

CHAPTER II

TRACE METALS PARTITIONING OF SEDIMENTS

Types of Metal Association in Sediments

Metals can accumulate in sediments by associating with various components. Gibbs (1973) has described this association by the following chemical bonds :

- adsorptive bonding
- coprecipitation with oxides of Fe and Mn
- complexation of metal by organic molecules
- held inside the crystal lattice of minerals

Gibbs had also emphasized that the first 3 kinds of bonding, which are sensitive to physico-chemical properties, are strongly influenced by environmental conditions. It should be noted that these bondings are primarily associated with sediment of the size less than 63 μm (Förstner and Wittmann, 1981). The bonding will not hold metals permanently in the sediments, thus, allowing for remobilization of metals between sediments and the water column due to biogeochemical processes (James, 1978). Table 2 expands this categorization, including all main types of metal associations, such as occur in both natural and polluted water systems.

Adsorption is the first step in the ultimate removal of metals from hydrological cycle; the ultimate sink being the oceanic sediments. Changes in environmental parameters like pH, chlorinity

Table 2 Carrier substances and mechanisms of heavy metal bonding
(from Förstner and Patchineelam, 1976)

Minerals of natural rock debris e.g., heavy minerals		Metal bonding predominantly in inert positions
Heavy metal - hydroxides - carbonates - sulfides		Precipitation as a result of exceeding the solubility product in the area of the water course.
Hydroxides and oxides of Fe/Mn	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in fixed positions) Cocprecipitation as a result of exceeding the solubility product
Bitumen, lipids Humic substances Residual organics	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in $COOH$ -, OH -groups) Complexes
Calcium carbonate	pH-dependent	Physico-sorption Pseudomorphosis (dependent on supply and time) Cocprecipitation (incorporation by exceeding the solubility product)

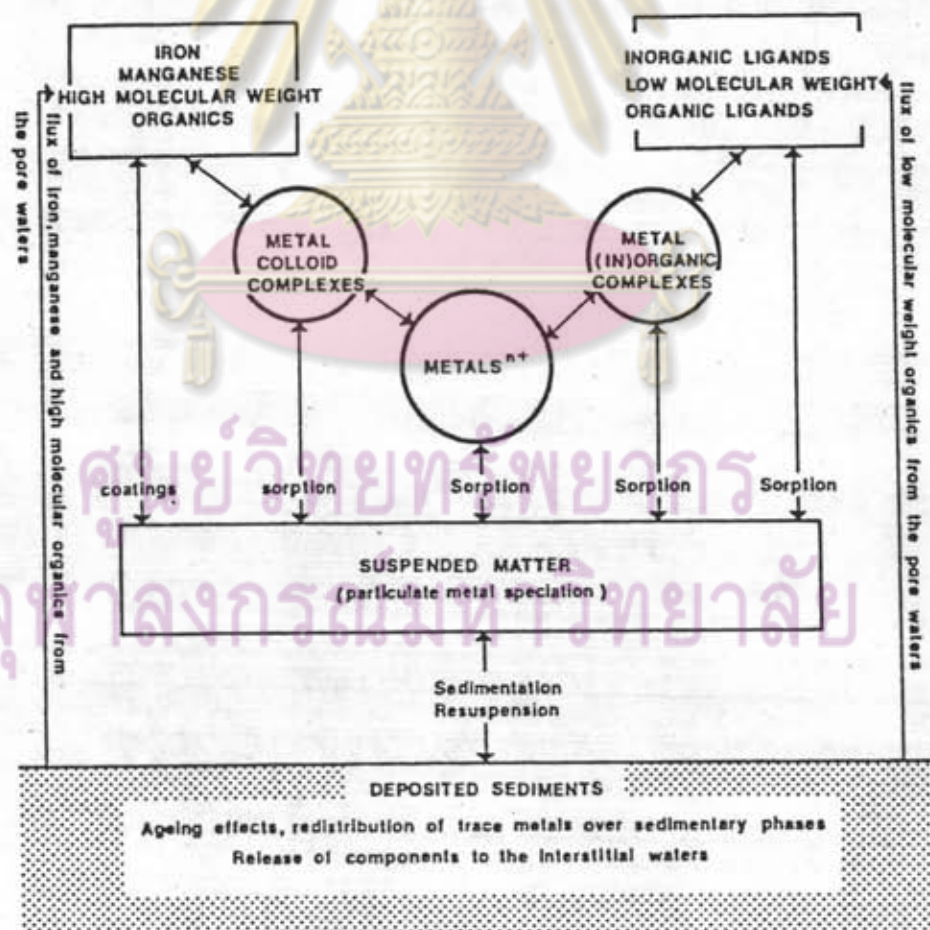


Figure 4 Summary of major processes and mechanisms in the interactions between dissolved and solid metal species in surface waters (after Salomons and Förstner, 1984).

(in estuaries) or the discharge of complexing agents all effect adsorption/desorption processes (Salomons and Förstner, 1984), as summarized in Figure 4.

1. Sorption Processes

The forms of sorption most commonly encountered with solute exchange between solid/solution interface are adsorption, chemi-sorption and ion exchange; there should be no difference between "sorption" and "coprecipitation" (Jenne, 1976; Laxen and Sholkovitz, 1981).

Physical adsorption on the external surface of particulate is based on Van der Waals forces of the relatively weak ion-dipole or dipole-dipole interactions. In addition, the reactions can occur with physical sorption on the particle's inner surface or in pores. Representative solid substances include Fe oxides, Al hydroxides, clay minerals and organic matters and molecular sieve (Lieser, 1975).

Chemi-sorption is characterized by the formation of chemical associations between ions or molecules from solution and the surface particles.

Sorption based on ion exchange is a chemical process which negative or positive charges in the minerals' lattice (such as in clay minerals) are compensated for by ions possessing opposite charges, which, more or less hydrated in the inner layers, are exchangeable by ions from the solution.

Several sediment-forming materials with a large surface area - particularly clay minerals, freshly precipitated Fe

hydroxides, amorphous silicic acids, as well as organic substances - are capable of sorbing cations from solution and releasing equivalent amounts of the other cation into the solution - i.e., by cation exchange. The mechanism which results in cation exchange is based on the sorptive properties of negatively charged anionic sites - SiOH^- , AlOH^{2-} , and AlOH -groups in clay minerals, FeOH -groups in Fe hydroxides, carboxyl and phenolic OH -groups in organic substances - towards positively charged cations. The balancing of negative charges of the lattice is a selective process which accounts for preferential adsorption of specific cations and the release of equivalent charges associated with the other species. Furthermore, all fine-grained materials with a large surface area are capable of accumulating heavy metal ions at the solid-liquid interface as a result of intermolecular forces. This phenomenon is termed "adsorption".

Guy and Chakrabarti (1975) established a generalized sequence of the capacity of solids to sorb heavy metals

$\text{MnO}_2 > \text{humic acid} > \text{Fe oxide} > \text{clay minerals}$

the sorption capacity of Fe oxides (crystalline phase goethite) for trace metals is at least 10 times less than that of the Mn oxides (Suarez and Langmuir, 1976). The hydrated oxides of Fe and Mn provide sorption sites for metals, some of which may be removed in the easily exchangeable fraction. This fraction may be very significant for several metals and is generally considered non-available under aerobic conditions. Rashid (1971) estimated that of a total bonding of 200-600 meq metal/100 g humic substance, approximately one-third can be attributed to the cation exchange and two-thirds to chemical sorption and organic complexation.

