within a given time period will vary with the following: the extent of aggregation and armoring of particles, the difference between the association constants of the metal-complexing agent and metal-adsorbent complexes, the complexing ligand concentration, and the number of absorption sites on the adsorbent. Consequently, multiple extractions and extended extraction times will be required when using complexing agents to determine the total quantity of metals sorbed by the major adsorbents.

A variety of acids of several different strengths have been widely used to correlate "bioavailable" metal fractions with the metal content of organisms associated with the soil or sediment. Acids have minimal selectivity for the various adsorbents since they may remove metals from sediments, both by competitive exchange and by partial dissolution of adsorbents. Recently, hydrochloric acid has become the acid of choice. Luoma and Bryan (1982) found that the quantity of metals extracted with 1N HCl correlated better with the metal burdens of two benthic organisms than did the metal concentrations determined using five other extraction methods. Some investigators who use hydrochloric acid include a neutral

salt to minimize readsorption of elements such as Sr (Spalding 1985), although alkali metals are largely ineffective in preventing adsorption of divalent metals onto high-energy sites (e.g., Wahlberg et al. 1965).

Adsorption resulting from complexation reactions at external surface sites is rapid and occurs in time periods ranging from minutes to tens of minutes for clays (Brown 1964) and oxides (Benjamin 1978). However, with the possible exception of highly crystallized oxides (e.g., $\alpha\text{-Al}_2\text{O}_3$) and certain nonaggregated clay minerals (Brown 1964), most sediments (Malcolm and Kennedy 1970) and oxides of Mn, Fe, Al, and Si generally exhibit a significant "time-dependent" component of sorption (Benjamin 1978). The rates of adsorption (and presumably of desorption) vary between fresh and aged oxide precipitates (Lijklema 1980) and probably with particle size. The equilibrium time allowed by various investigators varies from 2.5 h^(a) to weeks (Cutshall et al. 1973). The time-dependent component of adsorption probably results from the slow diffusion of metals into the absorption sites on the interior of aggregates and/or particles. The commonly observed curvilinear portion of sorption versus time curves (e.g., Loganathan and Burau 1973) is postulated to result from a decrease in the amount of the element sorbed per unit time. This decrease occurs because of the longer time periods required for an adsorbate to equilibrate with sites that are progressively more remote from the bulk solution. Desorption rates measured in the laboratory may be slower than measured sorption rates because the concentration gradients are generally

(a) Theis, T. L. and L. W. Kaul. "Rate Studies on the Sorption of Inorganic Ions at the Geothite-Water Interface." In ACS Symposium Series, Surface Processes in Aqueous Geochemistry, ed. J. A. Davis (in press).

lower during desorption than during sorption experiments. These observations imply that, depending on diffusion restrictions, short but fixed-time desorption procedures will extract variable portions of the sorbed metals present in sediments. The lengthy time period required to reach desorption equilibrium might be largely avoided if the entire quantity of reactive amorphous Fe and cryptocrystalline Mn is solubilized, as discussed in the following section.

SELECTION OF METHODS

Partitioning the quantity of metals adsorbed onto external sites (i.e., the "exchangeable" or "readily available" fraction of metals) from those adsorbed onto internal sites is a qualitative process and is inherently dependent on the fractionation method used. This dependency exists because of a probable gradation in structural properties between external and internal sorption sites; variation in selectivity for a given metal on a given adsorbent; and variation in the rates of diffusion between external and internal sites, which depends on the mineralogy and the extent and nature of armoring of sediment particles. Acetate salts, which were classically used to extract exchangeable metals, solubilize some Mn oxides and RPOC. Ammonium does not appear to effectively displace trace metals from sites on the exterior surfaces of metal oxide. Magnesium also competes rather weakly with trace metals such as Cd and Zn sorbed onto goethite, and its use may therefore underestimate the quantity of metals sorbed on external sites of oxide adsorbents.

