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The Chemical Behavior of Heavy Metals at the Water-Sediment Interface of Selected Streams in Maine Based on Ternary Partitioning Diagrams

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Dale Henry Rezabek

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THE CHEMICAL BEHAVIOR OF HEAVY METALS AT THE WATER-SEDIMENT INTERFACE OF SELECTED STREAMS IN MAINE BASED ON TERNARY PARTITIONING DIAGRAMS

By

Dale Henry Rezabek

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

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ABSTRACT

THE CHEMICAL BEHAVIOR OF HEAVY METALS AT THE WATER-SEDIMENT INTERFACE OF SELECTED STREAMS IN MAINE BASED ON TERNARY PARTITIONING DIAGRAMS

By

Dale H. Rezabek

The many chemical and physical controls on heavy metal activities in natural aqueous systems have impeded the development of a quantitative model for predicting metal behavior. This research studies the partitioning of metals in stream sediment adsorbents to determine if systematic trends in metal adsorption behavior are reproducible and consistent with adsorption theory and experimental results. The techniques used are: sequential selective chemical extractions, normalization to equal adsorbent concentrations, and the plotting of data on ternary diagrams. The results show: 1) unique fields of metal behavior can be depicted on the ternary diagrams, 2) the distributions of naturally-added metals are consistent with those of anthropogenically-added metals and with the results of adsorption studies, 3) the absolute abundances of adsorbing phases are apparently not as important as relative abundances in controlling metal partitioning, and 4) these techniques do not quantify the data sufficiently to be used alone in predicting metal behaviors.

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CHAPTER ONE

Introduction

This study examines whether there are systematic trends in metal adsorption on sediments in natural aqueous systems. The purpose of this type of research is to develop a model for making predictions of metal behaviors in exogenic systems.

The Problem

At the water-sediment interface, trace metals are controlled by kinetic and thermodynamic components of precipitation-dissolution, oxidation-reduction, and adsorption-desorption reactions (Stumm and Morgan, 1981). The chemical speciations of dissolved metals to predict precipitation-dissolution reactions have been interpreted successfully with the development of thermodynamic models such as WATEQ2 (Ball et al., 1978), EQ3NR (Wolery, 1983), and MINEQL (Westall et al., 1976). Laboratory experimentation has led to the development of models for the adsorption of metals on single substrates under well-defined conditions, which can theoretically predict the adsorption behaviors of metals in simple natural systems (Balistrieri and Murray, 1983; Davis and Leckie, 1978; Gadde and Latinen, 1974; Leckie et al., 1980; Lion et al., 1982). However, natural systems are usually guite complex and have more than one adsorbing substrate. Therefore, integrated models such as MINTEQ (Felmy et al., 1984), which combine precipitationdissolution and adsorption-desorption, are tenuous. At

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present, the fate of a metal at the water-sediment interface can only be described qualitatively.

One way to overcome the present lack of a useful model would be to derive the equilibrium constant for the adsorption of each metal on an adsorbing substrate or phase (Oakley et al., 1981). These constants could then be used to study metal adsorption distributions similar to the way thermodynamic equilibrium constants for precipitationdissolution reactions are used for calculating metal speciation in the chemical modeling programs. However, it may be difficult to use this technique since adsorption is controlled by the system pH, pe, ionic strength, etc., and the constant would need to be adjusted (if possible) for all variables.

Tessier et al. (1985) calculated apparent equilibrium constants for the adsorption of Cd, Cu, Ni, Pb, and Zn onto a natural substrate, iron oxyhydroxide, collected from lake systems in Canada. These results compared favorably with equilibrium constants obtained from simple experimental systems reported by Balistrieri and Murray (1983) and Oakley et al. (1981), and with theories on iron hydroxide adsorption (Leckie et al., 1980). The differences between the calculated constants for certain metals and the results of the experimental systems were interpreted to be caused by variations in the pH's of the systems and the formation of ternary complexes which were not accounted for in the calculations. Clearly, the complexity of natural systems

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necessitates a more comprehensive study of metal behaviors in multi-substrate systems before calculations like those made by Tessier et al. (1985) can be reliably made. This study explores a different approach to the development of a quantitative model for predicting metal adsorption in natural systems, by looking at natural metal behaviors on ternary diagrams after normalizing adsorption data to equal amounts of substrate.

Metal Partitioning in Sediment

Metals added to the sediment from the water (or those metals that can be easily released to solution from the sediment by environmental alterations) are associated with the hydromorphic fraction of the sediment (Gibbs, 1977). This fraction is composed of clay minerals, carbonates, iron and manganese (and other metal) hydroxides, sulfides, and organic matter (Gibbs, 1977). The association of the metals with these chemical phases (or substrates) is by adsorption, coprecipitation, complexing, or ion exchange of the metal with the phase. Non-mobile metals (frequently called the detrital or residual fraction) are found within the lattice structures of clay and silicate minerals (Gupta and Chen, 1975). Table 1 introduces the terminology which will be used throughout this report.

Adsorbed-metal concentrations can be measured to help understand the factors that control metal exchange on hydromorphic phases of the sediment. One method of measuring metal concentrations associated with hydromorphic phases is

Table 1: Terminology for sediment fraction.

Sediment Fraction	Sediment Substrate	Chemical <u>Phase</u>
Hydromorphic	Clay minerals	Exchangeable
	Carbonates,	Acid soluble
	Mn-ov amorphoug	ACIU SUIUDIE
	Fe-ox	Easily Reducible
	Fe-ox	Moderately Reducible
	Organics, sulfides	Oxidizable
Detrital	Silicate minerals	Residual

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to define the sediment substrates in terms of chemically alterable phases. This can be determined in a series of sequential selective, chemical extractions (Luoma and Davis, 1983). A number of studies have utilized sequential selective chemical extractions to determine the partitioning of heavy metals associated with the hydromorphic phases of sediment (Chao, 1972; Malo, 1977; Gatehouse et al., 1977; Tessier et al., 1979). In theory, a specific reagent will attack one chemically-reactive phase and release any bound (adsorbed, coprecipitated, complexed or ion exchangeable) metals into solution. If reagents are applied in a sequence to release metals from the weakest-bonded to strongestbonded of the different phases, they may provide a quantitative method for determining adsorbed metal concentrations from these "operationally defined" phases. Although there can be problems with readsorption of metals during the attacks (Rendell et al., 1980) and limited selectivity of chemical for a phase (Forstner and Patchineelam, 1980), the method of sequential selective, chemical extractions remains an important tool in the development of quantitative models for metal behaviors in sediment-water systems (Luoma and Bryan, 1981).

Phase Concentration Factor

In natural systems, substrates have wide ranges of surface areas. One method of study to overcome this problem of the variable surface areas available for adsorption involves the proportionating of trace metal concentrations

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according to the concentrations of the defined phases (Filipek and Owen, 1979). Calculating the ratio of a metal concentration to a substrate concentration provides information on the competition of substrates to adsorb metals, on competition among different trace metals for binding sites, and for characterizing the chemical and physical processes that control metal partitioning behavior. This would be very difficult using only the total concentrations of adsorbed metals and adsorbing substrates (Nowlan, 1976).

An estimate of the relative importance of the association for a phase with a metal can be made in two ways: 1. by calculating the ratio of a metal concentration with the concentration of the adsorbing substrate (Filipek et al., 1981), or 2. by calculating a phase concentration factor (PCF value) which is a ratio of the percentage of a metal among the phases to the percentage content of a respective phase within a sample (Forstner and Patchineelam, 1980). This can be shown in equation 1:

 $PCF = M/M_{T} \text{ divided by } P/P_{T} \qquad (1)$ where M = concentration of a metal in a phase, M_T = total concentration of the metal in all phases, P = concentration of a phase, and P_T = total concentration of all phases. A high value for the ratio indicates a high association of the metal with the phase.

Carpenter et al. (1978) looked at relative associations of metals with iron oxides and manganese oxides by using a normalization ratio shown in equation 2:

$$(M_{Mn-ox} / M_{Fe-ox})$$
 divided by $(Mn_{Mn-ox} / Fe_{Fe-ox})$ (2)

where M_{Mn-ox} = metal concentration in Mn-oxide extraction, M_{Fe-ox} = metal concentration in Fe-oxide extraction, Mn_{Mn-ox} = Mn concentration in Mn-oxide extraction, and Fe_{Fe-ox} = Fe concentration in Fe-oxide extraction.

Chemical extractions of sediment samples were used to distinguish between metals adsorbed on Mn and Fe oxides. By using this ratio technique, Carpenter et al. (1978) found Fe-oxides had a high association with Zn and Ni, and Mnoxides had a high association with Cu, upstream from a mineralized zone. Downstream from this zone, high associations with Zn and Cu by these oxides were reversed. Pb was associated mostly with Fe-oxides both upstream and downstream from the mineralized zone.

To detect anomalies in metal concentrations among iron and manganese oxides, a number of authors have suggested the use of ratios of metal concentrations to Fe and Mn concentrations (Tessier et al., 1982; Nowlan, 1976; Robinson, 1982). Filipek and Owen (1979) normalized metal concentrations to the weight of sediment dissolved in a given extraction rather than the total sediment weight. This was done to differentiate metal inputs from detrital

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components, which would represent nonmobile forms of metals in the sediment unavailable to the environment.

Luoma and Bryan (1981) used a statistical filtering method for correlation coefficients to investigate competition of substrates for metals and to see if substrate concentrations in the sediment influenced that competition. The filter functioned by isolating substrates with strong correlations with metals. If two substrates (Fe-oxides and Mn-oxides) competed for a metal, the substrate with a low concentration would show higher correlation with the metal. High concentrations of substrates would be filtered out to see, for example, if correlations between Fe and metals improved (meaning that Fe had a higher association with the metal). This study was interesting, but did not utilize sequential extractions, which have been shown to be very important in characterizing metal partitioning by Tessier et al. (1979). Therefore, the results of Luoma and Bryan (1981) cannot be compared to other investigations using chemical extractions.

Past Work by Gephart (1982)

Tessier et al. (1979) developed a technique for releasing metals from the following chemical phases (and speculated on the chemical nature of the phases): exchangeable (weakly adsorbed metals), acid soluble (carbonates), reducible (Fe-Mn-oxides), oxidizable (organic matter and sulfides), and residual (silicates). These

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chemical extractions will be discussed in detail in Chapter Three.

Gephart (1982) modified the procedure developed by Tessier et al. (1979) by splitting the reducible phase into easily and moderately reducible phases. With this procedure Gephart (1982) studied the partitioning behavior of Cr, Pb, Cu, Ni, and Zn adsorbed on the sediments of the Grand River, Lansing, Michigan. The Lansing area is highly populated and industrial. Automobile assembly, metal plating, and tanning operations are major sources of metals to the riverine system. The study concentrated on metal partitioning in sediment substrates; Mn-oxides, Fe-oxides, and organic matter. For most natural, oxic systems these appear to be the most important substrates (Gibbs, 1977). The concentrations of metals associated with other phases (exchangeable, acid soluble, and residual) were measured in order to distinguish them from the concentrations of metals associated with the three most important phases.

Since it is difficult to quantify the concentration of a metal associated with Mn-oxides, Fe-oxides, or organic matter, a more general identification was used (and will be also used in this study) based on the chemical response of the substrates to the chemical extractions; respectively easily reducible (ER), moderately reducible (MR), and oxidizable (OX) phases.

Gephart (1982) used a modification of the PCF to study the partitioning of the metals among the three substrates.

The modification was in the calculation of substrate concentrations, which are estimated from the chemical extractions. For example, ER phase concentration was estimated from the concentrations of Fe (dissolved amorphous Fe-oxides) and Mn (dissolved Mn-oxides) in the extraction solution after the chemical attack. In the report by Gephart (1982), this calculation for ER phases was done incorrectly, with the wrong Mn concentrations used. The corrected PCF values are calculated as percentages and plotted on ternary diagrams (Figure 1). These plots represent the partitioning of the metals relative to the substrates being present in equal concentrations (i.e. these are normalized metal data).

In multi-substrate systems, if the relative masses of the adsorbing substrates alone controlled the partitioning behaviors of metals, then the normalization of partitioning data for a metal to equal amounts of adsorbing substrates present in the systems would be expected to plot as a point on a ternary diagram. Predicting metal partitioning in a natural water-sediment system could then be done by estimating substrate abundances from the results of sequential selective chemical extractions. However, the data for each metal in the study by Gephart (1982) are scattered, and this suggests that the assumption of a one to one change in adsorption as a function of change in the mass of adsorbent is not valid and may not by itself explain why the data is scattered. Other variables such as surface area of adsorbent, solution pH, pe, ionic strength, etc. may cause









Figure 1: A summary of the results of Gephart (1982).

the scatter and need to be considered in modeling the behavior of metals at the water-sediment interface. In addition, this technique of normalizing partitioning data may be in error and needs study.

The normalized partitioning data plot in unique clusters for each metal. For example, in Figure 1, note that the normalized data for Ni, Pb, Zn, and Cu plot in clusters trending away from the ER phase apex. These clusters appear to rotate around the ER apex away from the ER-OX phase boundary in the order Cu < Pb < Ni < Zn, with the Zn data clustering along the ER-MR phase boundary. Four general metal behaviors can be interpreted from the diagrams: 1. Except for Cr each metal plots in a fairly tight cluster, 2. Cu plots in a cluster essentially along the OX-ER phase boundary, 3. Cr plots in a scatter with most of the points clustered near the center of the diagram and some plotting near the ER-MR phase boundary, and 4. Ni, Pb, and Zn cluster in the upper part of the diagram along the ER-MR phase boundary.

The data handling techniques developed by Gephart (1982) (Fig. 1) appear to depict unique metal behaviors, but it is not known if this type of diagram depicts similar behaviors of the metals in all water-sediment environments. That is, if adsorption data are handled in the same way experimentally and numerically, will partitioning patterns of metals on ternary plots such as Figure 1 be the same for various environments? These patterns may be artifacts of
t Ċ t b t i b ₽ i ĪN (01 te gu sy th th Pa sha ada exp abb anthropogenic metal sources. Therefore, this study will examine the application of these techniques in an area with natural additions of metals to streams.

<u>Hypothesis</u>

This research examines whether similar trends as found by Gephart (1982) exist for metal partitioning in the different sediment adsorbents in natural aqueous systems. If this is found to be the case, then metal adsorption behaviors among substrates can be studied by normalization techniques in which the relative partitioning of a metal is identified rather than the absolute partitioning. This would be significant because this might provide a technique for predicting quantitatively the adsorption behaviors of metals in sediments.

The hypothesis for this study is that the normalized metal distributions among the phases ER, MR, and OX depicted on ternary diagrams that were determined by the above techniques reflect systematic trends in metal behaviors among adsorbing substrates for any water-sediment system. By systematic, it is meant that there is some universality in the way these metals are associated with the adsorbents. If this hypothesis is true, then these metal distribution patterns should be found in different aqueous systems and it should also be possible to interpret the data in terms of adsorption theory and the results of laboratory experimentation. The test was performed in this study by applying these techniques of chemical extractions,

normalization to equal amounts of substrate, and ternary diagram construction to sediments from streams located in areas where natural sources of metals to streams are greater than anthropogenic inputs. The process of normalization was also evaluated to determine whether its use in studying adsorption behaviors is actually advantageous for developing models.

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Chapter Two

Description of the Study Area

The criteria used for choosing an area to test the hypothesis were that the area should be a stream environment with active sedimentation, that the area should be free from anthropogenic sources of metals such as industrial waste discharges or landfills, and that the area should have a natural source of metals in adequate concentrations for measurement with an atomic absorption spectrophotometer. A search was conducted in the literature to locate potential sites that were accessible and met the above criteria.