The matter becomes more complicated as clay minerals may act as nucleus in which hydroxide of Fe, Mn, Al and Cr, and organic compounds is coated upon. Therefore, clay mineral of coated and uncoated nature will differ greatly in their sorption behaviour and capacity.

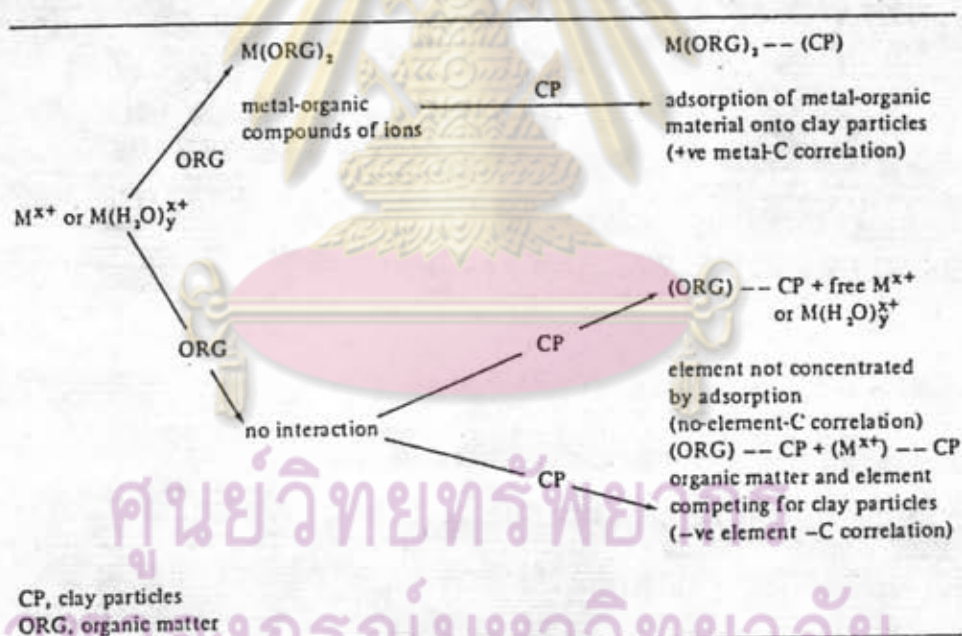
2. Complexation

The affinity of heavy metals for organic substances and for their decomposition products is of great importance for the behaviour of trace substances in aquatic systems. Singer (1977) summarized the influence of dissolved organics on the distribution of metals as follows: dissolved organic substances are capable of (1) complexing metals and increasing metal solubility, (2) altering the distribution between oxidized and reduced forms of metals, (3) alleviating metal toxicity and altering metal availability of aquatic life, (4) influencing the extent to which metals are adsorbed on suspended matters, and (5) affecting the stability of metal-containing colloids.

The organic matter of aquatic systems consists of the remains of biologically produced compounds as well as of synthetic organic substances. Synthetic organic substances originate from industrial and agricultural applications and have been suggested for use as detergent additives to replace polyphosphate, e.g., nitrilotriacetic acid. (Decomposition of higher-weight organic substances with high molecular mass is mostly due to microbiologic action, thus forming the smaller and more soluble fragments.)

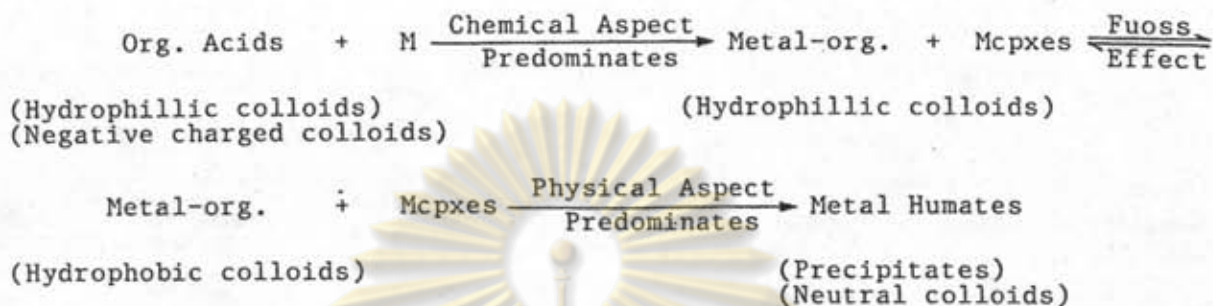
Saxby (1973) suggested 3 major processes leading to the incorporation of particular metal-organic species onto a sediment: (1) reaction between a metal ion and an organic ligand in solution leading to a species which can either precipitate directly or be adsorbed on sedimentary material, (2) incorporation in a sedimentary pile of all or part of an organism containing biologic coordination compounds, and (3) adsorption on a sediment of molecules resulting from the solubilization of minerals (sulfides, carbonates, etc.) by natural waters containing organic ligands (Table 3).

Table 3 Generalized metal-organic-solid reaction scheme as proposed by Curtis (1966).



In general the trace metal-organic complexes in natural waters represent a mixture of allochthonous and autigenic substances. These originate from solutions seeping through or running over the surface of soils (Shapiro, 1963) or are formed directly in the aquatic system by microbial and chemical processes. The behavior of humic acids during coagulation was summarized by Ong and Bisque

(1968), and Ong, Swanson and Bisque (1970) in the following schematic description of the reaction types :-



The behaviour of trace metals and organic material at the river/sea water interface finds particular attention in recent years. A fraction of the river water's organic matter and certain metals co-flocculate in the downstream reaches of the river and in the estuary (Beck, Reuter and Perdue, 1974). Rashid (1974) inferred that several metals, Co, Cu, Mo, Ni, Pb and Zn, may be removed to a considerable extent during or subsequent to flocculation of organic substances.

In organic role of Fe and Mn oxides as direct adsorbants of metal ions is either overshadowed by competition from the more reactive humic acids and organo-clays, or is obscured by coatings of organic matter (Jonasson, 1977). Organic flocculation coatings greatly affect the adsorption capacities for trace metals of sediment and suspended matter (Pillai, Desai, Mathew, Ganapathy and Ganguly, 1971; Sholkovitz, 1976).

3. Co-precipitation

Hydrous Fe and Mn oxides constitute a highly effective sink for heavy metals in aquatic systems where oxidizing occurs (Lee, 1975; Groth, 1971). Co-precipitation with carbonate may be an

important elimination mechanism for metals such as Zn and Cd when carbonate content occurs as a major component, i.e., when the other substances, particularly hydrous Fe oxides or organic substances, are less abundant (Förstner and Wittmann, 1981).

Under oxidizing condition, e.g., in the presence of D.O. ferric iron (Fe^{3+}) is only species found in the slightly acid to alkaline pH range. Some water bodies contain colloidal ferric hydroxide ($\text{Fe}(\text{OH})_3$), other ferric hydroxide or other ferric species that can pass through filters and appear to be part of the dissolved Fe (Hem, 1975). The concentration and chemical behaviour of dissolved Fe, as well as of other metal, may also be influenced by organic complexing agents. $\text{Fe}(\text{OH})_3$ can, in the presence of CO_2 (from the decomposition of organic substances), be converted to produce FeCO_3 , if the reduction potential becomes strongly negative as a result of the lack of oxygen.