The use of a series of selective extractants to fractionate absorbed trace metals among individual adsorbents appears to be highly qualitative. Extractants that use the processes of complexation or combined hydrogen exchange and dissolution provide minimal selectivity because of their attack on multiple adsorbents. At this time, any extractant proposed for Mn oxides will also solubilize a fraction of the amorphous Fe, and those extractants that are acidic also, at least partially, dissolve carbonates.

Because of the major limitations of the existing extraction methods in fractionating trace metals among the major adsorbents, an alternative approach must be used, such as simultaneously determining the total amount of metals sorbed by the three most generally important adsorbents and the quantities of poorly crystallized Fe and Mn adsorbents. The importance of the attack of an acidic extractant on carbonates, with the accompanying release of occluded trace metals, must be addressed experimentally.

INTERIM EXTRACTION METHODS

Two interim methods are selected for further evaluation and optimization. The acidic hydroxylamine hydrochloride method is selected as the best available extractant for simultaneously estimating the quantities of metals sorbed by amorphous Fe, cryptocrystalline Mn, and RPOC. This extraction method will also be used to estimate the quantities of the amorphous Fe and cryptocrystalline Mn adsorbents. The hydroxylamine extraction method of Chao and Zhou (1983), as used by Jenne (1984), is described below:

Prepare a solution that is 0.25M with respect to hydroxylamine hydrochloride and 0.25M hydrochloric acid. Place 95 mL of this solution in 100-mL stoppered Erlenmeyer flasks, bring temperature to 50°C, and add 0.400 g, on an air-dry basis, of either moist or air-dry sediment. Place the flask in 50°C water-bath shaker for 30 min. Cool the solution for 10 min in a cold water bath, separate the phases using a high-speed centrifuge, and filter the supernatant through 0.22- μ m membrane into a 100-mL volumetric flask. Bring filtrate to volume with deionized water. Make dilutions as needed with 2% HCl. Note that if the sediment is enriched in Fe and/or Mn oxides, the solid-to-sediment ratio may need to be reduced. The reproducibility of the extractions is increased if smaller grain size fractions and/or a larger sample mass are used.

Hot potassium hydroxide is selected as the interim method to estimate the RPOC. The method of Jenne (1984) is described below:

Bring 100 mL of 0.5N KOH to incipient boil in a 400-ml stainless steel beaker. Add 0.50 g of air-dry sediment and continue heating with stirring for 30 min. Place beaker in a cold water bath, and add 100 ml of cold distilled water to cool. Separate phases in a high-speed centrifuge, decant into 250-ml volumetric flask and bring to volume with distilled water. Analyze dissolved organic carbon in a carbon analyzer (inductive heating, infrared measurement of CO₂) or spectrophotometrically (Luoma and Bryan 1981).

RATIONALE FOR INTERIM EXTRACTION METHODS

The discussion in earlier sections suggests that sorbed metals could be determined by the same extractant used to quantify the amorphous Fe and cryptocrystalline Mn adsorbents. This approach is possible if the trace metals sorbed by RPOC are also recovered in this extract because of mass action displacement by the high solution concentrations of ferrous iron and hydrogen.

The use of the reactive quantity of amorphous Fe and cryptocrystalline Mn (and RPOC) adsorbents in conjunction with the total sorbed metal to calculate metal activity in pore water assumes that the sorbed metal content is relatively constant throughout an individual adsorbent, whether the adsorbent is present as coatings or particulates. The available data that address this point are so limited that information on Fe-Si precipitates is included in the following discussion. Warnant, Martin and Herbillon (1981) found a nearly constant molar ratio of sorbed Cu to amorphous Fe (i.e., $5 \text{ to } 10 \times 10^{-3}$) in several German soils. Using the Chao and Zhou (1983) hydroxylamine method, Jenne (1984) found a relatively constant ratio of extracted Fe to Mn in four samples of Columbia River terrace sediment. Orange-colored floccules recovered from the bottom of a