Two USGS Mineral Resource Maps of Maine (Post and Hite, 1964; Post et al., 1967) were located which identified a number of remote areas with high concentrations of copper, zinc, and lead in stream sediments. Concentrations were plotted throughout the state based on a multi-year geochemical survey of over 2000 Maine streams. A study by Nowlan (1976) shows that three areas in particular on these maps meet the above criteria quite well. These areas are shown in Figure 2 and will be identified as Jackman Township Area, Topsfield Area (which includes Tomah Mountain), and Calais Area. Some background data on the state of Maine is described below.

Maine is the most northeastern and eastern state of the continental United States, approximately 80,277 square kilometers in area. Based on the average climatic data for northern and southern Maine from 1939 to 1979, Maine has a



Figure 2: Study area locations in Maine.

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yearly mean temperature of $5.6^{\circ}C$ ($42^{\circ}F$), with a yearly minimum and maximum of $0.5^{\circ}C$ ($32.9^{\circ}F$) and $10.6^{\circ}C$ ($51.1^{\circ}F$), respectively. Annual precipitation has an average of 99.8 cm, with an average snowfall of 238.5 cm (Ruffner and Bair, 1981).

Southeastern Maine is bordered by the Atlantic Ocean, so the topographic relief ranges from 0 meters (sea level) to approximately 1525 meters above sea level (ASL). Classes of land-surface forms include plains with hills and high hills, open high hills, and open low mountains (USGS, 1970). The major vegetation of Maine consists of Northern hardwoodspruce forests (Genera include Acer, Betula, Fagus, Picea, Tsuga), with some areas of Northern hardwoods (Genera include Acer, Betula, Fagus, Tsuga) and Northern spruce-fir forests (Genera include Picea, Abies). The geology (in general) of Maine comprises eugeosynclinal deposits of late Precambrian to mid-Paleozoic age, with intrusive granitic rock of late Paleozoic age in some areas. Although bedrock is exposed in many areas, there are many surface features throughout the state which show evidence of Wisconsinan glaciation, such as eskers, moraines, beach, glaciofluvial and glaciomarine deposits, and various deposits of till (USGS, 1970; Thompson and Borns, 1985).

Jackman Township Area

The surficial geology of this area (570 sq. km.) consists of hilly terrain with elevations ranging from 270 to 1130 meters ASL. Moderate to thin glacial drift (< 3

meters thick) covers the area, with many bedrock outcrops. Most exposed bedrock has a thin cover of soil and vegetation. It has many low, swampy areas with cedar bogs. Hills are covered with spruce-fir forests. The only anthropogenic activity in this area has been some logging operations. The bedrock is Ordovician quartz monzonite of the Attean Formation and fine- to medium-grained gabbro, and Devonian slate, metasiltstone, and metasandstone of the Seboomook and Tarratine Formations. Some of the mineralization noted by Nowlan et al. (1983) include pyrite (FeS₂), chalcopyrite (CuFeS₂), galena (PbS), sphalerite (ZnS), and cobaltiferous-nickeliferous pyrrhotite (Fe(Ni,Co)S).

Eight streams and tributaries were chosen for sampling in the Jackman Township area. Although some have names recorded on maps, others were unofficially named by the USGS during geochemical surveys. The streams, with widths ranging from 1 to 10 meters, are Pyrite Creek, West Pyrite Creek, Bean Brook, Parlin Brook, Chase Stream, Dead Stream, Cold Stream, and Alder Stream (Figure 3). Some streams that were sampled were in boggy areas, had high amounts of organic matter, and shallow depths as they flowed over glacial deposits. Other streams had rocky beds with boulders and exposed bedrock, and a few waterfalls. The streams in boggy areas have extremely high concentrations of manganese oxides in the form of black coatings on cobbles and boulders, and as discrete nodules in some places. This is prevalent in

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Figure 3: Jackman Area Map.

Maine for streams that drain swampy areas (Canny and Post, 1964).

Calais Area

This area (124 sq km) consists of relatively flat terrain with a few hills and elevations ranging from 45 to 150 meters ASL. There are numerous swamps, bogs, and lakes in low areas, surrounded by Northern hardwood-spruce forests (USGS, 1970). The surface geology of thin drift deposits also has many outcroppings of bedrock, and some fine-grained sediments of glaciomarine origin (Thompson and Borns, 1985). The bedrock in the areas sampled consists of Devonian intrusives (granite, guartz diorite, and ultramafic rock).

Four streams and tributaries were sampled in the Calais area: Eastern Stream, Western Stream, Mill Brook, and various branches and tributaries of the Magurrewock River in the Moosehorn National Wildlife Refuge (Figure 4). The streams had widths ranging from 1 to 5 meters. All the streams, except for Eastern Stream, had rocky beds with numerous bedrock boulders and cobbles. Eastern Stream (at the site sampled) flowed over a large, tabular exposure of ultramafic bedrock in a series of small waterfalls. Upstream from this area the stream bed contained boulders and cobbles.

Topsfield Area

This hilly area (31 sq km) has elevations ranging from 91 meters ASL to the highest point reached at Tomah Mountain (329 meters ASL). The thin drift on ridges and poorly



CALAIS, ROBBINSTON AREA

Figure 4: Calais Area Map.

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covered, steep bedrock slopes are forested by Northern spruce and fir, with swamp and bog valleys containing mostly cedars and alders. The bedrock consists of intrusive Devonian granite, Ordovician-Cambrian pelites and sandstones, and Ordovician ultramafic volcanics (Osberg et al., 1985).

Sediment and water samples were collected from Little Tomah Stream and a tributary (Cabin Creek) that drains Little Tomah Lake (Figure 5). Little Tomah Stream originates as a slow, narrow (1 to 3 meters wide) stream through an organic-rich swamp near the base of Tomah Mountain. Eventually the stream becomes fast-flowing, with a bedrock, boulder, and cobble bed and with numerous waterfalls that cut through bedrock fractures and joints, and over small faults in the granite and ultramafic rock.



Figure 5: Topsfield Area Map.

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Chapter Three

Selective Chemical Extraction Theory and Application

For any metal ion in solution, its total concentration will consist of the sum of all aqueous species in that solution, including complexed, colloidal bound, and aquocomplexed ions. Similarly, the total concentration of a heavy metal within sediment will consist of all states in which the metal is found, including interstitial (oxidized and reduced) soluble ions, adsorbed ions on clays, oxides, carbonates, organic matter, and sulfides, and ions within lattice structures of clay and silicate minerals in the nonmobile (residual or detrital) fraction (Gupta and Chen, 1975).

The distribution of trace metals among various chemical phases is very important to know in quantifying the behavior of metals in sediment. The manner in which a metal is partitioned among the various phases may reflect the chemical controls operating on adsorption in the watersediment system. It may also help determine various properties of the metal such as its bioavailability, abundance, and mobility. A quantitative description of trace metal partitioning is one of the objectives of selective chemical extraction techniques.

The solid material of sediment can theoretically be divided into distinct phases. A phase is defined in this report as a fraction of the sediment which can release adsorbed trace metals into solution after a change in

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environmental conditions. These phases can be extracted by using an appropriate chemical reagent which either degrades a phase or causes a desorption reaction and mobilizes a metal into solution. For the purpose of investigating the partitioning of heavy metals, these chemical extractions are done in a sequence where the weakest-bonded metal ions are extracted first and the strongest-bonded last. In this respect, the extractions are somewhat "selective", but this selectivity is limited in that the phase which releases adsorbed metal ions may not be a unique substrate but rather a suite of substrates which respond to the changing conditions caused by the reagent. For example, weakly-bonded metals that can be extracted with NH_AOAc may be located on exchangeable surface sites of clays, oxides, and humic acids, so the phase or fraction can only be identified as "exchangeable" (Posselt et al. 1968).

These extractions can represent an environmental change of the natural conditions that would affect the sediment phases. Exchangeable phases in sediment will release metals on exchange sites with a change in water ionic composition. Carbonate phases are susceptible to changes in pH and will release associated metals. Reducible fractions are those phases that are thermodynamically unstable under reducing, anoxic conditions. These include <u>easily reducible</u> (manganese oxides and amorphic iron hydroxides) and <u>moderately</u> reducible (iron oxides) <u>phases</u>. Oxidizable phases include organic matter and sulfide compounds that may be degraded

under highly oxidizing conditions, which leads to a release of associated trace metals. The strongest-bonded metals in the <u>residual phases</u> are not expected to be released under the conditions produced above by extractions over a reasonable amount of time because they are located within crystalline lattices of primary and secondary minerals (Tessier et al., 1979). The partitioning of heavy metals which is determined by sequential selective chemical extractions (SSCE) is identified as operationally defined by the methods used to release metals into solution.

The early developments of chemical extractions were made to address the problem of soil fertility and estimates of the availability of trace metals in soils for plants (Jackson, 1958). The non-detrital forms which were extracted included iron oxides, carbonates, plant organic matter, and clay minerals with exchange sites (Table 2). An application of these techniques to pelagic sediments (Chester and Hughes, 1967) used acids, reducing agents such as hydroxylamine hydrochloride, and combined acid-reducing agents to investigate the distribution of heavy metals (Ni and V) adsorbed on sediment particulate surfaces.

Iron and manganese oxides are strong scavengers of heavy metal ions, and reducing agents that were developed readily dissolve these phases to release the associated metals. Chao (1972) recognized the importance of developing a separate dissolution of iron and manganese oxides in determining interelemental relationships. Manganese oxides

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Table 2: Chemical phases and extraction methods.

Chemical Phase	Chemical Extraction Method
Cation exchange	BaCl ₂ ; MgCl ₂ ; NH ₄ OAc
Hydrogenous/lithogenous	0.1M HCl; 0.3M HCl; 0.1M HNO ₃
Carbonates	CO ₂ treatment; exchange columns; NaOAc/HOAc-buffer
Reducible	1M NH ₂ OH·HCl v/v 25% HOAC
Easily reducible (Mn-ox and amorphous Fe-ox)	0.1M NH ₂ OH·HCl in 0.01M HNO ₃ @ 25° C; 10% H ₂ O ₂ in 0.001M HNO ₃ ; 0.25M NH ₂ OH·HCl in 0.25M HCl @ 70°C
Moderately reducible (hydrous Fe-ox)	Oxalate buffer; sodium dithionite with sodium citrate; hydrazine chloride; 0.04M NH ₂ OH·HCl in 25% v/v HOAc @ 96 ^o C
Oxidizable (organic matter and sulfides)	30% H_2O_2 @ 95 ^O C, with 1N NH ₄ OAc or 0.01M HNO ₃ ; fat solvents, e.g. chloro- form, ether, gasoline, benzene, carbon disulfide; KClO ₃ + HCl-4N HNO ₃
Detrital silicates From Forstner and Patchineelam,	EDTA; HF/HClO ₄ ; LiBO ₃ @ 1000 ⁰ C + HF-HNO ₃ digestion 1980.

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differ in solubility from iron oxides in natural environments in response to changes in redox state, charge, and kinds of metals scavenged. Using sediment samples from Maine, Colorado, and Hawaii, Chao (1972) developed a technique to selectively dissolve manganese oxides with little dissolution of any iron oxides. A solution of 0.1 M hydroxylamine hydrochloride prepared in 0.01 M nitric acid (pH = 2) was used. Iron oxides consist of crystalline Fe₂O₃, amorphous Fe(OH)₃, and some sort of intermediate iron oxyhydroxide. When MnO₂ is dissolved, some amorphous Fe(OH)₃ is hypothesized to be dissolved as well. For these samples from various states in the USA, the amount of iron was as much as ten times greater than the amount of manganese. Still, using this technique, the manganese oxides were preferentially dissolved.

This extraction was also tested in sediments from Maine with large amounts of manganese (0 to 20,000 mg/l) and iron (0 to 500 mg/l) by Chao and Sanzolone (1973). Oxides were extracted in order to determine the concentrations of associated Co, Ni, Cu, Pb, and Zn. The problem being investigated was whether microgram levels of these metals in solution could be determined by the manganese oxide extraction combined with APDC-MIBK chelation and atomic absorption spectrophotometry in solutions that contain large amounts of iron and manganese. Consistent and reproducible results were obtained in their experiments, which is significant since the sediment samples were taken from the

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same areas in Maine sampled in this study (Chao and Theobald, 1976).

This technique to distinguish between metals associated with manganese oxides and iron oxides was also used by Chao and Anderson (1974) to look at the behavior of silver in stream sediment from Colorado. They found that silver ion partitioning behavior is significantly controlled by manganese oxides while iron oxides were interpreted to play only a secondary role.

Gupta and Chen (1975) used SSCE to study the partitioning of various heavy metals in dredged sediments to determine potential mobile concentrations. In their sequence of extractions, they determined metal concentrations associated with the following sediment components: interstitial water, soluble solid minerals, exchange sites, metal carbonates, easily reducible phases (manganese oxides), organics and sulfides, iron oxides, and lithogeneous (mineral residual) fractions. One interesting aspect of their technique was the use of an oxidizing agent (for organics and sulfides) prior to the use of a moderately reducing agent (for iron oxides). Most studies reverse the order of these reagents, since metals are generally more strongly bonded with organic molecules than iron oxides (Stumm and Morgan, 1981). Gupta and Chen (1975) concluded that if the natural anaerobic conditions were left undisturbed when sediments were dredged, metals in the weakly bonded phases and interstitial water (which are a

small fraction of total available metals) would be the most mobile. A significant change in environmental conditions could release metals from the hydromorphic fractions.

Chemical extraction methods do not absolutely discriminate between metal concentrations present in the actual soil and sediment phases. However, they can give a general indication of the occupation of binding sites on operationally defined substrates, and they do provide a reproducible technique of analysis (Gatehouse et al., 1977). Even suspended particulates can be analyzed by extractions to determine the modes of metal transportation in streams among soluble, adsorbed, oxide coatings, solid organics, and crystalline minerals (Shuman et al., 1978). Tessier et al. (1980) found that, using SSCE developed in an earlier study (Tessier et al., 1979), most of the natural trace metals in suspended sediment of two southeastern Quebec rivers were in the residual fraction, while iron-manganese oxides and organic matter were important transport phases for bioavailable Co, Pb, Zn, Ni, and Cu. However, man-induced perturbations to the river trace metal input were found to increase relative concentrations in the reducible oxide phases and decrease the importance of the residual fraction as a sink for metals.

Robinson (1984) found that by comparing various techniques that extracted metals from exchangeable sites and carbonates, Mn-oxides, organics, and Fe-oxides on particulate coatings (Tessier et al., 1979; Filipek et al.,

1981; and Robinson, 1982), none were completely specific for releasing metals from a phase. Therefore, they produce some error in determining metal-substrate partitioning relationships. However, it was recognized that the quantitative information which can be learned from this type of study (which distinguishes among substrate phases) is quite important.

Forstner and Patchineelam (1980) also pointed out that extractions are often not selective. Repeated treatment of a reagent, for example, may show a further release of adsorbed metals as it attacks stronger phases to some extent. For example, metals can readsorb or precipitate after being released from organics by the action of dilute acids or hydrogen peroxide. Other chemicals have been found to attack different phases after a long extraction time or after a change in pH. One advantage in dissolving acid soluble phases prior to reducible phases is that the reducible extraction will then be more selective, since the buffering capacity of the sediment carbonates was eliminated by the acid.