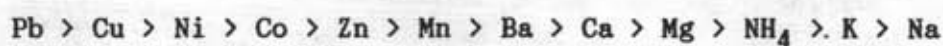
Müller, Irion and Förstner (1972) classified the conditions for CaCO_3 precipitation as follows : (1) CO_2 -loss or extraction as a result of changes in the p-T-conditions or by plant assimilation, either by macrophyta (e.g., potamogeton) or by microphyta (especially planktonic algae), (2) evaporation concentration or (3) mixing of different water bodies.

The third possibility is of the interest with respect to the co-precipitation of trace elements in carbonate. The solubility product of CaCO_3 is drastically reduced and CaCO_3 is precipitated in the mixing zones of an alkaline water body and river water, so that it carried heavy metals from solution with it.

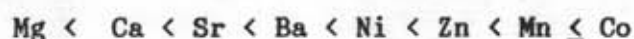
The main sink of phosphates in the ocean and in many lake consists of Fe (III) oxides on the surface of which phosphates become chemisorbed. This kind of chemisorb occurs referably on freshly precipitated ferric and Al hydroxide to a difference extent (Bache, 1963). Sorption of phosphates and polyphosphates onto clay minerals involves chemical bonding of the anions to positively charged edges of the clays as well as substitution of phosphates for silicates in the clay structure (Van Olphen, 1963); in general high phosphate adsorption by clay is favored by a lower pH (Stumm and Morgan, 1970).

These phosphate minerals during their precipitation will enrich trace element, such as U, Cd and As (McKelvey, 1956). However, little has been investigated as yet of the mechanisms involve the trace metals co-precipitate with these phosphate mineral.

Up to this point it is obvious that each carrier or sink influences the extent of removal of metals from natural water to a difference degree. On the other hand, one can say that metals are preferentially bonded to each phases of sediment. For example the process of cation exchange on organic and inorganic substances has higher affinity for heavy metal ions than alkaline earth and alkali ions, as illustrated by the following affinity series (Förstner and Wittmann, 1981) :



The affinity of the metals for the hydrous Mn-dioxide (MnO_2) surface followed the order :



and that the interaction can be characterized by its pH dependence

(Murray, 1975). Another study sorption of alkali metal ions on Fe oxide surfaces under alkaline conditions showed a series $\text{Li}^+ < \text{Na}^+ < \text{K}^+ \sim \text{Cs}^+$ and a sequence of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{M}^{2+}$ for transition metal ions (Vankataramani, Venkateswarlu and Shankar, 1978).

4. Incorporation in Crystalline Mineral

The presence of a large proportion of trace metals, particularly in the silt and fine-sand fractions of sediments. High proportions of quartz, feldspar, and detrital carbonates tend to have quite the opposite effect on the sedimentary heavy metals budget. This significant proportion of the total sediment bound metals is often represented by metals incorporated within the lattice of detrital minerals. Concentrations reflect the source minerals and may often serve to characterize separate drainage areas. These metals are inert and biologically unavailable.

Heavy metals as major, minor or trace components, frequently in inert lattice, can be transported and deposited in the mineral substances of natural rock debris. The silicate minerals feldspar and quartz usually have very low heavy metal contents.

The distribution of elements in minerals is determined by the physico-chemistry of the source medium (magma, lava, aqueous solution) and by the crystal-chemical factors, i.e., ionic radii, valences and electron configuration. Cu has not a strong tendency to be incorporated in any particular crystal structure of rock-forming minerals, but appears to be enriched more in the earlier counterparts (olivine, pyroxene) of magmatic differentiation series (Boven series) than in the late crystallization products (alkaline feldspar, quartz),

on the other hand, Zn is preferentially incorporated into distinct structural positions of silicate and oxides, where it replaces ferrous Fe (Fe^{2+}) and Mg. Biotites and amphiboles are often very rich in Zn. Some pure Zn minerals exist in both structural forms. Pb in the silicate structures replaces the position of large monovalent or divalent metals, especially potassium (K). This explains the enrichment in both muscovite and alkali feldspar (Wedepohl, 1972, 1974a,b).

Clay minerals, and particularly heavy metals contain significantly higher metal concentrations and frequently exhibit a close relationship to a specific source material of a regional nature (rock, ore dike).

Classification of Metals

In studying the association of metals into different phases of sediment it is recommended that one should choose a representative or representatives of metals in order to reduce the amount of work one can manage.

Choosing a representative or representatives one can pick an element/s based on its behaviour/s and/or characteristic/s in the hydrosphere (Table 4)

Metals react as electron-pair acceptors (Lewis acids) toward electron-pair donors (Lewis bases) in possibly the most important type of chemical reaction, which may be generalized by the equation :



Table 4 Estimation of the relative importance of mechanisms and substance in metal accumulation (after Salomons and Förstner, 1984)

	Detrital minerals, organic residues	Reactive organic matter	Trace metal precipitates, e.g., oxides, carbonates	Iron and manganese oxy-hydroxides	Calcium carbonate, non-apatite phosphates
Incorporation in inert positions, e.g. lattice-bound in crystals	XX			X	
Adsorption = physical sorption	C	X		X	
Chemical sorption and coprecipitation	CC	XX	X	XXX	XX
Precipitation of discrete minerals			XXX		
Complexation flocculation/ aggregation	CC	XXX		CC	C

C, CC: Effective via coatings on other substrates

The resulting species may be termed an ion pair, a metal complex, a coordination compound, or a donor-acceptor complex.

Pearson (1968a, b) has classified, on the grounds of experimental evidence, acceptors and donors into "hard" and "soft" categories to explain differences in the stability of the species AB. As a general rule, hard acceptors prefer to bind to hard donors and soft acceptors prefer to bind to soft donors to form stable compounds. Since this principle serves to systematize a great deal of chemical knowledge and is usually employed to explain various phenomena, an abbreviated list of metal acceptors and ligand donors is included in Table 5. Electron mobility or polarizability and electronegativity are the chief criteria for classification as hard or soft.

A hard acceptor is characterized by low polarizability, low electronegativity, large positive charge density (e.g., high oxidation state and small radius); the converse is true for a soft acceptor.

Table 5 Classification of acceptors and donors (adapted from Pearson, 1968a) R=alkyl or aryl (After Förstner and Wittmann, 1981)

<u>Hard acceptor</u>	<u>Intermediate</u>	<u>Soft acceptor</u>
H^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} ,	Fe^{2+} , Co^{2+} , Ni^{2+} ,	Cu^+ , Ag^+ , Au^+ , Tl^+
Ca^{2+} , Mn^{2+} , Al^{2+} , Cr^{3+} ,	Cu^{2+} , Zn^{2+} , Pb^{2+}	Hg^{2+} , Pd^{2+} , Cd^{2+} ,
Co^{3+} , Fe^{3+} , As^{3+}		Pt^{2+} , Hg^{2+} , CH_3Hg^+
<u>Hard donor</u>	<u>Intermediate</u>	<u>Soft donor</u>
H_2O , OH^- , F^- , Cl^- ,	Br^- , NO_2^- , SO_3^{2-}	SH^- , S^{2-} , RS^- , CN^-
PO_4^{3-} , SO_4^{2-} , CO_3^{2-} ,		SCN^- , CO , R_2S , RSH ,
O^{2-} , RS^-		

Similarly, a hard donor is characterized by low polarizability, but high electronegativity and a high negative charge density, whereas the opposite holds true for a soft donor atom.

Since electron-pair acceptors are broadly classified as acids (Lewis), and electron-pair donors are referred to as base (Lewis), the preferential bonding between hard species in contrast to soft species, has become known as the HSAB principle (hard and soft acids and bases).