Japanese lake contained a surprisingly constant Fe:Mn:Si mass ratio of 1.0:1.4(± 0.3):3.1(± 0.1), where the plus or minus values indicate the range of the four observations (Kato 1969). The ubiquity of Si in the weathering cycle suggests that Si is a ubiquitous component of Fe and Mn oxides in sediments. The available laboratory information indicates that incorporating Si into amorphous Fe oxide by aging the fresh Fe precipitate in glass beakers had little effect on the adsorption strength of Co, Cu, or Zn, but did increase the amount of Cd adsorbed (Anderson and Benjamin 1985). These findings suggest that the successive layers of the amorphous Fe component of these particular soils and sediment samples are reasonably homogenous. Importantly, the adsorption of Np by four Columbia River fluvial-glacial sediments was satisfactorily modeled, assuming amorphous Fe to be the dominant adsorbent (Girvin 1984). The amount of amorphous Fe adsorbent was estimated using the hydroxylamine extraction method (Jenne 1984).

The selection of the hydroxylamine method is based upon the following factors: 1) the method is reported to effectively discriminate against crystalline Fe oxides, 2) the quantities of both amorphous Fe and cryptocrystalline Mn are obtained with one extraction, 3) the amorphous Fe and cryptocrystalline Mn fractions are dissolved rapidly enough (about 1 h) for laboratory efficiency but slowly enough to permit ready discrimination between amorphous and crystalline fractions, 4) the possible presence of multiple Fe or Mn subfractions of varying crystallinity can be evaluated by curve stripping or equation-of-line techniques, and 5) the interelemental ratios in these extracts can be used to evaluate the constancy of sorbed metal to dissolved Fe and Mn ratios during

dissolution. The major significant limitation of this method is its acidity, which is needed to provide for recovery of released trace metals, but will attack carbonates.

Strong alkali is the only available extractant with the potential to estimate the RPOC adsorbent in sediments. The choice of the stronger alkali is based on the extensive use of sodium hydroxide to extract the fulvic and humic acid fractions from soils and sediments, and its use in estimating the quantities of amorphous aluminosilicates (Langston and Jenne 1964). The choice of potassium hydroxide in preference to sodium hydroxide is based on the decreased alteration of layer aluminosilicates by potassium as compared to sodium hydroxide (Dudas and Harward 1971). However, applying the proposed approach (Jenne et al. 1986) to a wide range of sediments may require estimating the quantity of amorphous aluminosilicates and perhaps the clay minerals, also. Amorphous aluminosilicates are likely to be an important adsorbent in sediments derived largely from source materials that are high in volcanic ash. In addition, in sediments that have sufficiently low redox potentials to have caused the dissolution of poorly crystallized Fe and Mn oxides, amorphous aluminosilicates may be a major adsorbent. Alteration of layer aluminosilicates by the alkali extractant is a consideration because the general application of the proposed approach for developing sediment criteria for metals (Jenne et al. 1986) may ultimately require consideration of layer aluminosilicates as adsorbents.

OPTIMIZATION OF METHODS

Additional research is required to optimize these methods and establish their adequacy as part of the process for developing metals criteria for sediments. The optimum pH for oxide dissolution and recovery of sorbed metals, the extent of pH control during extraction, and the solid-to-solution ratio needs to be evaluated for the hydroxylamine method. The extent of dissolution of crystalline Fe oxides should be included in the evaluation of the hydroxylamine method. The pH of the extraction method is particularly important because buffering due to carbonates and other solid phases may vary markedly between sediments. The amount of carbonate minerals dissolved during evaluation of the hydroxylamine extraction method needs to be determined either from the CO₂ evolved or from the decrease in total inorganic carbon in the samples. Adequate evaluation of the carbonate problem may require a review of existing information on the trace metal content of the carbonates of various sediments.