Since particulates in sediment are a diverse mixture of phases (clays, oxides, organic debris), one would expect a wide variety of surface chemistry properties and therefore variable metal adsorption characteristics (Lion et al., 1982). Adsorption would also be expected to vary with any changes in relative proportioning of surface sites among the phases. Since observed experimental metal adsorption

behaviors in well defined, single component systems are consistent with conceptual models of adsorption, the use of chemical extractions to determine metal distributions in natural systems would be quite important in the attempt to make predictions of metal behavior in natural systems.

Heavy metals are an important group to study in natural aqueous systems because of their sensitivity to variations in environmental conditions, which make them ideal indicators of physicochemical processes (Van Valin and Morse, 1982). SSCE can reproduce potential variations in conditions and isolate how heavy metals behave in response to these changes. Chemical extraction technique efficiency was evaluated by Van Valin and Morse (1982) through a comparison of metal concentrations determined by extractions with neutron activation and X-ray fluorescence analyses of solid phases. They found that the three methods of analysis produce consistent results, and they concluded that SSCE are a useful method for characterizing the partitioning of trace metals associated with solid phases in sediment. They recommended that the sequential scheme of Tessier et al. (1979) (with slight modifications) would be very useful.

Although the above investigations suggest that SSCE are quite helpful in determining interelemental relationships, there are problems with the selectivity of reagents (which was described above) and readsorption of metals after an extraction. An experiment by Rendell et al. (1980) shows that significant readsorption occurred within sediment after

extraction with the reagents for dissolving various sediment phases. This suggests that a misinterpretation of extraction data could occur because the concentration of metals determined in the extraction do not represent the total amount associated with the phases extracted. However, the sediments in their study were extracted for 16 hours and were not applied in sequential order for extracting the weakest to strongest bonded metals. This sequential procedure is very important in identifying quantitative partitioning data and can be tested by conducting steady state tests on the chemical extraction time.

In the development of the easily reducible phases extraction, Chao (1977) measured the amount of manganese released versus time of extraction. After a period of 60 minutes, the concentration of manganese in solution leveled off until little manganese was added to solution. This was interpreted to mean that most of the oxide was dissolved. In fact, it was found that over 80% of the available manganese oxide (analyzed after acid digestion) in the sample was dissolved. The study by Chao (1977) is very significant because the extraction techniques were developed using stream sediments collected in the same study areas in Maine that were sampled for this study. Tessier et al. (1979) also measured the effect of extraction time on calcium and iron concentrations in extraction solution for carbonate and moderately reducible phases respectively. Based on these reaction time experiments, a schedule for dissolving the

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various phases was developed and is shown in Table 3:

Table 3: Tessier et al. (1979) extractions methods.

Chemical phase	Extraction method
Exchangeable	1M MgCl ₂ pH=7 at 25 ⁰ C for 1 hr.
Carbonates	1M NaOAc pH=5 at 25 ⁰ C for 5 hr.
Reducible	0.04M NH ₂ OH HCl in 25% v/v HOAc
Oxidizable Residual silicates	at 96 ⁰ C for 6 hr.
	30% H ₂ O ₂ + 0.02M HNO ₃ at 85° C
	for 3 hr., then $3.2M$ NH ₄ OAc in
	20% v/v HNO ₃ for .5 hr.
	HF-HClO ₄ dissolution, then
	12N HCl dissolution.

Gephart (1982) conducted steady state experiments to find the adequate reaction times for the extraction of exchangeable phases, carbonate phases, easily reducible phases, moderately reducible phases, and oxidizable phases. Based on these experiments, the methodology for this study was formulated (summarized in Figure 6).

A comparison test was done to determine whether wet or dry sieving should be done for the sediment samples. Using the stored sample Tom-4, a subsample was dried and sieved while another subsample was wet sieved. The samples were then extracted according to the methods described in Figure 6 (except for the residual fraction) and the concentrations

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SELECTIVE CHEMICAL EXTRACTIONS

sediment sample dries (30°C), sieved to (180 micron fraction, 5 gram sample taken for procedure

Acid-soluble Fraction (metals associated with exchange sites such as clays and easily acid soluble such as carbonates) Add 1.0 M NaOAc (pH=5) @ 25°C for 5 hours.

centrifuge and save extract

Easily Reducible Fraction (metals associated with Mn-oxides and amorphous Fe-oxides) Add to residue: 0.1 M NH₂OH.HCl v/v 0.01M HNO₃ @ 25°C for 30 minutes.

centrifuge and save extract

<u>Moderately Reducible Fraction</u> (metals associated with Fe-oxides) Add to residue: 0.04M NH₂OH.HCl v/v 25% HOAc @ 96°C for 6 hours.

centrifuge and save extract

<u>Oxidizable Fraction</u> (metals associated with organic matter and sulfides) Add to residue: 0.02M HNO₃ + 30% H₂O₂ (pH=2) @ 85°C for 5 hours, then 3.2M NH₄OAc @ 25°C for 30 minutes.

centrifuge and save extract

<u>Residual Fraction</u> (metals associated with silicates and other chemically resistant minerals) To 0.2 grams of residue: Fusion with LiB₄ @ 1000⁰C, then dissolution with HNO₃.

Figure 6: Flow chart of chemical extractions for this study.

of iron, manganese, chromium, copper, zinc, nickel, and lead were measured on the AAS and converted to ppm whole rock.

The percent differences in dry vs. wet sieved samples were calculated for each metal. For the carbonate extraction, the percent differences for all metals had a mean of 7.4%; for the easily reducible extraction the mean was 14.3%; for the moderately reducible extraction the mean was 15.9%; and for the oxidizable extraction the mean was 34.4%. For a total of 28 measurements (7 metals, 4 extractions), the mean percent difference was 18%, and there was no consistency for either sieving method being more or less precise. The largest differences were found in the oxidizable extraction, which ranged from 13% difference for chromium and zinc to 77% difference for copper. However, since copper is known to complex with dissolved organics quite readily (Stumm and Morgan, 1981), the wet sieving may have included non-sediment phases (such as interstitial water) which would increase the concentration of copper extracted. Based on these results, the decision was made to dry sieve the sediment samples.

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Chapter Four

<u>Methods</u>

Field Methods

The study areas chosen in Maine (Figure 2) to test the hypothesis were sampled during the summers of 1983 and 1984. The streams with the highest reported concentrations of Zn, Ni, and Pb in sediment were first located on maps of Maine (Post and Hite, 1964; Post et al., 1967; and Nowlan, 1976). The first year (1983) in which samples were collected was used to determine exact locations of streams, their accessibility, and the quality of the sediments in regard to fulfilling the requirements of the research objectives. During the second sampling year (1984), additional field techniques were employed, based on the initial findings.

Sediments were collected from oxic zones at the watersediment interface in the stream beds with a polyurethane scoop, to reduce any metal contamination. Water was allowed to run off the sediment sample before transferring it to a one gallon polyethylene bag, which was knotted, double sealed, and transported from the site by backpack. The bags were placed in an ice-packed cooler for storage during the trip back to Michigan, where they were temporarily stored in a walk-in cooler kept at 2°C. Cold storage is required to inhibit bacterial activity which may produce a change in the reactivity of surface sites on sediment particulate surfaces. In 1983, 35 sediment samples were collected in three different areas of Maine: 24 from the Jackman Township

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Area (Figure 3), 3 from the Calais Area (Figure 4), and 8 from the Topsfield Area (Figure 5). In 1984, 30 sediment samples were collected: 16 from the Jackman Township Area (Figure 3), 6 from the Calais Area (Figure 4), and 8 from the Topsfield Area (Figure 5), for a total of 65 samples.

In 1984, stream water was also sampled at each site where sediment was collected. First, a 250 ml polypropylene bottle (containing 5 ml of formaldehyde to kill bacteria) was filled with raw water. This was to be used later to analyze the sulfate concentration. Next a 125 ml polypropylene bottle with no preservative was filled with raw water. This would be used to measure alkalinity at the end of the sampling day. Finally, a 500 ml polypropylene bottle was filled, to be used later for the laboratory analysis of concentrations of major cations and anions. This sample of the stream water had to be immediately filtered and acidified with concentrated nitric acid to pH < 1 upon collection, so as not to unnecessarily mix it with the atmosphere. Filtering was done by using a hand operated lever action pump (attached by rubber hose to a vacuum flask) to pull stream water through a 0.45 micron (pore diameter) Millipore filter. The filtered water was then carefully poured into the bottle containing 2-3 ml of acid. All bottles were acid washed with hydrochloric acid, rinsed with double distilled water in the laboratory, and sealed prior to sampling. The 250 ml bottle was prefilled in the laboratory with 5 ml of formaldehyde. The other bottles were

rl A] Mi tł Βı tł st Ca wi Up th di st bo de ac aį eq sa ٥f a]) the Wat rinsed in stream water at each site prior to being filled. All bottles were kept chilled during and after transport to Michigan.

Temperature and pH were also measured at the same time that water samples were collected. Bottles of standard pH Buffer Solution (pH=4 and pH=7) were placed in a bucket of the stream water to allow them to equilibrate to the ambient stream temperature. These buffers were then used to calibrate an Orion Research pH Meter (Model 399A) equipped with a pH electrode (Orion Combination pH, Model 91-05). Upon calibration to temperature and the buffers, the pH of the stream water was recorded by placing the electrode directly into slow streams or into a fresh bucket from fast streams.

At the end of the sampling day, the chilled 125 ml bottles were used to calculate alkalinity. This is determined by a titration method using a buret of sulfuric acid solution and a pH meter, as described by Skougstad et ai. (1979). A sulfuric acid solution (0.01639 N) with 1 ml equivalent to 1.00 mg CaCO₃, is used to titrate a volume of sample to a pH of 4.5, which is the true equivalence point of bicarbonate-carbonic acid under ideal conditions. Total alkalinity is calculated as CaCO₃ in mg/l. Values for all the streams were quite low (2.2 - 26.6 mg/l CaCO₃). All water analysis results are recorded in Appendix 3.

Laboratory Methods

A test was done using one sediment sample to determine if there were any differences in conducting chemical extractions (described in Chapter Three) using wet-sieved or dry-sieved sediments. Wet-sieving involves placing fresh, damp sediment into a clean nylon 180 micron pore diameter sieve, rinsing with double distilled water, and collecting the < 180 micron fraction for drying. Dry-sieving involves drying sediment in clean 1 Liter beakers in a convection oven for 24 to 48 hours at 30°C, and sieving dry sediment with a clean Nb. 80 Mesh U.S. Standard Sieve to collect the < 180 micron fraction for storage in waxed containers. Results of the test (described in Chapter Three) suggested that there were few differences between the methods of sieving. Therefore, the sediments were dry-sieved, since this method disturbed the samples the least.

The filtered and acidified stream water samples were used to determine the concentrations of major cations: sodium, potassium, calcium, and magnesium. The analyses were completed using a Perkin Elmer Model 560 atomic absorption spectrophotometer (AAS). Results of the major cation analyses are presented in Appendix Three. Major anions are HCO_3^- , SO_4^{-2} , and Cl^- . Bicarbonate is calculated from the alkalinity measurement. Sulfate will be discussed below. Chloride concentrations greater that 10 mg/l are typically analyzed with Mohr's titration. However, since the cation concentrations were very low (Appendix 3), another method

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Chloride concentrations were analyzed using a silver ion electrode. The instruction manual for the Orion Research Model 94-16 electrode describes a titration technique for measuring chloride concentrations less than 5 ppm $(10^{-4} M)$. A volume of sample is titrated with a dilute solution of silver nitrate while measuring the change in electric potential (in millivolts) with a silver ion electrode and an Orion Model 399A pH meter. The chloride concentration is determined from extrapolating from a linear plot of milliliters of titrant used vs. change in millivolts, on 10% volume-corrected Gran's plot paper. The extrapolated point is used to calculate ppm Cl (1 ml titrant = 0.5 mg Cl). Results are shown in Appendix 3, and the chloride concentrations were guite low. In order to carry out the titration, titrant had to be added to the sample until the millivolt reading was within the range for the blank (distilled water) titration, which was > 290 mv. Six of the sixteen samples were much less than 290 mv in spite of the amount of titrant added. It was assumed that these samples had some type of chemical interference which reduced the electrical potential, possibly a dissolved constituent which complexed or neutralized silver ions as quickly as they were added with titration. Therefore, chloride concentrations for these samples could not be measured.

Five sediment phases were chosen for this study with SSCE: acid-soluble (including exchange sites on clays, carbonates, and chromium hydroxides), easily reducible phases (manganese oxides and amorphous iron oxides), moderately reducible phases (iron oxides), oxidizable phases (organic matter and sulfides), and residual phases (silicates, lithogeneous minerals).

Five gram subsamples were collected from the <180 micron fraction of 61 of the 65 sediment samples (some samples did not have enough fine sediment for extraction). The subsamples were then subjected to the sequential extraction procedures outlined in Figure 7. The residual fraction was determined from a 0.2 gram subsample of the sediment that remained after the oxidizable attack. The 0.2 gram sample was fused with 1.0 gram of lithium metaborate in a graphite crucible at 1000° C for 15 minutes, dissolved with 5 mls concentrated HCl, and then diluted to 100 mls. All extraction solutions were collected in polyethylene bottles and acidified to pH<2. The concentrations of Mn, Fe, Cr, Zn, Cu, Ni, and Pb in solution were determined with a Perkin Elmer 560 atomic absorption spectrophotometer using standards made up with the extraction chemicals to account for matrix affects.

In order to carry out estimations of the concentrations of the important sediment phases, it is necessary to determine the amount of total organic carbon (TOC) in the sediment on a percentage basis. A titration technique

developed by Gaudette et al., (1974) was used for measuring organic carbon.

Construction of Ternary Diagrams

The phase concentration factor (PCF) (developed by Forstner and Patchineelam, 1980, and Filipek et al., 1981) was modified by Gephart (1982) in the estimation of phase concentrations and is described below. The amount of each phase must be known or estimated to use a PCF. By making some assumptions about the phases chemically attacked in the sequential selective chemical extractions, the concentrations of the three major phases can be calculated in the following procedure:

Organic matter: This is estimated by multiplying the percentage of total organic carbon (TOC) determined analytically in a sample by 10,000 ppm (an approximation for the mean molecular weight of organic molecules) and by 2.2, which is a constant used by Filipek et al. (1981) for organic carbon in biologic material.

<u>Manganese oxides</u>: It is assumed that MnO_2 and amorphous Fe(OH)₃ are dissolved in the easily reducible extraction (Chao, 1972). The weight percent of Mn and Fe in MnO₂ and Fe(OH)₃, respectively is approximately 63.2%. Therefore the concentration of easily reducible phases is estimated by multiplying the sum of Mn and Fe concentrations (in ppm) in the extract solution by 1.6 (100% / 63.2% = 1.6) (Gephart, 1982).

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Iron oxides: It is assumed that FeOOH is dissolved by the moderately reducible extraction, and Fe is 62% of FeOOH by weight. Therefore, the concentration of this phase is estimated by multiplying the Fe concentration (in ppm) in the extract solution by 1.6 (100% / 62% = 1.6) (Gephart, 1982). These phase concentrations are used to calculate the phase concentration factor (PCF) for a metal partitioned in each of the three major phases. An example of this calculation is shown in Figure 7 for sample Tom-6 from the Topsfield area.

The PCF for a metal in a phase can represent the association of that phase with the metal. However, it would be valuable if this PCF could be used to measure the relative association of the phase with that metal in comparison with the other phases. This can be accomplished for a three component system (easily reducible phases, moderately reducible phases, and oxidizable phases) by plotting the relative percentages of these PCF values on a ternary diagram (Gephart, 1982).