The hard acids, for example, Mg^{2+} , Ca^{2+} , Al^{3+} , form strong bonds with the hard bases, e.g., O^{2-} or CO_3^{2-} . Conversely, soft acids, Hg_2^{2+} or Hg^{2+} , or Pb^{2+} prefer soft bases such as As^{2-} . Hard acid-soft base, or soft acid-hard base combinations according to HSAB, do not form strong bonds; their ores will have been leached away by water prior to any ore recovery.

For those transition-metal cations having between 0 and 10d electrons, a reasonably well-established rule for the sequence of complex stability, the Irving and Williams (1948) order, is valid. According to this rule the stability of complexes increases in the series



Therefore, in this study Cr, Zn and Cd are chosen as the representative for hard acceptor, intermediate acceptor and soft acceptor respectively.

The Application of Sequential Leaching Technique in Studying Trace Metals Partitioning in Sediments

The extent of metal association with sediments has been widely studied using sequential extraction techniques (Gupta and Chen, 1975; Malo, 1977; Chester, 1978; Filipek and Owen, 1979; De Groot and Zschuppe, 1981; Chester and Voutsinou, 1981, etc.). With this approach it is possible to determine the extent of each type of bonding which is strongly influenced by the mineralogy of the sediment and the chemical behaviour of metals. Studies of this kind may lead to a better understanding of geochemical relationship between metals and sediment types. It should be stressed, however, that methods presently used in sediment studies are not necessarily suitable to the study of near-shore sediment because the methods used were originally developed for rock and deep-sea sediment.

The conception of sequential leaching method is due to "the solid material can be extractes selectively by using appropriate

reagents. Selection of extraction sequence and chemical reagent are based on chemical reactivities assuming that equilibrium is achieved during the time of contact. As we know that many factors can influence that rate of heterogenous processes, and differences between samples may arise from variatives in physical characteristics, as well as from different distribution patterns between components.

1. Factors Controlling Sequential Extraction Technique

The extraction sequence should be designed for specificity, to minimize manipulative losses, and to minimize variations in the proportions of ions extracted due to non-uniform or incomplete extraction, pH effect, or readsorption of solubilized ions. The followings strongly influence the success of every sequential leaching method.

1.1 Disaggregation

Ultrasonic is one of the method use to disaggregate and disrupt the sediment (Edwards and Bremner, 1967; Watson, 1971; Genrich and Bremner, 1972). However, the extent of disaggregation by probes is depend on energy output and treatment time (Watson, 1971; North, 1976). Robbins, Lyle and Heath (1984) concluded that the relatively dispersed nature of surficial deep-sea sediments augmented by the disaggregating effect of freze-drying obviated the need for intensive disaggregation. Microwave oven has been recently recommended as well (Mchan, Foderaro, Garza, Martinez, Maroney, Trivisonno and Willging, 1987), because it can provide heating at the same time as dispersing

1.2 Mixing of Sample and Leach

Differences in extraction rates due to the thoroughness and rate of mixing of sample and leachate have been reported for sediment extractions with $\text{NH}_2\text{OH}\cdot\text{HCl}-\text{HNO}_3$ (Chao, 1972) and for soils extraction with DTPA (Soultanpour, Khan and Lindsay, 1976). Vortex mixing provides very rapid, uniform mixing of the extracting solution with the sediment, little abrasion of particles, and avoids problems with container shape or the type and speed of the shaker. To disaggregate particles and dislodge coatings and grains, samples are dispersed in an ultrasonic bath following with vortex mixing. This treatment increases reaction rates between extractant and the susceptible sedimentary fraction, thereby ensuring complete extraction. In the case of organic matter, for example, ultrasonic treatment (using a probe) has been shown to increase the efficiency of extraction through the partial separation of humic substances (Felbeck, 1959; Edwards and Bremner, 1967; Kyuma, Hussain and Kawaguchi, 1969; Hinds and Lowe, 1980).

Saly (1967) found that 4-5 min. of ultrasonic bath dispersion has been used successfully for particle dispersion, providing that the temperature rise of the transducer must be kept to a minimum. The depth of immersion of the container tube in the water should be deep enough to ensure reproducibility (Pritchard, 1974).

1.3 Buffering Reactant Solution

Reactions of extractant and sample often result in the release or consumption of H_3O^+ ions. The resultant changes in the pH of the sediment/extractant system can profoundly affect the

concentration of elements extracted (Lindsay, 1979). To minimize effects due to differences in the final pH of the various sediment/extract systems, all extractants used in the procedure should have high capacities and intensities. Therefore, the buffering capacity of such reagent like of the HOAc-NaOAc extractant solution must be sufficient for the first repetitive extract to dissolve all the CaCO_3 in 0.5 g of a carbonate-rich sample that contain 68% CaCO_3 , resulting in a final pH of 5.5. Similarly, the first repetitive $\text{NH}_2\text{OH}\cdot\text{HCl}$ -Na-citrate extract of 0.5 g of nodule material containing 44% Mn as MnO_2 produced a pH increase from 5.0 to only 5.2.

1.4 Readsorption

A metal-spiked extractant can lose some of the metal to the sediment via adsorption (Rendell, Batley and Cameron, 1980). This phenomenon could result in underestimation of the metals released from solid phases and could contribute to "downstream" errors when a succession of extractions is carried out. To minimize such readsorption errors during extractions, repetitive extraction is recommended (Robbins et al., 1984). The concentration of reactants in each extract must be high enough to ensure theoretically complete reaction with the component of interest within the first two repetitive extractions.

1.5 Temperature and Time

Temperature should be adjusted for each reactant because of the differences in its extraction rate. By means of the new technique in using microwave (Mahan et al., 1987) more time can be saved than using conventional heating.

1.6 Extraction Sequence

The extraction sequence is usually designed to minimize cross contamination of one phase with another and should reduce effect of one reactant on any phases. It is commonly found that carbonates fractions must be extracted prior to the removal of the metal from another component in order to avoid dispersion of fine clay-size carbonate particles into the another fraction.

1.7 Chemical Reactivity and Kinetic Effects

If the extraction is to be succeeded the chemical equilibrium must be during the time of contact between sediment and extractant. Normally, the use of controlled experimental conditions hopefully ensures that in comparison studies reaction proceed to the same extent so that observed variations are attributable to composition effects rather than through kinetic effect. Theoretically, if equilibrium has been reached, further extraction with the same reagent will either retrieve no more of the species sought or it will release a fairly constant fraction of the residual sample component to each successive volume of extractant. Therefore, the time of shaking must be sufficient to ensure achievement of an equilibrium stage in the chemical interaction of interest.

Type of extractant normally chosen for sequential leaching study can be grouped as follows:

1.7.1 Acids

Extraction of a sediment with cold, non-oxidizing acid solution should, in theory, release exchangeable adsorbed

cations (particularly from sites having a high affinity for protons), reverse reactions involving proton transfer (e.g., promote dissociation of metal-humate complexes), dissolve disordered or non-aged hydroxy species and carbonate minerals, partially dissolve some silicate minerals and minor sample components, and precipitate some sparingly soluble species (e.g., humic acid).