Refining the RPOC extraction method requires a comparison between potassium and ammonium hydroxide extractants, optimization of alkali normality, and examination of solid-to-solution ratios. Examining the organic carbon-to-silica ratios in the extracts of the variable time extraction series may indicate the extent to which the dissolution of silica coatings is responsible for the release of POC. These data will assist in evaluating the optimum extraction time.

Further evaluation of the selected methods must include a range of extraction times to ensure that the quantity of the sorbed metal that is extracted represents the entire reactive portion of amorphous Fe,

cryptocrystalline Mn, and RPOC adsorbents, and does not include an appreciable quantity of crystalline Fe and Mn oxides nor of POC isolated from pore waters.

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APPENDIX 1. "Selective Extractants" Used to Partition Metals Among the Various Presumptive Adsorbates

Exchangeable or Adsorbate Target (a)	Extractant (b)	Concentration (c)	pH	Temp. (°C)	Time (d)	Solid:Soln (d) (g/ml)	Sample Quantity (d)	Reference
Non matrix	HNO ₃ + HCl	4.0N + 0.7N		70-90	2 h	1:100	1 g	Agemian and Chau (1977)
Non matrix	HCl	0.5N		room	overnight	5:100	5 g	Agemian and Chau (1977)
Non matrix	NH ₂ OH·HCl + HOAc	1N + 25%		70-90	2 h	1:100	1 g	Agemian and Chau (1977)
Non matrix	EDTA	0.05N	4.8	70-90	2 h	1:100	1 g	Agemian and Chau (1977)
Fe(OH) ₃ (A)	EDTA	0.01M-0.1M	4.4-10.5	room	h - months	1:10 - 1:1000	?	Borggaard (1976, 1979, 1981, 1982, 1984)
Fe(OH) ₃ (A)	(NH ₄) ₂ C ₂ O ₄	0.2N	3.0	room	2 h - months	?	?	Borggaard (1976, 1979, 1981, 1982, 1984)
Al, Fe and Si oxides	Tiron	0.1N	9.5-11.0	80-100	25-60 min	?	?	Biermans and Baert (1977)
Fe oxides(A)	(NH ₄) ₂ C ₂ O ₄ + H ₂ C ₂ O ₄	0.175M + 0.100M			4 h	1:250	0.100 g	Chao and Zhou (1983)
Oxides, carbonates	HCl	1-4 M		room and 92	30 min	1:250	0.100 g	Chao and Zhou (1983)
Fe oxides(A)	(NH ₄) ₂ C ₂ O ₄ + H ₂ C ₂ O ₄	0.25M + 25%		70	4 h	1:250	0.100 g	Chao and Zhou (1983)
Fe oxides(A)	NH ₂ OH·HCl + HCl	0.25M + 0.25M	1.0	50 and 70	1/2 - 2 hr	1:250	0.100 g	Chao and Zhou (1983) Ross et al. (1985)
Al and Fe oxides	H ₂ C ₂ O ₄	3%		92	15 - 60 min	1:250	0.100 g	Chao and Zhou (1983)
Mn oxides	NH ₂ OH·HCl + HNO ₃	0.1N + 0.01N		room	30 min	?	?	Chao (1972), Chao and Theobald (1976)
Fe oxides(A)	NH ₂ OH·HCl + HCl	0.25M + 0.25M		70	30 min	?(e)	?(e)	Chao and Theobald (1976)
Fe oxides(C)	Na ₂ S ₂ O ₄ + Na ₃ C ₆ H ₅ O ₇	?	4.75	50	30 min	?(e)	?(e)	Coffin (1963), Chao and Theobald (1976)
Sulfides	KClO ₃ + HCl + HNO ₃	4N + ? + ?		92	20 min	?(e)	?(e)	Chao and Theobald (1976)
Matrix	HF + HNO ₃				?	?(e)	?(e)	Chao and Theobald (1976)

APPENDIX 1. (contd)