The concentrations of Cr, Cu, Zn, Ni, and Pb extracted from the three phases were plotted on ternary diagrams as percentages of the amount of metal associated with each of the three phases. PCFs were calculated and plotted as percentages on ternary diagrams to see how metals would be distributed if the phases were present in equal concentrations. In this way some of the variability in the data was reduced. Low concentrations of a substrate will

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Fig

PCF for Nickel in Sample Tom-6. Maine:

A. Calculation of Phase Concentrations

1. Oxidizable phase (OX): 2.70 TOC * 10000 * 2.2 = 59400

2. Moderately reducible phase (MR): Fe concentration in leach (1572 ppm) * 1.6 = 2515

3. Easily reducible phase (ER): Mn and Fe concentrations in leach (51.75 + 57.5 ppm) \star 1.6 = 174.8

4. Total equals 62090 and therefore the absolute distribution of the phases in percents:

<u>ox</u>	MR	ER
95.7%	4.0%	0.3%

B. Nickel concentration in each phase as a percent:

	<u>Ox</u>		MR		ER	
Ni	1.8 ppm	80%	0.2 ppm	8.9%	0.25 ppm	11.1%

C. Calculation of phase concentration factors (PCF) for plotting on ternary diagram (calculations in B / calculations in A.4.):

PCF	<u>0X</u>	<u>MR</u>	<u>ER</u>	
	0.84	2.19	39.5	
as %	2.0%	5.2%	92.9%	

The percentage values are plotted on the ternary diagrams.

Figure 7: Example calculation of PCF value for sample Tom-6.

have a va asso dist norm the asso inte stat conc value hypot = 2.2 remaj PCF v = 4.0 the p and E Figur Altho With the M dramat \$ descri ^{range}, have a higher PCF value than high concentrations (closer to a value of one) and therefore will have a higher apparent association with a metal, even if the metal is actually distributed equally among the substrates before normalization. This is why the easily reducible phases in the Grand River sediments tend to have such high apparent associations with Zn, Ni, Pb, and Cu (Figure 1). Any interpretations of ternary diagrams must consider this statistical weighting or bias of PCF values on low concentrations.

As an example of this statistical bias, consider the values in Figure 7 if the percentages of phases were hypothetically the following: OX = 95.6%, MR = 2.2%, and ER = 2.2%. With the percentages of nickel in the phases remaining the same (80%, 8.9%, and 11.1% respectively), the PCF values calculated would be the following: OX = 0.84, MR = 4.05, and ER = 5.05. For plotting on a ternary diagram, the PCF values as a percent would be: OX = 8.5%, MR = 40.7%, and ER = 50.8%. The actual percentages as calculated in Figure 7 were: OX = 2.0%, MR = 5.2%, and ER = 92.9%. Although the ER phases still have the highest association with nickel, the importance of ER phases in comparison with the MR phases in this hypothetical case would be dramatically reduced.

Substrate concentration data were reduced by descriptive techniques to determine values for mean, median, range, and standard deviation. Three areas in Maine were

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sampled, but it was not clear whether the three data groups could be pooled without introducing additional variability into the data. Therefore, a test of the variation was done to determine if the substrate concentration data of the three areas (Jackman, Topsfield, and Calais) were significantly different. The relative percentages of substrates in the Maine samples were also compared with those of the Grand River to look at substrate abundance differences. The three areas in Maine were also compared individually for substrate abundances to study the effect of abundance variabilities and their influence to the normalization procedures.

CHAPTER FIVE

Results and Discussion

The raw metal concentrations for all the chemical phases of the Maine samples are tabulated in Appendix 3. The percentage Phase Concentration Factor (PCF) values for each metal on ternary diagrams will be referred to as the <u>normalized data</u>. The metals Cr, Cu, Ni, Pb, Zn are shown on Figures 8, 9, 10, 11, and 12 respectively. Also plotted on each ternary diagram are the percentages of metal concentrations among the three substrates prior to normalization, which will be referred to as <u>raw data</u>.

The distribution of Cr (raw and normalized data) is shown in Figure 8. The raw Cr data show a distribution mainly between the oxidizable (OX) and moderately reducible phases (MR). Generally the highest percentage of Cr associated with the easily reducible phases (ER) is less than 15% in most samples. The normalization of data to equal amounts of substrate modifies the distribution so that Cr data clusters near the center of the diagram. However, there is quite a range from high association with the ER phases to high associations with the OX-MR phases.

The normalized Cr data cluster location and range (Figure 8) is similar to that observed by Gephart (1982) (Figure 1). This pattern was interpreted by Gephart (1982), Takacs et al. (1983), and Long and Gephart (1982) to indicate that the distribution of Cr may be caused by its ability to exist in two oxidation states ,+3 and +6, in



Figure 8: Ternary diagram for chromium partitioning in Maine sediments.

natural environments. The adsorption and therefore relative partitioning behaviors of Cr species would be different than other metal ions with only one dominant valence state. In a stream with a pH in the range of 6 to 7.5, Takacs et al. (1983) defined a model for the two Cr species: Cr^{+6} existing as the thermodynamically stable ion CrO_A^{-2} and Cr^{+3} existing as the kinetically stable ion $Cr(H_2O)_4OH_2^{+1}$. The negative Cr species can be adsorbed by moderately reducible (MR) phases (such as Fe-oxides), or reduced by organic matter (James and Bartlett, 1983). The positive Cr species can be adsorbed on clays, adsorbed by Fe-oxides, oxidized by O_2 , and can be adsorbed, oxidized, and desorbed by Mn-oxides. The technique of analysis presented in this study shows a systematic behavior of chromium partitioning, whether the metal comes from a natural source (Maine) or an anthropogenic source (Grand River, Michigan). That is, the normalized data for this study are clustered similarly to the clusters in the Grand River study (Figure 1).

The ternary diagram for Cu (Figure 9) shows that the raw data are clustered mostly near the OX phases (> 70%), somewhat with the MR phases (0 to 50%), and very little with the ER phases (< 30%). Normalized Cu data are mostly clustered near the OX and ER phase (> 50%) and somewhat clustered near the MR phases (generally < 30%). Normalized Cu data plot in quite a scatter, resembling the plot of Cr data in Figure 8. The distribution of Cu in this study is similar to that of Gephart (1982) (Figure 1) in that the OX



Figure 9: Ternary diagram for copper partitioning in Maine sediments.

and ER phases show the highest association with Cu. However, the MR phases show a higher association with Cu in the Maine sediments than in the Grand River sediments (Figure 1). A systematic behavior for Cu is not indicated. The differences in Cu partitioning behavior between the two studies will be discussed below.

Raw Ni data in Figure 10 are clustered mostly with the MR and OX phases, with ER phases showing little association with Ni (< 30%). The normalized Ni data show that the ER and MR phases have higher associations with Ni than the OX phases (< 20%), which was also found in the results of Gephart (1982) (Figure 1). However, MR phases appear to have a higher association with Ni in the Maine samples than in the Grand River sediment samples. These two studies show a systematic behavior in the observed low association of the OX phases with Ni (< 20%).

Figure 11 is a plot of raw and normalized Pb data. The raw concentration data show that the MR phases have the highest association with Pb (40 to 90%), the OX phases have a lower association with Pb (< 40%), and ER phases have little association with Pb (<20%). Normalization of the data to equal amounts of phases shows that Pb clusters mostly with the ER and MR phases and is weakly associated with OX phases (<40%). In comparison with the Pb distribution of normalized data in the study by Gephart (1982), the results in this study suggest that the MR phases in Maine sediments have a higher association with Pb than those in Grand River



Figure 10: Ternary diagram for nickel partitioning in Maine sediments.



Figure 11: Ternary diagram for lead partitioning in Maine sediments.

sediments (Figure 1). The low apparent association of OX phases with Pb is observed to be a systematic behavior for Pb in the results of both studies.

The plot of raw Zn data in Figure 12 shows that the MR phases have a high association with Zn compared to the other phases. Normalization of the Zn data shows that Zn clusters mostly with the ER and MR phases (30 to 90%) and is very weakly associated with the OX phases (< 10%). The apparent association of the ER phases with Zn and the low association of OX phases with Zn show a systematic behavior for Zn in this study and in the results of Gephart (1982) (Figure 1).

In the Ni-Pb-Zn partitioning diagrams, where normalized data are generally clustered along the ER and MR phase boundary, Zn data (Figure 12) are less associated with the OX phases than Ni and Pb (Figures 10 and 11 respectively), and Zn data also show a stronger association with the ER phases. This trend for Zn data is similar to that found by Gephart (1982) (Figure 1) and suggests that the technique of analysis depicts a systematic trend for the natural partitioning behavior of Zn. However, normalized Ni and Pb data show a noticeable trend of a stronger association with the MR phases in Maine sediments than in the Grand River sediments. This will be discussed below.

It is observed that the partitioning behavior of the five heavy metals have similarities between the Maine sediments and the Grand River sediments from the study by Gephart (1982). For example, the normalized data for each of



Figure 12: Ternary diagram for zinc partitioning in Maine sediments.

the five metals appear to plot in distinct clusters among the three phases. Also, the two major trends found by Gephart (1982) can be seen in the Maine data: 1. clusters of normalized metal data rotate around the ER apex away from the ER-OX phase boundary in the order of Cu < Pb < Ni < Zn, and 2. for the association of Cr with all three phases, Cr data clusters near the center of the ternary diagram. Since there are some differences in the way the normalized metal data cluster on the diagrams in a comparison of these two studies, it is necessary to make a more thorough investigation of the any other differences in the two areas, as well as an investigation of the technique of normalization.

Differences in streams sampled in Maine

One factor which may account for the higher associations of Cu, Ni, and Pb with MR phases in Maine than in the Grand River is that two major types of streams were sampled in Maine; fast flowing and slow flowing, boggy streams. The distinction was in the amount aeration of stream waters observed in the field. The rates of flow in these stream types may cause a change in the oxidizingreducing environment. Although the values for redox and dissolved oxygen were not measured for the streams, the fast flowing streams would typically be more oxidizing while the slow flowing streams would tend to be reducing. The different redox conditions may cause a difference in the adsorption behaviors of metals.

The metal partitioning data for these two stream types were divided into two groups, Fast and Slow, but only 51 of the 61 sampling sites could be positively identified as being fast or slow flowing (some dry beds were sampled), with 26 in the Fast group and 25 in the Slow group. Figure 13 summarizes the distribution of metals between the two groups. No differences were detected in how partitioning data for Cu, Ni, and Pb were distributed in fast and slow streams, so it was necessary to consider some other explanation for the differences in adsorption behaviors of copper, nickel, and lead between the two studies.

It was found, however, that the Cr data in the slow streams seems to plot in two distinct groups. This may be caused by the fact that Cr exists in two valence states, Cr^{+3} and Cr^{+6} . If there was a factor in the slow streams which favored the existence of different adsorption behaviors of these two species, the differentiation of these behaviors may be identified.



Figure 13: Comparison of metal partitioning in fast-flowing and slow-flowing streams.



Figure 13: continued.

Differences in areas sampled in Maine

Since three distinct areas in Maine were sampled (Figure 2), with different bedrock types and mineralizations, it was hypothesized that the normalized partitioning data may plot distinctly as well. This may explain some of the variability in the data. The data were divided into the three sampling areas (Jackman, Calais, and Topsfield, Figure 2) and plotted on separate ternary diagrams. All the metals were studied in this manner in order to see if partitioning trends are similar among the three sampling areas.

Chromium

The three ternary diagrams for chromium (Figure 14) show that data from the Calais and Topsfield areas cluster either near the ER phases or only between the OX and MR phases, but that data from the Jackman area clusters almost equally among the three phases. One explanation for the data in the Calais and Topsfield areas plotting at such extremes is the low detectability of chromium by the methods used for this study (Flame AAS). For all samples, chromium was in low concentration in the extractant solutions. Therefore, since the normalization procedure is biased toward the phases with the lowest concentrations (ER), any concentration of chromium present would plot mostly with that phase. If that extractant solution had no detectable chromium, then the chromium would be distributed among the other two phases



exclusively, which can be observed in all three diagrams in Figure 14.

The Jackman area samples plot among all three phases almost equally. If the amount of ER phases were present in similar amounts to the other two types of phases, the normalization procedure would not be biased on ER phases as in samples from the Calais and Topsfield areas. This will be discussed in the next section on differences in substrate concentration data. The partitioning behavior of chromium in Maine sediments is consistent with the Grand River sediments, but the relative distribution of data may be affected by differences in substrate amounts and by the detectability of chromium in solution by Flame AAS. Zinc

With the exception of some Jackman area data which shows a slightly stronger association of zinc with the MR phases than results of Gephart (1982), zinc data plots in the same cluster pattern for Maine (Figure 15) and the Grand River (Figure 1). The high association of Jackman zinc data with MR phases may be explained by the high amount of ER phases in this area. Zinc data would not biased on these phases and would therefore cluster nearer the MR phases than the other two areas of Maine. The possibility of variable substrate concentrations and their affect on normalization will be explored in the next section.



Nickel

Nickel data for the Jackman area samples cluster equally between the ER and MR phases (Figure 16). The nickel data from the Calais and Topsfield areas cluster closer to the ER phases apex. This could again be caused by a lower weighting or bias on ER phases due to an increased amount of these phases present in the sediment. All three areas from Maine show a low association of OX phases with nickel, which was also noted in the Gephart (1982) study.

Lead

For the three areas in Maine sampled, Jackman area (Figure 17) shows that the MR phases have the highest association with lead. The Calais and Topsfield areas show a somewhat equal association of the MR and ER phases with lead. This is different than the Grand River sediments, in which the ER phases had the highest association with lead. Differences between the three areas are not as great for lead as they were for chromium, zinc, and nickel, so another explanation is needed. The association of OX phases (< 30% on the diagram) with lead among the three areas in Maine is similar to the results of the Grand River study by Gephart (1982).

Copper

For all three areas in Maine (Figure 18), there is an observed higher association of the MR phases with copper than in the Grand River samples. The samples from the Jackman area show a much higher association of MR phases










with copper than the Calais and Topsfield areas, in which copper is mainly clustered between the OX and ER phases. The partitioning behavior of copper may not be explained simply by the higher concentrations of ER phases in the Jackman area (as suggested for the other metals) since it is the MR phases that show a different association with copper. Therefore, other reasons for copper partitioning behavior will be explored below.

In summary, normalized Cr partitioning data is found to have a larger range of associations with the three phases in Maine than is found in the Grand River, Michigan, and normalized Cu, Ni, Pb, and Zn partitioning data are found to have a greater association with MR phases in Maine than in the Grand River. Since the manner in which a metal clusters is related to the proportionating of metal concentrations with substrate concentrations, it is hypothesized that variability in the substrate concentrations of the Maine samples may be influencing the cluster patterns on the ternary diagrams.

Significant differences in substrate concentrations (especially ER phases) in the Maine sediments would be magnified by the normalization procedure. Since this type of research is attempting to model metal behaviors, statistical variations among the concentrations of substrates in the Calais, Jackman, and Topsfield areas may explain some of the differences in partitioning behaviors of metals in the Maine and Grand River sediments. It may also be necessary to take

a close look at the normalization procedures to see if they impart a significant influence on the metal partitioning behaviors. The program Statgraphics (made by Statistical Graphics Corp., 1986) was used on a Zenith 158 PC to perform statistical tests on substrate concentration data.

Differences in substrate concentrations

Three questions must be addressed in studying the effect of substrate concentrations and normalization on metal partitioning behaviors: 1) are there substrate concentration differences between the three areas of Maine which cause the variance from the Grand River study? 2) are there differences in the absolute and relative substrate concentrations of the Grand River sediments in comparison with the Maine sediments? and 3) does the normalization of metal partitioning data actually take into account the differences in substrate concentrations? These questions will be looked at in the following discussion.