The use of weaker acid (e.g., acetic) should ensure minimum attack on crystalline components, but at the same time, dissolution of dissolved hydrous oxides may also become partial and both clays and humic acids can retain measurable amounts of metal ions at pH ~3. The recovery levels can be increased by the use of ammonium oxalate, an acidic electrolyte solution, adjusted to pH 3.2 which can minimize the amount of metals retaining on both clays and humic acids at pH <4 (Beveridge and Pickering, 1980; Farrah and Pickering, 1976a, b)

1.7.2 Electrolyte Solutions

Salt solutions (e.g., of K^+ , Na^+ , Ca^{2+} , NH_4^+) of concentrations of 0.1-1.0 M should promote displacement of other cations from accessible exchange sites and weakly bonding adsorption sites. Having no buffer capacity, the extractant solutions tend to adopt the pH of the sediment suspension, and in some cases its pH is lowered. This may cause the exchange capacity to vary since the exchange capacity varies with the pH used and displacing ion selected.

1.7.3 Synthetic Chelating Agents

Conversion of cations into stable anionic

complexes of cations into stable anionic complexes or chelates should also promote their release from many components of sediments. Chelating solutions possess the ability to dissolve some sparingly soluble solids, but the rate of attack varies markedly with the degree of crystallinity or "aging" time, particle size to solid, nature of the chemical compounds, pH and concentration of the reagent, and effective stability of the chelate all serve to control the extent of such dissolution processes. For example, EDTA and DPTA have been widely used as extractants, due in large part to their ability to form very stable, water-soluble complexes with a wide range of polyvalent cations. The amount extracted is a comparative measure of the sum of exchangeable and displaceable absorbate plus organically bound.

2. Selective Release of Fractions Bound in Different Modes or Associated with Specific Sediment Components

The grouping used in describing the distribution patterns are somewhat arbitrary. Commonly considered fractions appear to be the ion exchange, the weakly adsorbed, organic-bound, hydrous oxide, and lattice component material. Views differ on the type of reagent required for the release of specific types of fraction.

2.1 Exchangeable Fraction

This fraction is easily exchange with environment, and is generally the result of cation exchange and often metals are defined as loosely sorped to many of the mineral phases, both organic and inorganic, of sediment. By far, this is believed to be the most biological available fraction in normal aerobic environments.

This fraction, may be subdivided into the water soluble fraction and exchangeable fraction. Soluble cations, that are dissolved in the porewaters in sediments, are extracted by rinsing sediments with polar or non-polar solvents which causes a major loss of exchangeable cations (Gupta and Chen, 1975; Polemio and Rhodes, 1977; Neal, 1977; Sayles and Mangelsdorf, 1977; Förstner and Patchineelum, 1980).

Table 6 summarizes the various kinds of extractants employed for extracting metal ions from exchangeable fraction.

Table 6 Some examples of extractants used to release metal ions from exchangeable fraction.

<u>Reagent</u>	<u>References</u>
1 M NH_4OAc , pH 7	Peech et al., 1947; Jenne, 1968; Gibbs, 1973; Ackermann, et al., 1979; Förstner & Wittmann, 1981 Förstner et al., 1981; Förstner & Calmano, 1982; Gibson & Farmer, 1983
1 N NH_4OAc (at ambient sediment pH under oxygen free conditions)	Engler et al., 1977; Adams et al., 1980
1 M NH_4OAc (deaerated), pH 2	Gupta & Chen, 1975
5 M NH_4Cl , pH 8	White, 1957; Zaytseva, 1958, 1962
1 M HCl	Stanton & Burger, 1966
0.05 M CaCl_2	Mclaren & Crawford, 1973

Table 6 (cont.)

<u>Reagent</u>	<u>References</u>
0.2 M BaCl ₂ -thiethanolamine, pH 8.1	Patchineelum, 1975; Forstner & Patchineelum, 1980
1 M BaCl ₂	Meguellate et al., 1983
0.5 M MgCl ₂	Eisenreich et al., 1980
1 M MgCl ₂	Martens, 1968; Stewart & Berger, 1965; Gibbs, 1973; Shuman et al., 1978; Shuman, 1979;
LiCl-LiOAc, pH 8.2	Yaalon, et al., 1962
ethanolic LiCl-CoCl	Neal, 1977
ethanolic NaOAc-NaCl, pH 8.2	Polemio & Rhoades, 1977
NaOAc, pH 8.2	Bascomb, 1968

Displacement of exchangeable cations by NH₄Cl (White, 1957; Zaytseva, 1958, 1962) or by NH₄OAc (Peech et al., 1947; Ackermann, Bergmann and Schleichert, 1979) causes considerable dissolution of CaSO₄ (Rhodes and Krueger, 1968), CaCO₃ (Papanicolaou, 1976), BaCO₃, BaSO₄ (Okasaki et al., 1962), and Mg as carbonates and sulfates. Neutral NH₄OAc causes dissolution of Mn-oxyhydroxides (Jenne, 1968) and metal oxide coatings in general (Gibbs, 1973). Rhodes and Krueger (1968) reported that NH₄⁺ can cause excessive cation extraction from zeolitic and feldspathoid-type minerals. The use of ammonium salts was also affect the dissolution of organic matter via the formation of ammoniated organic matter complexes

(Frink, 1964).

Some dissolution of CaCO_3 was occurred when using BaCl_2 . MgCl_2 can be used instead BaCl_2 ; however, BaCl_2 or MgCl_2 concentration should be optimized (Meguellate et al., 1983). 1 M MgCl_2 reagent was preferred (Gibbs, 1973) over NH_4OAc (ammonium acetate) for the determination of exchangeable Mn and Cu, because the acetate appear to dissolve some hydrous oxide coatings.

Attempts to displace cations from exchange sites with LiCl-LiOAc , pH 8.2 which (Yaalon, Van Schuylenborgh and Slager, 1962) had only been partially successful (Papanicalaou, 1976). Ethanolic LiCl-CoCl can produce complete exchange, but results in carbonate dissolution (Neal, 1977). Bascomb (1964) reported little dissolution of CaCO_3 caused by using NaOAc (pH 8.2). Nonetheless, Rhodes and Krueger (1968) have shown that this extractant can dissolve structural cations from silicates. Polemio and Rhoades (1977) proposed the use of ethanolic NaOAc-NaCl , pH 8.2 to remove exchangeable cations concede that NaOAc may not completely saturate exchange sites in competition with di- and tri-valent cations. Bower (1950) found NaOAc extractant can release interlayer cations in 2:1 layer silicates into solution, in contrast to NH_4^+ which collapses the edges of 2:1 layer silicates, especially vermiculite.

Patchineelum (1975) chosed to use 0.2 M BaCl_2 -thiethanolamine solution, pH 8.1 because of its chelating effect and formation of metal-chloro-complexes, which are dissolved in the solution.

From the review it is noted that there is still no extractant that is specific enough to give a meaningful and realistic result. In addition, as mentioned earlier that this fraction is susceptible to handling and preparation, thus in this study, this fraction will be extracted along with carbonate fraction.

2.2 Carbonate Sorbed Fraction

Co-precipitation of metals with carbonate is effectively immobilized the metals with respect to biological availability. However, pH changes in the water may cause dissolution of the carbonate phase and results in metal remobilization. For the examples of extractants see Table 7.

Table 7 Some examples of extractants used to release metal ions from carbonate fraction (precipitated or co-precipitated on carbonate)

<u>Reagent</u>	<u>References</u>
acidic cation exchanger or buffered	Förstner & Wittmann, 1981
1 M NaOAc solution, pH 5	Ackermann et al., 1979
acidic cation exchange resin	Lloyd, 1954; Deurer et al., 1978; Patchineelum, 1975; Förstner & Patchineelum, 1980
0.4 M HOAc	McLaren & Crawford, 1973
1 M HOAc*	Gupta & Chen, 1975
1 M NaOAc-HOAc, pH 5	Jackson, 1956; Tesseir et al., 1979;

Table 7 (cont.)