Exchangeable of Absorbate Target (a)	Extractant (b)	Concentration (c)	pH	Temp. (°C)	Time (d)	Solid:Soln (d) (g/ml)	Sample Quantity (d)	Reference
Exchangeable	CuSO ₄	0.05M		room	1-3 wk	?	?	Cutshall et al. (1974)
Exchangeable	MgCl ₂	1N	7	room	1 h	?	?	Gibbs (1973), Diks and Allen (1983)
Carbonates	NaOAc	1N	5	room	5 h	?	?	Tessier et al. (1979) Diks and Allen (1983)
Mn and Fe oxides	NH ₂ OH·HCl + HNO ₃	0.1N + 0.01N	2	room	30 min	?	?	Chao (1972) Diks and Allen (1983)
Organic	H ₂ O ₂ + NH ₄ OAc	30% + 1 M		85	5 h	?	?	Gupta and Chen (1975), Diks and Allen (1983)
Fe oxides	NH ₂ OH·HCl + HOAc	1N + 25%		96	6 h	?	?	Chester and Hughes (1967), Diks and Allen (1983)
Organics, sulfides	H ₂ O ₂ + HNO ₃ + NH ₄ acetate → HNO ₃	50% + 0.025M + 1N + 6%		dryness room	? + 30 min	?	?	Filipek et al. (1981)
Fe oxides	NH ₂ OH·HCl + 25% HOAc	0.25M + 25%		75	4 h	?	?	Chester and Hughes (1967), Filipek et al. (1981)
Silicates	HF-aqua regia+HCl	?-con+10%			?	?	?	Filipek et al. (1981)
Exchangeable	HOAc	1M			2 h	?	?	Filipek et al. (1981)
Exchangeable, Mn, oxides, carbonates	NH ₂ OH·Cl + HNO ₃	0.1M + 0.01M		room	30 min	?	?	Chao (1972) Filipek et al. (1981)
Exchangeable, Carbonates, Mn and Fe oxides	HOAc	1M			90 min	1:50	?	Gupta and Chen (1975)
Organics, sulfides	HNO ₃	0.01M			?	?	?	Gupta and Chen (1975)
Ferrihydrate	(NH ₄) ₂ C ₂ O ₄ + H ₂ C ₂ O ₄	0.2M + 0.2M	3.0.		2 h	?	?	Schwertman (1964), Karim (1984)
Extractable	HNO ₃	Con			?	1:20	?	Luoma and Bryan (1981)
Extractable	HCl	1N	0.1		2 h	1:10	1 g	Luoma and Bryan (1981)

APPENDIX 1. (contd)