<u>Substrate data:</u>

The concentration values for the ER, MR, and OX phases in the study by Gephart (1982) were calculated in the same manner as described in Chapter Four of this paper. Table 4 shows the summaries of descriptive statistics determined from estimated substrate concentrations by Gephart (1982) for the 27 Grand River samples. This table shows results for both raw values and for log base 10 values. It was determined by a Chi-squared goodness of fit test (see Appendix 4) that these three phase concentrations are Table 4: Summary statistics for raw phase concentrations and log phase concentrations in Grand River sediments.

Raw Values (ppm)

	ER phases	MR phases	OX phases
Sample size	27	27	27
Mean	558	6442	14768
Median	365	6592	10120
Variance	3.17E5	1.14E7	3.12E8
Stan. dev.	563	3374	17667
Stan. error	108	649	3400
Minimum	24	2195	748
Maximum	2820	12237	88000
Range	2796	10042	87252
	Lo	g Values	
•••••••	ER phases	MR phases	OX phases
Sample size	27	27	27
Mean	2.59	3.75	3.88
Median	2.56	3.82	4.00
Variance	0.16	0.06	0.31
Stan. dev.	0.40	0.25	0.56
Stan. error	0.08	0.05	0.11
Minimum	1.38	3.34	2.87
Maximum	3.45	4.09	4.94
Range	2.07	0.75	2.07

approximately lognormally distributed.

The descriptive statistics (raw and log base 10) for the three phase concentrations for the 61 samples from Maine are shown in Table 5. The Chi-squared goodness of fit test (see Appendix 4) suggests that the three phase concentrations are also approximately lognormally distributed. The descriptive statistics of phase concentration data from each of the three areas sampled in Maine are shown in Table 6.

As stated in guestion 1 above, one cause for the variability of metal behaviors between sediments in Maine and the Grand River, Michigan may be that three areas in Maine with varying geology and stream sizes and types were sampled. If the substrate concentrations in the three areas in Maine come from more than one population (for example, if the concentrations are significantly different), this may be a reason why the Maine metal data are clustered differently than the Grand River metal data. To test this, a one-way analysis of variance (ANOVA) was done with log phase data from the three sampling areas in Maine. The ANOVA table for the OX phases (Table 7) was interpreted to show that the mean concentrations for the three areas in Maine are not significantly different (P >> .05, where P represents the 95% confidence level). The ANOVA for the MR phases (Table 8) was interpreted to show that these means are significantly different (P < 0.05). The ANOVA for the ER phases (Table 9) shows that the means are significantly different (P <<

Table 5: Summary statistics for raw phase concentrationsand log phase concentrations in Maine sediments.

	ER phases	MR phases	OX phases
Sample size	61	61	61
Mean	4634	14076	31431
Median	819	13408	23100
Variance	7.66E7	7.36E7	7.30E8
Stan. dev.	8750	8577	27026
Stan. error	1120	1098	3460
Minimum	118	2515	2420
Maximum	35128	41290	149600
Range	35010	38765	147180
	Lo	g Values	
	ER phases	MR phases	OX phases
Sample size	61	61	61
Mean	3.12	4.06	4.38
Median	2.91	4.13	4.36
Variance	0.43	0.08	0.11
Stan. dev.	0.65	0.29	0.33
Stan. error	0.08	0.04	0.04
Minimum	2.07	3.40	3.38
Maximum	4.55	4.61	5.17
Range	2.47	1.21	1.79

,

Raw Values (ppm)

Table 6: Summary statistics for the raw phase concentrations (ppm) for each of the three areas sampled in Maine.

.	ER phases	MR phases	OX phases
Sample size	9	9	9
Mean	1085.2	15111.1	25691.1
Median	607.2	13760	19360
Variance	1.19E6	5.61E7	1.53E8
Stan. Dev.	1090.7	7492.9	12383.1
Stan. Error	363.6	2497.6	4127.7
Minimum	283.2	5760	15620
Maximum	3170	32416	49280
Range	2886.8	26656	33660
		Topsfield Area	
	ER phases	MR phases	OX phases
Cample dize	13	13	13
Mean	498 3	8806 2	50580 8
Median	450.5	7328	36250
Variance	67798 7	3 9287	2 1 AE9
Stan Dev	22250.7	5,52B7 6257 1	46298 3
Stan Prror	69 7	1735 A	12840 8
Minimum	17A Q	2515 2	2420
Marinum	1025 6	2512.2	149600
Range	850.8	23468.8	147180
•		Jackman Area	
	ER phases	MR phases	OX phases
Sample Size	39	39	39
Mean	6831.1	15594.2	26332.3
Median	1783.6	15584	22660
Variance	1.07E8	7.99E7	2.83E8
Stan. Dev.	10335.5	8936.3	16816.1
Stan. Error	1655.0	1431.0	2692.7
Minimum	118	2764.8	2860
Maximum	35128	41280	83600
Range	35010	38515.2	80740

•

<u>Calais Area</u>

Table 7: ANOVA for Maine log oxidizable phase concentrations.

One-way Analysis of Variance

Number of Groups: 3 (Jackman, Calais, and Topsfield Areas) Confidence Level: 95

	Anal	ysis of	Variance		······
Source of Variation	Sum of Squares	d.f.	Mean Square	F-ratio	Sig. Level
Between groups	0.18623	2	0.09312	0.850	0.4327
Within groups	6.35527	58	0.10957		* _
Total	6.54150	60			
Table 8: ANOVA conce	for Mainentrations	e log m •	oderately red	ucible ph	ase
	Ana	<u>lysis o</u>	f Variance		.
Source of Variation	Sum of Squares	d.f.	Mean Square	F-ratio	Sig. Level
Between groups	0.64273	2	0.32136	4.375	0.0170
Within groups	4.25997	58	0.07345	·····	* -
Total	4.90270	60			
Table 9: ANOVA conce	for Mainentrations	e log e	asily reducib	le phase	
	Ana	lysis o	f Variance		_ _
Source of Variation	Sum of Squares	d.f.	Mean Square	F-ratio	Sig. Level
Between groups	5.36605	2	2.68302	7.679	0.001
Within groups	20.26521	58	0.34940		# -
Total	25.63126	60			

.

0.05). This may be explained by the fact that there were a number of very high concentrations of ER and MR phases in the Jackman Township Area, which was described above.

Since the phase concentrations in Maine sediments are only approximately lognormally distributed, the nonparametric Kruskal-Wallis analysis was also done to compare the three areas in Maine. In this analysis, the data are ranked from smallest to largest, the ranks are summed for each sample, and a test statistic value is calculated and compared with tabulated values from a Chi-squared distribution. The results of this analysis for the three phases are summarized in Table 10. These results are interpreted to show that the means for the OX phases from the three areas are not significantly different (P > 0.05) while the means for the ER and MR phases are significantly different (P < 0.05). These results are similar to those of the ANOVA.

Therefore, it has been found that there are statistically significant differences in substrate concentrations between the three areas sampled in Maine, suggesting that three distinct populations were sampled. This may be a cause for the variance seen between the two studies.

To address question 2, the absolute (raw) and relative (percentage) concentrations of the substrates will be compared for the Maine and Grand River studies, and compared among the three sampling areas in Maine. The phase

Table 10: Kruskal-Wallis analyses for log phase concentrations in Maine sediments. Number of Levels: 3 (Jackman, Calais, and Topsfield Areas) Confidence Level: 95 Kruskal-Wallis analysis of Log Ox phases Level Sample Size Average Rank 39 29.2949 Jackman Calais 9 28.5000 Topsfield 13 37.8462 Test statistic = 2.47207 Significance level = 0.2905 Kruskal-Wallis analysis of Log MR phases Level Sample Size Average Rank Jackman 39 34.3462 9 Calais 34.2222 Topsfield 13 18.7308 . Test Statistic = 7.89209 Significance level = 0.019331 Kruskal-Wallis analysis of Log ER phases Level Sample Size Average Rank 39 36.8718 Jackman 9 Calais 25.2222 Topsfield 13 17.3846 .

Test statistic = 12.8662 Significance level = 1.60743E-3

concentration values in both studies have approximately lognormal distributions. The medians rather than the means will be used as measures of central tendency (Sokal and Rohlf, 1969) to compare substrate concentration data, because a few very high concentration values tend to bias the mean values (Sokal and Rohlf, 1969). Also, the larger values for phase concentrations have been suggested to influence metal partitioning in the normalization procedure.

In the Maine sediments, the median absolute concentrations of the three phases were almost twice as large as the concentrations found in the Grand River sediments (Table 11). However, the relative concentrations of phases (calculated as percentages) for the two study areas are very similar:

Maine		<u>Grand River</u>					
ER	=	2.2%		ER	=	2.1%	
MR	z	35.9%		MR	=	38.6%	
ox	=	61.9%		ох	=	59.3%	

.

Since the partitioning behaviors of the metals among the adsorbing phases between the two study areas are very similar, and the relative abundances of the phases are also quite similar, this suggests that the relative abundances of a phase are more important than the absolute abundances in controlling metal partitioning.

To address question 3, the process of normalization will be examined by looking at how metal partitioning behaviors in the three areas in Maine are affected by Table 11: Comparison of sediment phase concentrations (ppm) for Maine streams and the Grand River, Michigan.

Median Values

	<u>Maine</u>		<u>Grand Ri</u>	<u>Grand River</u>	
Phase Type	Conc.	Rel. %	Conc.	Rel. %	
Easily Reducible	819.0	2.2	365.0	2.1	
Mod. Reducible	13408.0	35.9	6592.0	38.6	
Oxidizable	23100.0	61.9	10120.0	59.3	

normalizing the data. The absolute and relative abundances of substrate concentrations for each of the three sampling areas in Maine are shown in Table 12. The absolute abundances for the substrates from the Topsfield area are quite different from the Calais and Jackman substrate concentrations. The relative percentages for the substrates in the Topsfield area are also different from the Calais and Jackman areas (%ER and %MR in Topsfield are lower than in the other two areas, and %OX in Topsfield is higher than the other two areas).

Although the relative percentages for substrate concentrations in Topsfield differ from the other two areas, the partitioning data for the Topsfield and Calais areas have been shown to cluster similarly on the ternary diagrams. Therefore, it in concluded that in spite of substrate concentration differences among sampling areas, there are still similarities in metal partitioning behaviors.

Variability in substrate or metal concentrations is reduced by normalization, but very low substrate concentrations will have higher apparent associations with metals simply because of the calculation technique. However, normalization does not appear to influence the partitioning of the data on ternary diagrams, even if absolute and relative concentrations of substrates vary.

When the Maine results for Cu partitioning are compared with the Grand River results, Cu has a higher association

Table 12: Comparison of sediment phase concentrations (ppm) for three sampling areas in Maine.

Median Values

Calais Area

Phase Type	Conc.	<u>Rel. %</u>
Eas. Reducible(ER)	607.2	2
Mod. Reducible(MR)	13670	41
Oxidizable(OX)	19360	57
	Topsf	ield Area
ER	463.2	1
MR	7328	17
ox	36250	82
	Jack	man Area
ER	1783.6	4
MR	15584	39
ox	22660	57

with MR phases in Maine sediments. This is not explained by the substrate differences and the discussion above which addressed the three questions. Since it was found that large concentrations of substrates can affect normalization and also the partitioning behaviors depicted on ternary diagrams, it was hypothesized that perhaps large metal concentrations would also affect metal partitioning.

In Appendix 3, which has a tabulated listing of the raw metal concentrations found for each of the five chemical extractions, all samples with very high concentrations of Cu in the hydromorphic fraction (> 100 ppm whole rock) were isolated and are listed in Table 13. This concentration of Cu was chosen because it was equal to the mean of the highest concentrations of Cu that were found in the residual phases (i.e. Cu with an origin in mineralization) from all areas sampled in Maine. Of the 17 samples with high Cu concentrations, 15 (88%) of these were found to be highly associated with MR phases on the ternary diagram. However, these 15 samples represent only 38% (15 out of 40) of the total number of samples which show the high association of Cu with the MR phases.

This leaves 40 of the 61 samples (66%) which have a high association with MR phases, but these 40 samples do not have a high Cu concentration, so high Cu concentrations do not explain all of the variability. The difference in Cu behavior between Maine and the Grand River studies may be caused by the source of the metal, since Cu in the Grand

Table 13: List of samples with high concentrations of copper (> 100 ppm) in the hydromorphic phases.

<u>Calais Area:</u>	Topsfield Area:	<u>Jackman Area:</u>
Cal-2	Tom-1	Jac-14
Cal-6	Tom-3	Jac-16
	Tom-4	Jac-17
		Jac-19
		Jac-21
		Jac-22
		Jac-23
		Jac-27
		Jac-28
		Jac-31
		Jac-33
		Jac-35

.

.

River is more likely to have come from an anthropogenic source while Cu came from a natural source of weathered rock (especially mineralized zones) in Maine. However, the effects of mineralization were not explored in this study. The literature suggests that an association of Cu with MR phases (especially Fe-oxides) is not uncommon in experimental and field studies (to be discussed below).

The following findings were made from the comparison of the Grand River and Maine substrate data:

1. The substrate concentration data from the Grand River and Maine study areas are approximately lognormally distributed.

2. Both analysis of variance and Kruskal-Wallis analysis show that the OX phase concentrations for the three areas sampled in Maine are not significantly different, and the concentrations for the ER and MR phases are significantly different.

3. In a comparison of the substrate concentrations of the Gephart (1982) study and this study, the absolute concentrations are different, but the relative concentrations are guite similar.

4. In a comparison of the substrate concentrations among the three areas sampled in Maine, the absolute and relative abundances of substrates in one area (Topsfield) are different from the other areas (Calais and Jackman). However, metal partitioning behaviors in sediments of Topsfield and Calais are very similar.

5. The analyses of variance and Kruskal-Wallis analyses are interpreted to mean that the ER and MR phase concentrations are significantly different among the three areas studied in Maine. This could be caused by some very large concentrations of these phases which are found in the Jackman Township Area.

6. The normalization technique is not weighted on the ER phase concentrations in Maine sediments, as it is in the study by Gephart (1982). In some samples, ER phases made up a large fraction of the sediment in Maine. This could explain why there is an even clustering of Ni, Pb, and Zn between the ER and MR phases on the ternary diagrams (Figures 10, 11, and 12 respectively). This is different than the results of Gephart (1982), where these metals are mostly distributed among the ER phases.

In conclusion; 1. there are significant differences in ER and MR substrate concentrations which may cause the variability in the results of the Maine and the Grand River studies; 2. the absolute abundances of substrates are not as important as relative abundances in controlling metal partitioning; and 3. the process of normalization is able to take substrate concentration differences into account in the

construction of ternary diagrams to depict partitioning behaviors.

Metal Behaviors and Past Research

The partitioning behavior of chromium has been discussed by Gephart (1982). Cr data is mainly associated with the MR phases in the raw data, but normalized data show a significant association of Cr with the ER phases. This is supported by other studies of Cr in natural sediments (Moore et al, 1984) where the adsorption of the Cr^{+6} species by iron oxides is dominant in natural waters with a pH between 6 and 8, while at the same time the adsorption of the Cr^{+3} species by manganese oxides and subsequent oxidation to Cr^{+6} can also take place (Leckie et al., 1980).