<u>Reagent</u>	<u>References</u>
1 M NaOAc-HOAc, pH 5 (cont.)	Förstner et al., 1981; Förstner & Calmano, 1982; Gibson & Farmer, 1983 Robbins et al., 1984
1 M HOAc + 0.6 M NaOAc 35 ml, 5 hrs	Meguellite et al., 1983
CO ₂ -treatment of suspension	Patchineelum, 1975
* remove some Fe & Mn oxides)	

Adsorption of trace metals onto Fe oxyhydroxides increases abruptly at pH values >5.0 (Gadde and Laitinen, 1974; Forbes, Posner and Quirk, 1976; Davis and Leckie, 1978; Benjamin and Leckie, 1981). So that pH 5 HOAc should desorb these "specifically bound" cations. For Mn oxyhydroxides the adsorption edge (the point where metal ion sorption rapidly increases) occurs at pH <5.0 (Gadde and Laitinen, 1974). Thus, the HOAc-NaOAc treatment may remove proportionally less specifically bound metals from Mn oxyhydroxides. For minimize the effect, several successive extraction of each samples should be used (Robbins et al., 1984).

HOAc buffered at pH 5 with NaOAc (Jackson, 1956; Tessier et al., 1979; Förstner et al., 1981, etc.) is capable dissolving carbonates because of its effectiveness and minimal impact on other phases. The use of strong inorganic or unbuffered weak organic acids is not suitable due to the vulnerability of silicate, particularly iron-rich phyllosilicates and zeolites (Rich, 1968), to dissolve at low pH (Coleman and Harward, 1953; Low, 1955; Aldrich and

Buchanan, 1958). Robbins et al. (1984) found only 0.38% of the total Al and 0.4% of the total Si were dissolved by using HOAc-NaOAc in the study of phillisite. While the acid intensity at pH 5.0 is low, so the capacity is sufficient to cause complete dissolution of CaCO_3 within a short period of time. Dolomite, which is not detectable in most marine samples, has been considered resistant to HOAc attack (Ray, Gault and Dodd, 1957; Emiliani, 1955; Copeland, 1970; Horder, 1979, etc.), but Tessier et al. (1979) reported that HOAc-NaOAc, pH 5, causes the disappearance of dolomite XRD peaks in sediment samples. This is consistent with Chester and Hughes (1967) finding that $\text{NH}_2\text{OH}\cdot\text{HCl} + \text{HOAc}$ treatment caused 40% dissolution of dolomite.

However, the use of pH 5.0 NaOAc-HOAc extractant may be able to dissolve minimal amounts of sulfide and organic matter from sediments (Tessier et al., 1979). The NaOAc-HOAc treatment are found to extract virtually all (>99.9%) of the total CaCO_3 -bound Ca in carbonate-rich sediments (Robbins et al., 1984). This means that this reagent is effective enough to extract most of the metals bound in the carbonate fraction with less effect to the lattice held. Lyle et al. (1984) found a small portion of the total Fe, Mn, Cu, Ni and Zn was extracted from all samples during HOAc-NaOAc treatment. The variable metal to carbonate ratio suggests that such metals are sorbed to clays, not contained in the carbonates.

Robbins et al. (1984) found 1.0 N NaOAc concentration can completely dissolve the $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (which was dissolved during freeze-drying depends on the ionic strength of univalent Na-salts (Nakayama, 1971) from marine sediments). Grossman and Millet (1961) reported that organic carbon and free Fe concentrations in non

calcareous soil samples were unchanged after contact with this buffer for 9 weeks, but Nissenbaum (1972), Gupta and Chen (1975) and McLaren and Crawford (1973) found lower pH values lead to a partial attack of Fe and Mn oxides. In summary, pH 5 HOAc leach is capable of separating carbonate-bound, sea salt, exchangeable, and sorbed cations from sedimentary particles.

The time required for extraction of this fraction will depend upon such factors as particle size, percentage and type of carbonate present, and sample size (Kunze, 1965); however, for coarse bottom sediments with high carbonate content, longer leaching times and frequent pH adjustment might be necessary.

2.3 Organic Bound Fraction

This fraction is extremely important as a result of the formation of organo-metal complexes. Early decomposition processes may result in the release of such metals to the water or, by ingestion, directly to benthic organisms. After decomposition and mineralization of the organic matters have been completed, metals associated with this fraction may be considered as non-available.

The metal fraction associated with organic matter can be extracted through oxidation of this component with NaOCl or H₂O₂, by dissolving the segment using Na₄P₂O₇, through proton displacement (with 0.5 M HCl); by chemical competition (e.g., using 0.05 N EDTA) (Pickering, 1981) or through the using of surfactant to disperse the sediment (e.g., Sodium dodesyl sulphate, SDS) (Robbins et al., 1984).

The summary of extraction techniques for this fraction is shown in Table 8.

Table 8 Some examples of extractants used to release metal ions from organic fraction (complexation with organic matter).

<u>Reagent</u>	<u>References</u>
acidified 30% H ₂ O ₂ follow with 1 M NH ₄ OAc	Jackson, 1958; Chester & Hughes, 1967; Nissebaum, 1972; Engler et al., 1977; Gupta & Chen, 1975 Salomons & DeGroot, 1978; Filipek & Owen, 1979; Ackermann et al., 1979 Adams et al., 1980 Förstner & Wittmann, 1981; Förstner & Calmano, 1982 Meguellate et al., 1983
30% H ₂ O ₂ heat; evap out then dilute with 5% HCl*	Chester & Hughes, 1967; Presley et al., 1972; Ghobary & Latouche, 1981
a) 0.1 M NaOH for humates and fulvates	\ Förstner & Patchineelum,
b) 30% H ₂ O ₂ + 1 N NH ₄ OAc for organic residue and sulfide	1980 /
H ₂ O ₂	Shuman et al., 1978 Gibson & Farmer, 1983

* not suitable for near shore sediment because of high organic matter (Chester, 1978)

Table 8 (cont.)

<u>Reagent</u>	<u>References</u>
EDTA	Pickering, 1981
HCl	Pickering, 1981
0.1 M NaOH	Bucket & Metche, 1972; Patchineelum, 1975
0.4 N Napyrophosphate ($\text{Na}_2\text{P}_2\text{O}_7$)	Eisenreich et al., 1980
SDS, Na_2CO_3	Robbins et al., 1984
Organic solvents	Cooper & Harris, 1974
0.1 M NaOH/ H_2SO_4	Volkov & Fomina, 1974

Surfactants could be used in high-pH leaches as dispersant. Surfactants are especially effective dispersant where a substantial fraction of the component of interest is located at the phase boundary. The buffered surfactant solution is more suitable because most of the organic matter extracted by this extractant is largely fulvic acid rather than humic acid which can be flocculated by electrolytes (Evans, 1959). Both fulvic and humic acid have very high surface area in which surfactants will be adsorb to and disperse them (Robbins et al., 1984). The fulvic acid fraction is considered to be responsible for binding most organically complexed metals (Schnitzer and Desjardins, 1969). The buffered solution with high ionic strength will also help to flocculate clays and oxyhydroxides dispersed by the extractant (surfactant) (Ford, Greenland and Oades, 1969), thus helping to prevent cross contamination from these fractions.