Exchangeable or Absorbate Target (a)	Extractant (b)	Concentration (c)	pH	Temp. (°C)	Time (d)	Solid:Soln (g/ml)	Sample Quantity (d)	Reference
Extractable	HOAc	25%	2.2		2 h	1:30	2 ml	Luoma and Bryan (1981)
Extractable	$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4$	0.4N + 0.4N	3.3		2 h	1:30	2 ml	Luoma and Bryan (1981)
Extractable	$\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HNO}_3$	0.1N + 0.01N	2		30 min	1:10	2 ml	Luoma and Bryan (1981)
Extractable	NH_4OAc	1N	7		2 h	1:30	2 ml	Luoma and Bryan (1981)
Extractable	$\text{Na}_4\text{P}_2\text{O}_7$	0.1N	10		2 h	?	2 ml	Luoma and Bryan (1981)
Organic	NH_4OH	1N	11.6	room	1 wk	1:15	4 ml	Luoma and Bryan (1981)
Organic	NaOH	0.1N	12		1 wk	1:15	4 ml	Luoma and Bryan (1981) Thomas-Becker and Luoma (1985)
Surface coatings	$\text{S}_2\text{O}_4^{2-} + \text{C}_6\text{H}_5\text{O}_7^{3-}$	0.29M + 0.56M	3.0	80	3 h	?	?	Malo (1977)
Surface coatings	$\text{Na}_2\text{S}_2\text{O}_4 + \text{Na}_2\text{C}_6\text{H}_5\text{O}_7 + \text{NaHCO}_3$	0.57M + 0.3M + 1M 7.0	70	80	15 min	?	?	Malo (1977)
Surface coatings	$\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HOAc}$	1M + 25%		room	4 h	?	?	Malo (1977)
Fe oxides	$\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HCl}$	0.25M + 0.25M	1.0	room	16 h	1:250	0.10 g	Ross et al. (1985)
Fe oxides	$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4$	0.113M + 0.087M	3.0	room	4 h	1:40	0.25 g	McKeague (1978), Ross et al. (1985)
Fe oxides	$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4$	0.113M + 0.087M	3.0	room	4 h	1:250	0.1 g	Ross et al. (1985)
Exchangeable	$\text{Mg}(\text{NO}_3)_2$	1M			2 h	1:4	10 g	Sims (1986)
Organic	NaOCl	5.3%	8.5	100	30 min	+20 ml (e)	(b)	Sims (1986)
Mn oxide	$\text{NH}_2\text{OH}\cdot\text{HCl}$	0.1M	2.0		30 min	1:10	5 g	Sims (1986)
Fe oxide (A)	$\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HCl}$	0.25M + 0.25M		50	30 min	+50 ml (e)	(e)	Sims (1986)
Fe oxide (C)	$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4$	0.2M + 0.2M	3.0	100	30 min	+50 ml (e)	(e)	Sims (1986)
Carbonates	$\text{HCl} + \text{KCl}$	0.1 M + 0.5M			?	?	?	Spalding (1985)
Mn oxides	$\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HNO}_3$	0.1M + 0.01M			30 min	1:60	0.5 g	Suarez and Langmuir (1976)

APPENDIX 1. (contd)

Exchangeable or Absorbate Target (a)	Extractant (b)	Concentration (c)	pH	Temp. (°C)	Time (d)	Solid:Soln (d) (g/ml)	Sample Quantity (d)	Reference
Fe and Mn oxides	NH ₂ OH·HCl + CH ₃ COOH	1M + 25% (v/v)			2 h	?	?	Suarez and Langmuir (1976)
Exchangeable	MgCl ₂	1M	7.0	room	10 min (f,g)	1:8	1 g	Tessier et al. (1979, 1981)
Carbonates	NaOAc	1M	8.2	room	(f)	1:8	1 g	Tessier et al. (1979, 1981)
Carbonates	NaOAc	1M	5.0	room	5 h (g)	+8 ml (e)	(e)	Tessier et al. (1979, 1981)
Fe and Mn oxides	Na ₂ S ₂ O ₄ + Na ₃ C ₆ H ₅ O ₇ + H ₃ C ₆ H ₅ O ₇	0.3M + 0.175M + 0.025M			?	+20 ml (e)	(e)	Tessier et al. (1979, 1981)
Fe and Mn oxides	NH ₂ OH·HCl + HOAc	0.04 + 25% (v/v)		96	6 h	+20 ml (e)	(e)	Tessier et al. (1979, 1981)
Organic	H ₂ O ₂ + HNO ₃ + NH ₄ OAc + HNO ₃	30% + 0.02M + 3.2M + 20%	2	85	2 h	+8 ml (e)	(e)	Tessier et al. (1979, 1981)
Fe oxides (A)	NH ₂ OH·HCl + HNO ₃	0.1M + 0.01N	2.0		30 min	1:50	?	Thomson-Becker and Luoma (1985)
Fe oxides (C)	(NH ₄) ₂ C ₂ O ₄ + H ₂ C ₂ O ₄	0.2M + 0.2M	3.3		2 h	?	?	Thomson-Becker and Luoma (1985)
Matrix	HNO ₃ + H ₂ SO ₄	Con + con		room	2 h	>1:25	?	Thomson et al. (1980)
Matrix	HCl	0.5N		room	2 h	>1:25	?	Malto (1977), Thomson et al. (1980)
Matrix	HOAc	25%	2.2	room	2 h	>1:25	?	Loring (1976), Thomson et al. (1980)
Matrix	(NH ₄) ₂ C ₂ O ₄ + H ₂ C ₂ O ₄	0.4N + 0.4N	3.3	room	2 h	>1:25	?	Schwertmann (1964), Eaton (1979), Thomson et al. (1980)
NH ₂ OH·HCl + HNO ₃	0.1N + 0.01N	2.0	room	30 min	>1:25	?	?	Thomson et al. (1980), Chao (1972)
NH ₂ OH·HCl + HNO ₃	NaP ₂ O ₇	0.1N	10	room	2 h	>1:25	?	Thomson et al. (1980)
NH ₂ OH·HCl + HNO ₃	DTPA	0.00N	7	room	2 h	>1:25	?	Thomson et al. (1980)
NH ₂ OH·HCl + HNO ₃	NaOH	0.1N	12	room	1 wk	>1:25	?	Luoma and Bryan (1970), Thomson et al. (1980)
NH ₂ OH·HCl + HNO ₃	NH ₄ OAc	1N	7	room	2 h	>1:25	?	Thomson et al. (1980)
Organic	NaOCl + Na ₂ S ₂ O ₄ + Na ₃ C ₆ H ₅ O ₇	?	8.5		?	?	?	Gibbs (1977)