Copper, zinc, lead, and nickel are adsorbed by Mnoxides in the ER fraction. Using nine synthetic manganese oxides, McKenzie (1980) found that all of these oxides have a higher association with lead than with copper, zinc, and nickel. This was suggested as the reason that lead is found accumulated in the manganese oxides of soils. The results of lead adsorption on natural Mn-oxides in Maine and the Grand River differ from the results of McKenzie (1980) with lead not as highly associated with Mn-oxides as copper, zinc, and nickel. However, the use of synthetic manganese oxides in laboratory adsorption experiments may not be representative of the adsorption of metals in many natural systems, since there are many other factors which must be considered. Catts and Langmuir (1986) recognized that the application of the

results of adsorption experiments with synthetic oxides to adsorption on natural manganese oxides is somewhat tenuous and cannot predict the magnitude of changes in metal adsorption accurately.

For the study of stream <u>particulates</u> and <u>coatings</u> by Filipek et al., 1981 in the vicinity of a polymetallic sulfide deposit, <u>particulate</u> organics also were associated with the highest absolute concentrations of copper and zinc (as found by McKenzie, 1980), while lead was mostly associated with Mn-oxides. However, a competition analysis and normalization technique determined the following sequences for the relative importance of the association of coating phases with a metal: for Cu, organics > Fe-ox > Mnox, for Zn, Mn-ox = organics > Fe-ox, and for Pb, Fe-ox > organics > Mn-ox. These differed from the partitioning of metals in the particulates and from the results from Maine and the Grand River. However, if the phases extracted in the Maine and Grand River studies are considered a mixture of coatings and particulates in the sediment, the partitioning results that are found in these studies are similar to the results of the study by Filipek et al. (1981) which are shown above.

In the results from Maine, the high association of MR phases (including Fe-oxides) with copper was different than the copper distribution found by Gephart (1982) in the Grand River sediments. However, an association of copper with Feoxides after normalization to equal amounts of phases has

been noted in a number of other studies. Filipek and Owen (1979) found that the moderately reducible fraction of Little Traverse Bay sediments showed a moderate association with copper, containing an average of 24% of the nonlithogeneous copper. In stream sediment near a porphyry copper deposit in Arizona, 56% of the total normalized copper among the Mn-oxides, Fe-oxides, and oxidizable phases was found associated with the Fe-oxides (Filipek and Theobald, 1981).

The <u>non-normalized</u> distributions of metals that were found in Maine show a similarity to the adsorption characteristics of estuarine particulate matter studied by Lion et al. (1982). In that study, 65% of the copper was associated with the oxidizable phases (compared with 72% for Maine sediments) and 70% of the lead was associated with the reducible phases (compared with 76% for Maine sediments). The same types of chemical extractions were used in each of these studies.

Forstner and Patchineelam (1980) looked at the normalized partitioning of metals in the polluted sediments of the Rhine River and found lead, copper, and chromium mostly associated with MR fraction, zinc and copper associated with the ER fraction, and copper and lead associated with the OX fraction. These results are very similar to the normalized results from the sediments in Maine as well as those of Gephart (1982).

The raw data distributions of the 5 metals studied in Maine are also similar to the distributions found by Tessier et al. (1980) in the Yamaska and St. Francois Rivers of Quebec. Among hydromorphic fractions (exchangeable, carbonates, Fe-Mn oxides, and organics) non-normalized copper was mostly associated with organics (60%) and Fe-Mn oxides (23%), nickel was mostly associated with the Fe-Mn oxides (65%), lead was associated mostly with Fe-Mn oxides (56%) and organics (23%), and zinc was associated mostly with the Fe-Mn oxides (59%) and very little with the organics (8%). In the Maine hydromorphic fractions, the percent associations of non-normalized metal data are: copper with organics (72%) and Fe-Mn oxides (28%), nickel with Fe-Mn oxides (60%), lead with Fe-Mn oxides (80%) and organics (20%), and zinc with Fe-Mn oxides (86%) and organics (145). Similar results were found for another stream in Quebec which was located near a rock zone with Zn-Cu-Pb mineralization (Tessier et al., 1982).

Moore et al. (1984) have also found similar partitionings for non-normalized data for copper, zinc, nickel, and lead, especially result of the low concentrations of lead, zinc, and nickel associated with organic matter (5-10% for lead, 10% for nickel, and < 5% for Zn). Chromium was distributed among exchangeable (1.1%), easily reducible (2.7%), oxidizable (28.3%), and moderately reducible (67.9%) phases. These are similar to the percentages found in Maine for chromium.

Chapter Six

Conclusions

The impacts of particle-bound metals on bioavailability in natural systems are difficult to predict because of the differences that occur when metals are bound to different binding sites on particle phases. However, quantitative methods for describing metal partitioning among binding sites in natural sediments have not yet been developed. Quantitative descriptions in the past have involved the use of selective chemical extractions which remove heavy metals from sediment phases.

At equilibrium, the partitioning of a heavy metal ion among adsorbing substrates at the water-sediment interface is believed to be influenced or controlled by: 1) the binding capacity of each substrate or operationally defined phase; 2) the binding intensity of each metal ion to each phase; 3) the absolute abundance of the adsorbing phases in the sediment; and 4) parameters such as the pH, pe, temperature, and the concentrations of major cations and anions (Luoma and Davis, 1983).

The development of quantitative partitioning models will require the use of some assumptions regarding the binding characteristics of adsorbing phases, with concentrations of these phases measured by operational techniques (chemical extractions). Presently these techniques for studying metal partitioning are the only

suitable methods that provide consistent results in multicomponent, natural systems.

A major objective of this type of research is to quantitatively define natural water-sediment systems, in order to make predictions on how a metals in these systems will behave under certain environmental conditions. Attempts to accomplish this have involved measurements of as many conditions as possible in the natural system, and have reduced the amount of variability to the extent that the important controls on the system can be identified. The next step is to predict how the behavior of the specific component may be altered when these controls are changed. An important portion of the study of an aqueous system is the partitioning of the components adsorbed on surface sites at the water-sediment interface. This has been the focus of my study, and is important because systematic trends in natural metal distributions in sediments can be depicted with these methods and are consistent with metal behaviors determined from studies of other natural systems and from experimentation. This may help lead to the development of quantitative models of metal adsorption in natural systems.

The conclusions for this study are: 1. Using chemical extractions and the normalization of metal concentrations to equal amounts of adsorbing phases, distinctive cluster patterns for metal partitioning behaviors in natural systems can be depicted on ternary diagrams.

2. The additions of anthropogenic versus natural sources of chromium, copper, nickel, lead, and zinc show similar clustering patterns, and these partitioning behaviors are consistent with the results of other studies on adsorption behaviors for these metals.

3. An evaluation of the normalization of data to equal amounts of substrates has shown that large ranges of values in substrate concentrations can cause a bias towards the least abundant component in the depiction of metal partitioning on a ternary diagram. However, the patterns of metal behavior can still be interpreted in light of adsorption theory and experimentation.

4. A comparison of the absolute and relative concentrations of adsorbing phases in the Grand River sediments with the three sediment sampling areas in Maine has shown that the absolute abundances of an adsorbing phase are apparently not as important as the relative abundances in controlling metal partitioning.

5. Although distinct metal behaviors are indicated on the ternary diagrams, normalized data on the diagrams do not quantify the data sufficiently to be used alone in predicting metal behaviors in various water-sediment environments. The effect of other quantifiable factors on metal partitioning behaviors depicted on ternary diagrams should be analyzed.

APPENDIX 1: Geochemistry of Heavy Metals

APPENDIX 1

Geochemistry of Heavy Metals

Our understanding of the behavior of heavy metals in natural aqueous systems will be very important as we increase industrial metal additions to our environment. The behavior of metals in adsorption/desorption reactions are a function of many variables, including their basic chemistry in natural geologic systems. Therefore, it is important to evaluate geochemical characteristics of metals in order to adequately model and predict adsorption behaviors.

Metal atoms are characterized by their tendency to form positive ions (Murray and Dawson, 1980). As a class of solid substances (i.e. "metal"), they have properties of high electrical and thermal conductance, reflectivity, and mechanical strength and ductility (Cotton and Wilkinson, 1980). One exception to this is metallic mercury, which is a liquid at standard temperature and pressure. Most metals exist in the form of compounds and minerals.

There are four main categories of metal ores: 1. Highly electropositive metals (Group IA: Li, Na, K, Rb, Cs; and Group IIA: Be, Mg, Ca, Sr, Ba) are primarily found as salts such as halides, sulfates, nitrates, and carbonates. Group IIA elements are most abundant as sulfates and carbonates. 2. Aluminum and the more electropositive transition elements (Sc, Ti, V, Cr, Mn, Y, Zr, Nb, La) form naturally-occurring oxides. 3. Other transition elements (Co, Ni, Cu, Zn, Cd, Hg), Group IIIA elements (Ga, In, Tl), and Group IVA

elements (Ge, Sn, Pb) are usually found as sulfide minerals. 4. Relatively unreactive metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) occur naturally as free metals or in a compound (such as a sulfide, AgS, or substituting for another element in a mineral, such as Rh-rich molybdenite) (Murray and Dawson, 1980).

Goldschmidt (1954) formed a set of rules to describe the distribution of elements in the earth's crust. Primary distribution was interpreted to show that most elements can be classified in the following groups: <u>siderophile</u> if they are relatively inert and commonly exist with native iron (includes Group VIII elements Fe, Co, Ni, etc and Mo, Ge, Sn), <u>lithophile</u> if they characteristically are found concentrated as silicates (Groups IA, IIA, IIIB, and IVB including Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, W, Mn; also O, halides and rare-earth elements), <u>atmophile</u> if found as natural gases (for example H, N, C, O, halides, and inert gases), and <u>biophile</u> if they are enriched in organisms (includes many elements common in all the other groups) (Goldschmidt, 1954; Krauskopf, 1979).

For the secondary distribution of elements (especially heavy metals, which for this paper are considered to be the first row transition elements), Goldschmidt (1954) believed that the behavior of an element in the formation of crystal lattices was controlled by their ionic radius. Three general rules were empirically deduced: 1. If two ions have the same radius and charge, they will be incorporated into a crystal

lattice with equal facility. 2. If two ions have the same charge and similar radii, the smaller ion will be preferentially incorporated and will form a stronger bond. 3. If two ions have similar radii but different electrical charge, the more positively charged ion will be preferred and will make the stronger bond (Burns, 1970; Mason and Moore, 1982).

Although these principles helped to explain some of the trends in trace metal distributions in rocks and minerals, there were several exceptions to Goldschmidt's Rules, such as the behavior of zinc in ferromagnesian silicates (Burns, 1970). Although zinc and iron have identical charge and ionic radii, zinc can substitute for either iron or magnesium (magnesium has a smaller ionic radius) (Wedepohl, 1969). Ringwood (1955) modified these rules with the deduction that the relative bond strengths of ions in crystal lattices can be based on their respective electronegativity. If two ions have similar ionic radii and electric charge, the ion with the lower electronegativity value will be preferentially incorporated into the lattice and will form a stronger, more ionic bond than the other ion (Burns, 1970).

These rules by Goldschmidt (1954) and Ringwood (1955) lack generality in interpreting trace element distributions, particularly with the heavy metals. For example, the geochemical distribution of nickel in magmatic crystallization is unusual and cannot be explained by its

ionic radius and electronegativity alone. Nickel would be expected to behave like magnesium since it has essentially the same radius and charge. However, nickel behaves as if its effective radius were less than that of magnesium, which can be observed by comparing unit cell lengths of Ni_2SiO_4 (281 Angstroms) and Mg_2SiO_4 (292 Angstroms) (Mason, 1966). For reasons such as this, other chemical properties have been applied to more accurately describe metal distribution behaviors.

The crystal field theory (CFT) of chemical bonding in transition metals has been used to help explain heavy metal behaviors that are exceptions to the above rules. CFT assumes that the only interactions between metal ions and ligands are electrostatic ones (Huheey, 1972). The angular distribution of electron density about a nucleus in terms of wave functions can best be represented by molecular orbitals.

The partial filling of the 3d orbitals with electrons characterize the first row transition elements. Induced magnetic and electric fields by coordinating ligands can cause an energy separation of the normally degenerate orbitals. In this case, ions with the same charge can each have different crystal field stabilization energy (CFSE) and therefore may form different types of complexes. Differing energy environments cause a unique energy separation (or crystal field splitting) for each transition metal. The magnitude of the splitting is dependent on: 1. Valence of

the ion. 2. Nature and type of coordinating ligands. 3. Interatomic distance. 4. Symmetry of the coordinating ligands (Burns, 1970; Huheey, 1972).

Evidence for the importance of CFSE can be seen in making predictions of the lattice energies for heavy metals. Predictions were good for Mn^{+2} and Zn^{+2} , for example, but discrepancies for the metals Cr^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , and Cu^{+2} were all explained by CFT. CFT also explains unusually stable aqueous complexes that have been found. Although aqueous Co^{+3} is thermodynamically unstable and is easily reduced to Co^{+2} by water, if certain ligands are present in an aqueous solution, Co^{+3} is a perfectly stable ion (Huheey, 1972).

In summary, the distributions of heavy metals in geochemical systems are related to ionic size, charge, and bond character. The unique d-orbital bonding properties of transition elements facilitates the interpretation of their geochemical behavior in rock and sedimentary environments. However, metal behaviors are also controlled by the physical and chemical properties of the environment. For example, in an aqueous system, some of the important conditions to consider include the system's oxidation-reduction potential (pe), pH, temperature, solution-mineral equilibria, aqueous complexation, aqueous ion speciation, and elemental and hydromorphic adsorbent concentrations (Stumm and Morgan, 1981). The prediction of the behavior of a metal in any system is dependent on the quantification of these factors.

APPENDIX 2: Adsorption Theory and Experimentation

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APPENDIX 2

Adsorption Theory and Experimentation

One important objective of this study is to interpret the metal adsorption behaviors which are found using the techniques of Gephart (1982) in light of current metal adsorption theory and the results of laboratory experimentation. By doing this I will assess the ability of these techniques of chemical extractions and normalization of partitioning data to describe metal partitioning in natural systems. This is a necessary step if we are able to develop models for predicting metal adsorption in multisubstrate systems.

Adsorption Theory

At a liquid-solid interface (or water-sediment interface in this study), adsorption can be described as an attachment of solute ions to the surface of the solid. Although there is no generally accepted model for adsorption that explains all observed surface phenomena, several models have been developed and refined that can account for many experimental observations. Two accepted principles in adsorption theory are that the solid-solution interface has an associated surface charge and an electric potential gradient that extends from the interface into the liquid (or solution) (Leckie et al., 1984). Adsorption can be referred to as non-specific (electrostatic bonding) or specific (caused by London-van der Waals forces, covalent bonding, hydrogen bridges and bonding, hydrophobic bonding, steric

effects, or specific ion effects that form a charged surface).

The surface charge on a solid which will be a potential binding site for dissolved ions can originate in three ways: 1. Chemical reactions which involve the surface and ionizable functional groups on dissolved species. Some of these functional groups are -OH, -COOH, and $-OPO_3H_2$. The charge that results is strongly dependent on the pH of the solution. A more basic pH will tend to form a negatively charged surface. A more acidic pH will form a positively charged surface. 2. Lattice imperfections at the solid surface can result in isomorphic replacement of atoms by similarly sized ions with a different charge. This will cause a charge imbalance which can be satisfied by the attraction of charged aqueous ions to the surface site. For example, Al^{+3} could replace Si^{+4} in an array of SiO_2 tetrahedra and result in a positive charge deficiency and potential binding site. 3. The adsorption of a surfactant ion can produce a surface charge. These ions may be bound by London-van der Waals force interactions and hydrogen or hydrophobic bonding (nonspecific adsorption), such as with some organic surfactant ions. The binding site available to charged solute ions is made up of the charged, adsorbed surfactant ion bound to the solid surface. These surface charge sites are examples of nonspecific adsorption.