Among the surfactant used SDS (gel electrophoresis grade) is considered to be better than iso-octyl ethoxylate (Triton

X-100), alcohol ethoxysulphate (Neodol 25-35) and alcohol ethoxylate (Neodol 25-12), because of its availability in pure form and its ease of handling. However, the buffered surfactant solution having a basic pH with Na salts is recommended (Evans, 1959; Schnitzer and Skinner, 1967 and Robbins et al., 1984).

H_2O_2 is also one of the popular extractant because its effectiveness in breaking down organic material. However, it needs to be acidified in order to prevent the scavenging of metals ions by Fe(III) hydroxy precipitate formed at higher pH value. Because under mildly acidic conditions, H_2O_2 effectively solubilized Mn oxides and their occluded elements (Jenne, 1968) making the results of earlier studies to be overestimated (Engler et al., 1977; Gupta and Chen, 1975). In any case, pH-controls of the extracts after treatment are the pre-requisite to obtain comparable results. In addition, the use of acidified H_2O_2 is found to have the following disadvantages :

a) H_2O_2 does not destroy the refractory organic matter in samples (Martin, 1954; Jackson, 1958; Harada and Inako, 1977);

b) Sedimentary sulfides were oxidized to varying degree (Jackson, 1958);

c) It is catalytically decomposed (often violently) by MnO_2 (Jenne, 1968; Canadian Society of Soil Science, 1978), with a resultant suppression of organic matter oxidation;

d) Brown (1953) and Martin (1954) found it related to from oxalic acid leading to the precipitation of insoluble Ca-oxalate, while the dissolution of oxyhydroxides was found by Farmer and Mitchell (1963) and Jenne (1968);

e) Poorly buffered, organic-rich (Douglas and Fiessinger, 1971) or sulfide-rich (Van Breeman, 1973) sediments become very acidic when treated with H_2O_2 , leading to dissolution of silicates (Presley et al., 1972; Langeveld, Van der Gaast, and Eisma, 1978; Tessier et al., 1979, 1982) and

f) Metals release by H_2O_2 treatment are susceptible to scavenging by Mn oxyhydroxides in the sediment (Guy, Chakrabarti, and McBain, 1978).

Therefore, if one want to use acidified H_2O_2 , one must employ it after the extraction of hydroside fraction.

Using EDTA and HCl will release metal ions associated with both organic and oxide phase (Pickering, 1981), and this has led to these being used as extractants for the evaluation of the total non-detrital fraction.

NaOH has also been used to extract metal-organic complexes (Bucket and Metche, 1972). The NaOH disperses organic in the pH buffer system.

More efficient methods for destroying organic matter do exist (e.g., conc. HNO_3 used separately or in combination with HCl or $HClO_4$), but they usually suffer from a lack of specificity in the sense that they may also effect a partial attack of silicate lattice (Tessier et al., 1979).

2.4 Reducible Fraction

For the reducible fraction, so called oxyhydroxide bound fraction, in marine sediments consists primarily of poorly

crystalline material, but can contain more crystalline Fe oxides such as goethite and detrital magnetite. These crystalline oxides, which are more resistant to extraction than non-crystalline oxyhydroxides, are uncommon in most surface sediments in the pelagic environment. An extractant for this fraction should not attack silicates.

Ferro-manganese oxyhydroxides are relatively easy to extract, but the fine-grained silicate fraction contained easily degradable authigenic minerals. The susceptibility of such silicates to attack by potential oxyhydroxides extractants played a major role in the final choice of an extractant.

Some works subdivided this fraction into another sub 3 subfractions. The summary are shown in Table 9. The co-precipitation of metals with hydrated oxides of Fe and Mn is well known, these oxides provide sorption site for metals, some of which, may be removed in the easily exchangeable fraction. This fraction may be very significant for many metals and is generally considered non-available under aerobic conditions. Under anaerobic condition the resulting reduction of the Fe and Mn oxides, may cause solubilization of the associated metals. However, under some conditions these can become linked with another fraction of the sediment (e.g., to a sulphide phases).

Table 9 Some examples of extractants used to release metal ions from reducible fraction (or oxyhydroxide fraction).

<u>Reagent</u>	<u>References</u>
(a) Easily reducible phase (mainly Mn oxides)	
0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.01 M HNO_3 , pH 2*	Jackson, 1958; Chao, 1972; Gupta & Chen, 1975; Salomons & De Groot, 1978; Ackermann et al., 1979; Adams et al., 1980; Förstner & Patchineelum, 1980; Förstner & Wittmann, 1981; Förstner & Calmano, 1982; Gibson & Farmer, 1983
* extract Mn oxides and partly amorphous Fe oxyhydrates (Gupta and Chen, 1975; Chao, 1972; Förstner et al., 1981; Förstner and Calmano, 1982)	
(b) Moderately reducible phase	
0.2 M ammonium oxalate + 0.2 M oxalic acids, pH 3*	Schwertmann, 1964; Ackermann et al., 1979; Förstner & Wittmann, 1981; Förstner et al., 1981; Förstner & Calmano, 1982
1 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 25% HOAc	Förstner & Patchineelum, 1980; Gibson & Farmer, 1983
* amorphous and poorly crystalized Fe oxyhydrates	

Table 9 (cont.)

<u>Reagent</u>	<u>References</u>
(c) Non silicate iron phase	
Na-dithionite-citrate	Holmgren, 1967; Anderson & Jenne, 1970; Shuman et al., 1978; Tessier et al., 1979; Ackermann et al., 1979 Förstner & Wittmann, 1981;
oxalate buffer reagent	Schwertmann, 1964; Health & Dymond, 1977
1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 25% HOAc	Chester & Hughes, 1967;

Acid ammonium oxalate is commonly used as an alternative to $\text{Na}_2\text{S}_2\text{O}_4$ for the dissolution of ferro-manganese oxyhydroxides (Tamm, 1922; Deb, 1950; Schwertmann, 1959, 1964; DeEndredy, 1963; Segalen, 1970). Landa and Gast (1973) reported that this solution dissolves oxyhydroxides without attacking silicates or crystalline goethite to any great degree. Even Health and Dymond (1977) found it to be slightly more specific for oxyhydroxides than acidified hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), but analytical problems occur because insoluble Ca and Ba oxalate precipitates are formed (Brown, 1953; Martin, 1954; Taylor, 1964).

Sodium dithionite-citrate buffer system ($\text{Na}_2\text{S}_2\text{O}_4$ -Na-citrate- NaHCO_3 , pH 7.3), developed by Mehra and Jackson (1960), is most commonly used by clay mineralogists for dissolving both

crystalline and amorphous oxyhydroxides, but not suitable for use with pelagic sediments because it attacks Fe-rich layer silicates (Coffin, 1963) particularly fine-grained authigenic nontronite (Robbins et al., 1984). $\text{Na}_2\text{S}_2\text{O}_4$ tends to be contaminated with Zn (Shuman, 1982; Tessier et al., 1979) and the extractant solution can readily lose metals by precipitation of metal sulfides (Shuman, 1982).

Tessier et al. (1979), using concentration prescribed by Anderson and Jenne (1970), found substantial precipitation of trace metals, presumably due to the formation of sulfide as result of the disproportionation of dithionite. Gupta and Chen (1975) reported the consistently lower leachates by dithionite-citrate than in those with $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-HOAc}$; the differences were greatest for those trace metals which form the most insoluble sulfide salts.