APPENDIX 1. (contd)

Exchangeable of Absorbate Target (a)	Extractant (b)	Concentration (c)	pH	Temp. (°C)	Time (d)	Solid:Soln (g/ml)	Sample Quantity (d)	Reference
Matrix	LiBO ₂ + HNO ₃	?		1000	?	?	?	Gibbs (1977)
Surface Coating	Na ₂ S ₂ O ₄ + Na ₂ C ₆ H ₅ O ₇	?	7.0		?	?	?	Gibbs (1977)
Exchangeable	MgCl ₂	1N			?	?	?	Gibbs (1977)
Carbonates, oxides, sulfides	NH ₂ OH·HCl	0.1M	2		?	?	?	Soloman and DeGroot (1978)
Organic	H ₂ O ₂	30%	2.5		?	?	?	Soloman and DeGroot (1973)
Exchangeable	CaCl ₂	0.5M	5.0		5 days	3:10	30	Suarez and Langmuir (1976)
Matrix	HF + HClO ₄	5:1			?	?	?	Tessier (1980)

(a) (A) and (C) signify amorphous and crystalline states, respectively, matrix = silicate minerals, and non matrix = extractable fraction.
 (b) Chemical composition and names of extractants are as follows:

Formula	Name
NH ₂ OH·HCl	hydroxylamine hydrochloride
C ₆ H ₅ O ₇ ⁻³	citrate
C ₂ O ₄ ⁻²	oxalate
C ₂ H ₃ O ₂ ⁻	acetate (OAc ⁻)
P ₂ O ₇ ⁻	pyrophosphate
S ₂ O ₄ ⁻²	dithionite
H ₂ C ₁₀ H ₁₄ O ₈ N ₂ ·2H ₂ O	EDTA (ethylenediaminetetraacetic acid)
C ₁₃ H ₂₃ O ₁₃	DTPA (diethylenetriaminopentaacetic acid)
C ₆ O ₈ H ₄ ⁻	Tiron (di-sodium salt of catecholdisulphonic acid)

(c) Concentrations are indicated in the same order as the extractants in the preceding column, ? = concentration not given, con = concentrated, % = concentration in volume percent.
 (d) ? = value not given
 (e) Solid from previous extraction added to specified volume.
 (f) Tessier et al. (1979).
 (g) Tessier et al. (1981).