The electrical potential gradient for an interface is usually defined by a pair of ions that are present on the

surface and in solution, and are called potentialdetermining ions (PDIs). On an oxide surface, for example, H⁺ and OH⁻ are usually chosen for the PDIs. Each system has a condition at which both the PDIs (at unique concentrations) are equally adsorbed, known as the zero point of charge (ZPC). For an ideal system, the surface charge and surface electric potential gradient are zero at the ZPC. ZPC is expressed as a pH for solid phase oxides. Ideally, when solution pH is greater than the oxide ZPC, the oxide surface will have a negative charge, and when solution pH is less than the oxide ZPC, the surface will have a positive charge. Ions of opposite charge in solution will be attracted to the charged surface (Leckie et al., 1984).

The distribution of charges, ions in solution, and an electrical potential at the solid-solution interface make up an electric double layer (EDL). One layer is the fixed or surface charge of the solid and the other layer is the diffuse distribution of charged ions in solution. This is referred to as the Guoy-Chapman diffuse charge model, and considers only electrical interactions. Charged ions in the diffuse layer can be counterions (opposite charge of the surface) or co-ions (same charge as surface).

Stern (Grahame, 1947) refined this theory to account for nonelectrostatic adsorption. Specifically adsorbed ions are closest to the fixed charge layer (or they account for the charge themselves) and form the "Stern Layer". Ions in the Stern Layer can be subjected to electrostatic and/or

specific interactions. Ions in the more diffuse, bulk solution extending from the surface make up the Guoy Layer. This was based on the hypothesis that an ion retains its hydration sphere during adsorption. Grahame (1947) refined the theory even further by suggesting that only specifically adsorbed ions (resulting from non-electrostatic interactions) can lose their hydration spheres in their approach to the surface. Together, these are referred to as the Guoy-Chapman-Stern-Grahame (GCSG) adsorption model, although it is still considered an oversimplification of surface phenomena (Leckie et al., 1984).

Further developments of this model by other workers have explained observed anomalies (such as the unusually large surface charge of metal oxide/solution interfaces), and the assumption of interfacial ion pair formation by adsorbed ions has led to the most refined model to date, known as the Stanford Generalized Model for Adsorption (SGMA) (Leckie et al., 1984). Another method to model adsorption is by studying the thermodynamics of adsorption reactions (James and Healy, 1972). The total free energy of adsorption (ΔG_{ads}) was hypothesized to be the sum of three components: electrostatic work (ΔG_{coul}), total specific adsorption energy (ΔG_{chem}), and the change in secondary solvation energy (ΔG_{solv}).

Adsorption Experimentation

The adsorption of heavy metals by organic matter and hydrous metal oxides in sediments is usually described in
the context of the above theories. Hydrous oxides of iron and manganese have a pH-dependent surface charge which enables them to adsorb heavy metal ions (Jenne, 1968). Adsorption by organic matter is more complex. Organic matter can be regarded as having three components: humic acids (soluble in basic solutions), fulvic acids (soluble in both basic and acid solutions), and insoluble humins. There are no distinct divisions among these three, as all are part of a heterogeneous polymer system of molecules. Basic differences to distinguish between them are in elemental composition, acidity, molecular weight, and degree of polymerization. Reactive functional groups on these molecules include carboxyl, phenolic and alcoholic hydroxyls, methoxyl, carbonyl, and guinone groups. The negative charge of organic species is often due to the ionization of acidic carboxyl and hydroxyl groups. The charge can be neutralized by an interaction with a charged metal ion in solution. Attractive interactions could range from weak forces that make the metal ion easily replaceable (physical adsorption) to strong forces similar to chemical bonding (chemical or specific adsorption) (Jackson et al., 1978).

Studies by Gibbs (1977) and others have established the importance of hydromorphic phases as significant scavengers of heavy metals in stream and lake sediments, and in numerous laboratory experiments. Experiments with

synthetic and natural sediment phases have identified a variety of adsorption behaviors for heavy metals.

Krauskopf (1956) noted the importance of adsorption in controlling the distribution of a number of heavy metals in seawater, especially zinc, copper, and lead. The distributions of chromium and nickel were resolved to be controlled by organic reactions. Concentrations of heavy metals in freshwater sediments are significantly controlled by hydrous iron and manganese oxides (Jenne, 1968), organic molecules, and other hydromorphic phases such as clays, carbonates, and sulfides (Gibbs, 1977).

Hydrous manganese oxides are able to adsorb metal ions from solution quite rapidly in laboratory experiments when pH and ionic strength are controlled variables. Posselt et al. (1968) found that exchange reactions are a principle mechanism in metal uptake. Group I metals undergo nonspecific adsorption under electrostatic interactions. Manganese dioxides, which in colloidal hydrous form exhibit a negative surface charge within the pH range of 5 to 11, can have surface areas of 150 to 300 square meters per gram. The negative charge results from an increase in the ratio of OH⁻-bound to H⁺-bound ions, especially as pH increases. Heavy metals such as nickel, copper, and cobalt with smaller Cr ystalline ionic radii than Group I metals (and therefore 9^r eater hydrated ionic radii) appear to undergo specific ad sorption in which the metal ions exchange with H⁺ ions and

form stronger, bidentate bonds with adjacent surface-bound hydroxyl ions.

When zinc is adsorbed on manganese dioxide, it can replace Mn⁺² in the lattice, on the basis of crystal field theory, or it can interchange with bound H⁺ sites, in which 2 moles of H⁺ are released per 1 mole of Zn⁺² (Loganathan and Burau, 1973). However, although this suggests that crystal field stabilization energies control adsorption selectivity on manganese dioxides, the selectivity order of transition metals for manganese dioxides (Mn>Co>Cu>Zn>Ni) does not follow the Irving-Williams order (Zn<Cu<Ni>Co>Fe>Mn) and CFT is therefore not the only factor involved in metal ion selectivity (Murray, 1975).

Murray and Dillard (1979) investigated the oxidative properties of manganese dioxide. Co^{+2} can be readily oxidized to Co^{+3} , for example, when adsorbed at the MnO_2 solution interface. However, Ni^{+2} cannot be oxidized unless it is present at very high concentrations. This suggests a mechanism for the geochemical separation of NI and Co in surface aqueous systems. Lead can be readily adsorbed by MnO_2 and was hypothesized to be oxidized to form PbO_2. However, McKenzie (1980) found no evidence for the oxidation of lead on nine synthetic manganese oxides, and attributed the binding of lead to be caused by a special affinity of manganese oxides for lead, such as was found for cobalt. Lead appears to be more strongly adsorbed on many oxides than copper and zinc.

Catts and Langmuir (1986) studied the applicability of the site-binding model of the electric double layer to the adsorption of copper, lead, and zinc by synthetic manganese dioxides. Adsorption was controlled by surface reactions with divalent metal cations up to a pH of 6. At greater pH, metal hydroxide-complex reactions with the surface were a better fit with the model. In general, predicted behaviors fit experimental adsorption data, but were limited by a lack of quantification in predicting the magnitude of adsorption after changes in solution conditions. They suggested that equilibrium binding constants would have to be determined for conditions found in natural systems in order to be modeled. Features to be considered include ionic strength, sorbent concentration, surface characteristics, and competing metal concentrations. Streams with actively precipitating manganese oxides were suggested to best represent the optimum natural system to test the model.

Gadde and Laitinen (1974) found that there was appreciable adsorption of lead, cadmium, and zinc near the ZPC of hydrous manganese oxides. This was not expected since the surface charge at this pH is essentially neutral. This adsorption behavior was attributed to specific (nonelectrostatic) adsorption reactions. Similar behaviors were also noted for copper, nickel, and cobalt adsorption on hydrous manganese oxides in experimental studies, and also for lead and cadmium adsorption on hydrous iron oxides.

Metal adsorption can also be either enhanced or inhibited by the interaction of dissolved ligands and adsorbent surfaces. A ligand which is complexed with a aqueous metal ion may then be adsorbed at the surface and stay complexed with the metal to form a surface-ligand-metal adsorption complex. If a dissolved ligand is adsorbed onto a surface, it may also serve as a new adsorption site for aqueous metals on the surface or it may stabilize the surface binding site, thus inhibiting any adsorption of metal ions. A ligand may form a nonadsorbing complex in solution and compete with a substrate for coordination with a metal ion. It has been suggested that heavy metal distributions in natural systems may be controlled by a humic compound coating on oxide surfaces rather than simple metal reactions with oxide surface binding sites (Davis and Leckie, 1978).

The chemical modeling of heavy metal distributions is limited by the lack of knowledge of concentrations, identities of organic compounds, and stability constants for many metal-ligand and metal-surface interactions. Vuceta and Morgan (1978) examined chemical interaction and competition be tween metal ions and different components of natural waters in an experiment with controlled parameters. They us ed oxic fresh water with four major cations (Ca, Mg, K, Na), eight trace metals (Pb, Cu, Ni, Zn, Cd, Co, Hg, Mn, Fe), eight inorganic ligands (CO₃, SO₄, Cl, F, Br, NH₃, PO₄, OH) and a substrate with adsorption characteristics of SiO₂

(with calculated conversions to also represent $Fe(OH)_3$ and MnO_2). The investigation varied the following parameters: pH, types of adsorbing surfaces, surface area, and presence of organic ligands such as EDTA, amino acids, and citrate. This study stresses the importance of having a wellcharacterized environment in which to determine quantitative chemical adsorption behaviors of metals in natural aqueous systems.

Vuceta and Morgan (1978) found that dissolved Cu^{+2} will be expected to be substantially removed from solution by adsorption if complexing agents are absent or in very low concentrations. If organic ligands present in a solution have little affinity for Pb⁺², then the distribution of lead adsorption is dependent on the availability of substrate surface area. An increase in the substrate surface area and concentrations of organic ligands will cause an increase in the adsorption and complexation of Ni⁺², Co⁺², and Zn⁺².

It appears that the presence of both inorganic and organic complexing ligands may have a dramatic effect on heavy metal adsorption behaviors and on substrate surface Properties. Oxide surfaces can bind with either the metal or the ligand of a dissolved complex. By studying chloro- and sulfato- complexes of cadmium, Benjamin and Leckie (1982) found that if the metal end of a complex is adsorbed, a plot of percent metal adsorbed vs. pH is roughly parallel to that of a ligand-free system (but is shifted to a higher pH). If the ligand end is adsorbed, an increased ligand

concentration increases the amount of metal adsorbed in one pH range, while metal adsorbed decreases in a higher pH range. The adsorption behavior of complexes is apparently independent of the type of adsorbent, since similar results were found for a variety of substrates.

Solutions with high ionic strength would be expected to have a greater influence on the extent of adsorption than dilute freshwater. Using seawater, Balistrieri and Murray (1982) were able to estimate the binding energies of Cu, Pb, Cd, and Zn on goethite. The four metals showed no competition between each other for sites on the oxide. Although CO_3^{-2} , PO_4^{-2} , and SiO_2 had no effect on the adsorption of these metals, the concentration of Mg⁺² and SO_4^{-2} in solution did influence adsorption by competing with the metals for binding sites. The pH range of the "adsorption edge" for each metal ion is a function of substrate concentrations in a seawater system.

In a study of the adsorption of heavy metals on humic acids, Kerndorf and Schnitzer (1980) found a different binding strength sequence of metals for each of three different pH readings, 5.8, 4.7, and 2.4 (humic acids are insoluble at pH<6.5). At pH = 2.4, the order was Hg>Fe>Pb>Cu=Al>Ni>Cr=Zn=Cd=Co=Mn. At pH = 4.7, the order was Hg=Fe=Pb=Cu=Al=Cr>Cd>Ni=Zn>Co=Mn. At pH = 5.8, the order was Hg=Fe=Pb=Al=Cr=Cu>Cd>Zn>Ni>Co>Mn. They could find no COrrelations between the affinities of humic acids and metal at omic weights, atomic numbers, valencies, and crystal and

hydrated ionic radii. Apparently, metal ions compete with protons and with each other for the humic acid binding sites.

Robinson (1982) investigated the partitioning of copper and zinc adsorbed to five substrate coatings in stream sediments to determine important residence sites for the metals and to study the influence of stream water pH and metal concentration on the partitioning. The results show that over 90% of the total copper and zinc determined by selective chemical extractions of the coatings reside in manganese and iron oxide phases. He also concluded that stream water pH and metal concentration variations were not important in controlling the partitioning of the metals among the coating phases.

In the marine environment, the controlling mechanism of certain trace metal concentrations has been suggested to be adsorption by particles. Laboratory studies of adsorption often use natural particle phases or synthetic solids in well-defined solutions, such as seawater. The study of adsorption on synthetic solids has been primarily responsible for the development of surface adsorption theory. Balistrieri and Murray (1983) applied these concepts (which were developed using Cu, Cd, and Zn adsorption on we ll-defined goethite, FeOOH) to the interaction of Zn and ad sorbents in natural sediments to determine apparent equilibrium binding constants as a function of adsorption site density. They concluded that the calculated constants

are independent of density when sites are in excess, but are dependent on density when binding sites are in a limited quantity. This type of study is important because it shows that it is possible to quantitatively assess the role of adsorption in natural systems, even if the number of strong metal binding sites on phases may be small.

Leckie et al. (1984) studied competitive adsorption to determine the distribution and energy of surface binding sites, using Cd, Cu, Zn, and Pb in experiments with amorphous iron oxyhydroxides. Their results indicate that Cu has a smaller effect on the competitive adsorption of Cd than expected. This supports the hypothesis that there are discrete groups of binding sites and energies on oxide surfaces. Further experiments on high energy binding sites and competitive adsorption behaviors suggests that oxide surfaces also have large differences in site-specificity for individual metals.

Oakley et al. (1981) developed an equilibrium adsorption model to predict trace metal partitioning. Conditional equilibrium constants for Cu and Cd were determined using some artificial geochemical phases (bentonite, Fe(OH)₃, MnO₂, and humic acid) in seawater, which has fixed values for pH, pe, temperature, ionic strength, and major species concentrations. The thermodynamic modeling used mathematical equations identical with models of complexation and distribution of soluble metals among dissolved ligands. Although it was shown that

there is a potential for predicting metal adsorption behaviors from laboratory studies which derive equilibrium constants, experimental results are useful only for the experimental conditions and cannot be extrapolated to natural systems. However, adsorption experiments using natural sediment phases can be compared with the results using synthetic phases in order to test the applicability of laboratory-defined adsorption models, as discussed by Tessier et al., (1985).

In order to evaluate the characteristics of heavy metal-surface interactions, selective chemical extractions are often employed. Significant correlations have been found between the concentrations of trace metals extracted and the concentration of operationally defined sediment components, namely ion exchangeable phases, acid-soluble phases, easily reducible phases, moderately reducible phases, and oxidizable phases (Salomons and Forstner, 1984). Two Problems with the use of chemical extractions are 1) there is sometimes a lack of chemical specificity, and 2) there may be some alteration of phase-surface characteristics a fter the removal of extracted metals and/or components.

Lion et al. (1982) studied the role of iron/manganese \sim ide and organic surface coatings in the adsorption of Cd, \sim and Pb by estuarine particulate phases. The substantial = actions of Cd (50%) and Cu (65%) associated with \sim idizable organic coatings, and of Pb (70%) associated with = ducible coatings (Fe/Mn oxides) suggest that these

coatings are important in the binding of these metals to particulates. One important aspect of this study was the evidence that the use of extractant-determined metal/phase associations yielded consistent results on the binding of heavy metals, regardless of the flaws in the chemical extraction technique.

In summary, experimental studies of natural and synthetic adsorbents have shown: 1. The solution speciation of heavy metals may enhance or inhibit their adsorption onto mineral or organic surfaces. 2. The nature of the adsorbing phase or surface will determine the extent of metal adsorption.