Furthermore, several additional problems are raised by the utilization of the dithionite-citrate couple (Tessier et al., 1979): (i) dithionite is highly contaminated with Zn and its purification by a chelation-extraction procedure proves difficult (Brannon et al., 1977), (ii) frequent clogging of the burner is observed upon analysis of the aqueous extracts by flame atomic absorption spectrophotometry; due to the high salt content of the extraction solution; to minimize this problem, a chelation-extraction step is required before analysis (Jenne, Ball and Simpson, 1974). The acidified $\text{NH}_2\text{OH}\cdot\text{HCl}$ buffer can differentially reduce Mn-oxyhydroxide, while reduction of Mn oxide may require more time to complete this dissolution.

Chao (1972) and Shuman (1982) concluded that $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-HNO}_3$ was almost efficient as other reducing acids in dissolving Mn while removing little Fe. Increasing the $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration in extract solutions from 0.1 M to 1.0 M results in the extraction of more Fe (Chester and Hughes, 1967; Chao, 1972). Frampton and Reisenauer (1978) found that the greater effectiveness of $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-HOAc}$ over $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-HNO}_3$ in extracting Fe to the 10 times higher concentration of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in the former extractant.

The acid pH of $\text{NH}_2\text{OH}\cdot\text{HCl}$ -acid extractant is capable of dissolving calcite and partially dolomite, but does not dissolve amphiboles, apatite, barite, celestite, feldspars, glauconites, micas, pyroxenes, zeolite or zircon (Chao, 1972). The $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-HOAc}$ treatment also extracts low levels of Si from opal (Chester and Hughes, 1967), Al and Si from river sediments (Tessier et al., 1979), and Al from soils (Shuman, 1982), possibly due to the low pH (approximately 1.5) of the solution. So the increasing of the Fe-oxyhydroxide dissolution capacity of $\text{NH}_2\text{OH}\cdot\text{HCl}$ -based extractants by reducing the pH only enhances the dissolution of Fe-rich layer silicates. For all the reasons above, the low pH extractants should be reject for extracts this fraction.

The $\text{NH}_2\text{OH}\cdot\text{HCl}$ buffer with Na-citrate is considered by many workers to be more suitable than $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-acetate}$ because of its capability in removing a well-defined, reproducible Fe-oxyhydroxide fraction from most samples and all the Mn from nodules and oxic sediments (Tessier et al., 1979; Bowers et al., 1980; Robbins et al., 1984).

The use of citrate has advantaged of preventing acid attack on aluminosilicate, minimizing the readsorption of metal released by the extraction process, enhancing the dissolution of amorphous and poorly crystalline Fe-oxyhydroxide, minimizing the formation of the insoluble oxalate precipitate and if added in the form of Na salts will provide ionization suppression properties in AAS (Canney and Nowlan, 1964; Whitney, 1981; Robbins et al., 1984). The best concentration of this extractant is 1.0 N at pH 5.0 (Bowers et al., 1980).

2.5 Residual Fraction

Once the first several fractions have been removed, the residual solid should be mainly primary and secondary minerals, which hold trace metals within their crystal structure. Concentration reflects the source materials and may often serve to characterize separate drainage areas. These metals are inert and biologically unavailable or one can say that they are not expected to be released in solution over a reasonable time span under the condition normally encountered in nature. The summary of techniques in dissolving this fraction is shown in Table 10.

This fraction contains metals which are held in the lattice sediment and chemical resistant. Its concentration should provide the background level of metals in such sediment before it comes into contact with other environment. The method used in this fraction would be the same as in total digestion.

Table 10 Some examples of extractants used to release metal ions from residual fraction.

<u>Reagent</u>	<u>References</u>
Neutron Activation (NAA)	Shuman et al., 1978
HF-HClO ₄	Salomons & DeGroot, 1978; Förstner & Patchineelum, 1980; Förstner & Wittmann, 1981
HF-HNO ₃ -HCl	Bernas, 1968; Dolezel et al., 1969; Price & Whiteside, 1977
HF-HNO ₃ -fuming HNO ₃ , 95°C	Smith & Windom, 1972; Engler et al., 1977; Adam et al., 1980
HF-HNO ₃ -HClO ₄	Agemian & Chau, 1975, 1976; Gupta & Chen, 1975; Filipek & Owen, 1979; Meguellate et al., 1983
DDW-HCl-HNO ₃ -HF-HClO ₄	Sturgeon et al., 1982
HF-HClO ₄ -HCl	Chester & Hughes, 1967; Presley et al., 1972; Grobary & Latouche, 1981
conc. HNO ₃ 120°C	Förstner et al., 1981; Förstner & Calmano, 1982
Aqua regia-HF-Boric acid	Gibson & Farmer, 1983
HNO ₃ -H ₂ SO ₄ -HClO ₄	Scott & Thomas, 1977

Complete dissolution of the residual fraction requires vigorous digestion with strong acids or combination of strong acids. Sometimes the solubilization action is preceded by fusion of the sediment (e.g., Pratt and Bradford, 1958; Gibbs, 1973; Sulcek, Povondra and Dolozel, 1977). HF, in most cases in combination with one or more others acids or treatments, is always involved. The teflon bomb technique is recommended because of its advantages of working in a closed system and also in speeding up the digestion (Loring and Rantala, 1977).

The differences in the relative abundances of heavy metals in the crystal lattices of the individual minerals may result in different amount of metals solubilized by different digestion procedures, therefore, one must chose the digestion procedure that will bring a complete destruction of metalliferous minerals in sediments.

The use of HF-HNO₃-HCl(or HClO₄) in conjunction with the bomb digestion procedure is considered to be the digestion technique that gives the strongest attck on the metalliferous minerals (Bernas, 1968; Dolezel, Lenz, and Sulcek, 1969; Price and Whiteside, 1977; Gupta and Chen, 1975; Agemian and Chau, 1975, 1976).

In summary each type of extractant is not really perfect because it tends to underextract or overextract metals from the fraction of interest. Pickering (1981) has summarized the reactivity for each type of extractant ever employed inwhich it will give the reader an overall picture (Figure 5).

EXTRACTANT TYPE	RETENTION MODE						
	Ion Exchange Sites	Surface adsorption	Precipitated (CO ₃ , S, OH)	Co-ppptd. amorphous hydrates oxides)	Co-ordinated to organics	Occluded (crystalline hydrates oxides)	Lattice component (mineral)
Electrolyte	MgCl ₂						
Acetic Acid (buffer) (reducing)	HOAc	HOAc/OAc ⁻					
	HOAc + NH ₂ OH						
Oxalic Acid (buffer) dil. Acid (cold)	HOx + NH ₄ Ox					Light (UV)	
		0.4 M	HCl				
Acid (hot) Mixtures (+HF)	HCl + HNO ₃		HNO ₃ + HClO ₄				
		HCl + HNO ₃		HF			
Chelating Agents	EDTA	DTPA					
	Na ₄ P ₂ O ₇						
	Na ₄ P ₂ O ₇ + Na ₂ S ₂ O ₇						
	Na ₂ S ₂ O ₇ + citrate		HCO ₃ ⁻ (alk. ppt)		NaOH		
Basic Solns.					NaF		
Fusion (+ Acid leach)		Na ₂ CO ₃					

Figure 5 Schematic representation of the ability of different extractant solutions to release metal ions retained in different modes or associated with specific sediment fractions (dashed segments indicate areas of uncertainty) (after Pickering, 1981).

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