3. Surfaces alone can adsorb metals (specific or nonspecific adsorption) and the nature of binding sites is quite variable. 4. Hydrous iron/manganese oxide and organic coatings on surfaces can also adsorb metals. 5. The environmental conditions of a natural system must be well characterized before heavy metal adsorption behaviors can be quantified.

6 - Chemical extractions are useful methods for determining
the partitioning of trace metals in sediments.

APPENDIX 3: Tabulated Metal Concentration Results and Stream Water Concentration Data

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SAMPLE	EXTR	FE	MN	CR	CU	2 N	NI	PB	PHASE
CAL-1	AS	106.6	91.2	1.6	3.3	26.4	2.8	30.8	CUNC.
	ER	159.3	17.8	0.3	0.5	5.0	0.3	0.5	283.2
	MR	3600	21.6	2.0	2.0	13.4	0.6	12.4	5760
	OX	570	9.2	3.2	49.8	7.8	2.6	6.0	44880
	RE	16600	1400	295	40	75	330	380	
CAL-2	AS	181.7	2688	1.7	64.7	76.8	3.8	39.6	
	ER	248.8	1732.5	0	28.3	30.8	1.0	22.0	3170
	MR	9280	536	3.6	96.8	55.6	2.0	140.4	14848
	OX	452	28.2	2.6	139.8	7.4	1.2	32.4	24200
	RE	33700	1630	370	80	100	325	400	
CAL-3	AS	424.5	528	2.3	4	38.4	3	127.1	
	ER	230.8	81	0.5	0.5	5.5	0.3	4.3	498.8
	MR	6280	56	1.6	2.4	21	1.8	144	10048
	01	686	14.2	2 8	37.8	8.4	2 4	38	49280
	RE	22400	1565	395	30	80	570	360	
CAL-4	ΔS	452.8	600	27	3.6	18.4	3.8	23.6	
	EP	320	1402 5	<u> </u>	0 5	4 5	0 3	<u> </u>	2756
	MD	9080	274	26	36	28 6	1 4	11	14528
	OY	582	2/3	2.0	22 5	5 8	1 6	5	19360
	DF	30500	1390	370	50	110	610	360	1,200
CAL-5	AC	20200	512	1 3	37	21 6	2 6	26	
	70 70	72.7	168 3	0	1	5	0 5	1	384 4
	MD	8600	204 2	2 6	<u> </u>	J 26 2	1 4	14 9	13760
		A26	15 9	2.0	20	20.2 5 A	1 4	5	19260
		340	1100	200	29	110	1.1	365	10200
CAL-6	KB Ng	20300	202	370	30 0	E2 C	735	305 21 0	
	AJ ED	JJ.2 172	JJZ 407 5	1.2	33.3	17 0	2.5	1 2	020 0
	er Md	12190	10/.5	2 2	20.0	70 2	0.0	2.3	10400
	MK OY	12100	230	J. Z	30.0	10.2	2.4	20 7 C	10260
		029 55700	29.2	4.4 5.45	223.3	0.0	1.0	7.0	T3 200
CAL-7	RE	55/00	2250	242	125	120	090	320	
	AS	12.5	130	Ţ	3	17.2	Ј 0 Е	20.3	220 2
	ISR MD	20.3	149.5	0	0.0	4.0	0.5	0.5	323.2
	MK OY	/180	227	2.2	0	4 U.2	2.0	14.2	10260
	UX DD	632	29.8	4	27.8	8.0	1.0	2.2	TA20 0
CAL- D	RE	44800	1940	455	70	120	445	345	
	AS	706.4	1000	3.5	1.1	22.4	2.9	20.1	
	ER	314	191.8	1	0.3	3.8	0.3	0.5	809.2
	MR	8540	252	4.2	0	40.4	3.8	7.6	13004
	OX	1178	47.8	6	8.5	9.2	4.8	12.8	20900
CAL-O	RE	39250	1310	420	50	120	460	440	
3	AS	187.2	264	1.5	3.9	19.5	3.4	24.5	
	ER	241.3	138.3	U	2.3	4	0.8	0.5	607.2
	MR	20260	113.4	Z	7.8	21.8	2.6	11.6	32416
	ΟΧ	1014	15.4	3	21.3	5.6	2.2	6.6	15620
	RE	50800	1740	505	65	95	500	350	

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All Values in parts per million (ppm). AS = Acid Soluble phases

- BR =
- Acid Soluble phases Basily Reducible phases Moderately Reducible phases Oxidizable phases Residual fraction MR =**∞ X**0
- RE =

SAMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE Conc.
TOM-1	AS	671.2	1304	3.3	25	37.6	5.4	25.8	
	ER	266.5	171.8	0	1.3	4.8	0.5	1.8	701.2
	MR	16240	256	1.8	30.8	21.2	4.4	22.6	25984
	ΟΧ	1044	31.8	4.4	151.3	8.2	3.2	12.8	60280
	RE	28300	1040	385	50	85	390	330	
TOM-3	AS	152	1312	1.1	4.4	32	3.2	32.1	
	ER	104.8	287.5	0.3	0.3	2.8	0.5	0.3	627.6
	MR	4860	342	0.8	5.8	32	1	29	7776
	ΟΧ	732	27.4	2	121	6	2.4	21	128260
	RE	8850	655	260	25	50	315	395	
TOM-4	AS	29.7	1032	1	4.4	32	3.2	32.1	
	ER	84.8	226	0	0.3	2.5	0.5	1	497.2
	MR	5500	245.4	0.8	3.4	32.4	1.8	19.8	8800
	οχ	814	37.2	2.6	117.5	8.2	2.6	10.8	88440
	RE	17000	760	305	25	55	390	360	
TOM-5	AS	30.7	624	1.3	1.5	16	3.2	24.6	
	ER	66.5	133.3	0.3	0.3	2.5	0.3	0	319.6
	MR	3720	124.2	2.6	0	12.8	0.8	5.6	5952
	οχ	468	15.8	5.2	12.3	7.8	2.6	3	37180
	RE	19050	1035	300	35	90	240	380	
Tom-6	AS	46.4	384	1.2	1.6	20.8	2.7	25.2	
	ER	51.8	57.5	0.3	0.3	1.5	0.3	0.3	174.8
	MR	1572	61.6	1.2	0.6	17	0.2	11.4	2515
	οχ	452	12.2	3.4	23	5.6	1.8	4	59400
	RE	10400	635	295	40	55	345	320	
Tom-7	AS	128.1	984	1.3	6.8	52.8	3.8	22.2	
	ER	188.5	452.5	0	1.5	11.3	1	2.3	1026
	MR	10780	234	3.2	11.4	68	3.4	21.4	17248
	OX	420	18.4	2.8	24.8	9.4	2.2	6.2	12760
	RE	35600	1590	400	40	125	425	390	
TOM- 8	AS	69.5	45.6	1.1	1.5	7.2	2.6	17.3	
	ER	165	206	0	0.8	0.8	0.5	0	593.6
	MR	4840	60.4	3.2	1	6.4	0.6	3.2	7744
	OX	268	6.8	2.4	7.5	3.4	1	2.4	6380
	RE	21600	1005	340	35	70	360	345	
TOM-10	AS	23	448	1.3	3.7	20	2.9	27.1	
	ER	69.5	199.3	0	0.8	4.3	0.3	0.5	430
	MR	4580	242.6	1.6	8	22	1.8	1.8	7328
	οχ	664	18	5.2	99.5	5.8	2.8	2.4	36250
	RE	17500	880	330	50	70	380	290	
TOM-11	AS	9.6	728	1.2	3.1	27.2	3.4	27.4	
	ER	38.5	251	0	0.3	3	0.5	1.3	463.2
	MR	4080	236	1.4	3.2	34.2	3.6	11	6528
	οχ	630	19	4	44	7.6	2.6	4.2	32120
	RE	18550	1030	310	60	75	310	330	
TOM-12	AS	15.6	40	1	1.7	3.2	2.5	23.7	
	ER	32.3	104.3	0.3	1	0.5	0.5	1	218.4
	MR	4500	244	1.6	3.8	3.4	1.4	5	7200
	οχ	240	8.8	1.8	2.5	2.4	1	1.4	2420
	RE	30500	1545	370	70	85	425	365	

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SAMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE CONC.
T OM-14	AS	35.6	472	1.2	3.1	50.4	3.1	37.7	
	ER	68.3	97	0.3	0.5	5.3	0.5	1.3	264.4
	MR	2258	101	1	0	29.4	1	36	3613
	οχ	776	19.2	2.8	78.8	9	5.6	23.8	149600
-	RE	5650	775	260	50	55	310	335	
TOM-15	AS	30.2	1160	1.3	5.1	23.2	3	31.9	
	ER	89.5	422.5	0	1	6.3	0.5	0.5	819.2
	MR	2960	250	3	5	28.8	2.8	27.4	4736
	OX	402	24.4	4	85.8	7.2	2.4	6.8	35420
	RE	29850	1510	380	70	100	465	340	
TOM-16	AS	23.8	536	1.2	4	12.8	2.5	27.4	
	ER	56	158.5	0.3	1.3	1.5	0.3	0.3	343.2
	MR	5660	308	2.2	5.4	25.2	3.6	19.2	9056
	ох	414	22.4	2.8	16.8	6.6	2.4	5	10340
	RE	35550	1545	415	45	100	380	390	
JAC-1	AS	187.2	376	2.1	5.5	20	2.3	19.7	
	ER	311.5	175.8	0	2.8	7.3	0.3	3.8	779.6
	MR	11660	165.4	2.4	19.4	20.6	0.4	66.2	18656
	OX	61.4	6.2	3.2	41.3	6.6	0.4	12.8	14300
	RE	15450	595	335	70	95	415	395	
JAC-2	AS	2729.6	800	5.2	2.7	77.6	10.1	74.1	
	ER	430	147.5	0.3	0	21.8	1.5	1.3	924
	MR	14580	109.8	2.4	3.2	110.8	13.2	92.2	23328
	OX	504	22	6.8	65.5	35.6	8.8	42.2	83160
	RE	14200	750	310	45	100	475	330	
VAC-3	AS	15.7	7080	1.6	1.3	77.6	3.8	11.8	22422
	ER	262.3	18750	0.3	0.8	163	2	6.5	30420
	MR	18300	8180	2.0	8.4	241.2	43.0	290	29280
	OX DD	122	692 1075	2.4	46.8	121	10.4	310.0	83800
JAC-4	RE	44/50	10/5	480	65	240	5/0	430	
	AS	29.7	1264	1.4	1.9	17.0	4.0	21.1	22260
	er ND	305.5	20000	0.5	0.5	1/9.0	J .J	2.3	33309
	MK	25800	4900	0.2	10.0	204.2	20.0	494	41200
		1212	300 1065	4.0	31	00	1	120.2	54120
JAC-5	KE Ng	53100	1000	400	1 0	210	222	447	
•	AS	01.3	120 0	1.0	1.0	0	J 0 2	17.2	202
	BR MD	110	120.0	0.3		2.5	0.3	15 4	JOZ 12212
	MK OY	0320	434.4	Э э о	0.4	15.2	2.0	13.4	10000
		330	1455	J.0 505	0.J 50	1.0	200	4.4	13000
JAC-6	KE Ng	117 6	1433 760	202	50	30 24 Q	230	127	
	rd Rd	165	/00 707 E	2.I 0 5	1.0	24.0	2.0	12.7	1540
	MD	10920	676	4 6	2.3	50.0	6.5 6	26	17312
		124	020 20 A	4.0	2	50.4	2 1	20 7 A	20240
	UN De	133 25200	47.4 715	340	7 55	115	2.7 505	325	20290
JAC-7	<u>7</u> 6	125 0	83 2	1 2	3.7	0 K TT2	2 2 2 2	20 A	
	ED.	123.3	26 2	U 3	2.2	1.3	0 3	0.5	235 6
	MD	8380	165 2		8 6	11 4	3 1	11 2	13408
	ALC ALC	342	10	3.3	7	3.6	2	2.2	16720
	RE	29850	1280	445	55	80	540	390	24164

				t	L16				
S AMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE CONC.
JAC-8	AS	23.4	2224	1.2	1.7	72	3.9	12.2	
	ER	256.5	14650	0.3	0.3	158.5	3.3	4.5	23850
	MR	18260	4080	4.8	16.4	257.6	30.8	276.6	29216
	ΟΧ	520	281	4.2	34.3	63.6	6.6	129.4	38500
	RE	51600	1550	465	65	310	600	405	
JAC-9	AS	15.1	440	1.4	2.4	15.2	2.7	12.7	
	ER	72.8	290	0.3	0.5	5	0.3	0.5	580.4
	MR	9200	460	4.8	8.8	31	4	20.8	14720
	ΟΧ	166	32.8	7.4	35	10.6	4.6	10.8	40700
	RE	29550	835	425	70	120	560	305	
JAC-10	AS	11.4	55.2	1.2	1.5	12.8	2.1	16.8	
	ER	77.5	200.5	0.3	2.3	3.8	0.5	1.3	444.8
	MR	2480	109.4	2	2.2	14.2	1.8	6.2	3968
	ΟΧ	162	4	2.2	13	4	1.2	1.8	10780
T - -	RE	16350	1350	345	35	55	310	350	
JAC-11	As	16.1	108	1.5	3.2	20.8	3	16.8	
	ER	91	510	0.3	0.8	10.5	0.5	0.3	961.6
	MR	5680	294	3.2	11	30.8	3	16	9088
	ОХ	254	15.6	3.4	23	6.8	2.4	3.8	23540
7.5 -	RE	24100	1385	430	50	80	415	375	
JAC-12	AS	18.1	168	1.3	1	14.4	2.3	20.3	
	ER	47.8	26	0	0	2.3	0	0.8	118
	MR	3040	42.8	2.2	0	17.2	2.6	7.8	4864
	ΟΧ	266	6.4	3.4	10.5	7	1.8	2	21780
	RE	11550	555	285	45	55	300	380	
0AC-13	AS	22.7	296	1.6	3.2	12	2.2	11	
	ER	76.3	53.3	0.3	6.3	3	0	2	207.2
	MR	1728	108.6	1.6	9.6	11	0.6	7.2	2765
	ΟΧ	25	6.6	1.2	11	3	0.6	0.4	5060
JAC-14	RE	15300	710	300	55	65	525	325	
VAC-14	AS	129	1568	1.5	17.4	25.6	3.5	8.8	
	ER	225.5	1652.5	0.3	17	24.5	2.5	1.5	3005
	MR	11700	1286	2.2	109.6	46.2	6.4	31.6	18720
	OX	130	77.4	2.6	79.3	6.2	1.8	6.6	17820
JAC-16	RE	31300	1320	385	95	105	485	350	
10 10	AS	12.1	528	1.1	15.1	64	5.1	12	
	ER	542.5	19775	0.5	5.8	148.3	15.8	2	32508
	MR	11960	2218	4	127.2	198.4	35.8	47.6	19136
	OX	506	152.2	4	70	18.8	4.8	15	24640
JAC-17	RE	29850	375	375	45	130	630	435	
	AS	37.8	1552	1.1	9.9	30.4	3	12.6	
	ER	477.5	4100	0.3	4.3	33.3	1.5	U OO f	7324
	MR	14060	1358	4	94	73	9.2	29.6	22496
	UX D	426	92.2	3	88		2.6	8.2	25740
	RE	36250	805	435	50	125	530	460	

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SAMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE CONC.
JAC-18	AS	14.9	608	1	1.6	52.8	3	13.2	
	ER	298	4125	0	0.5	61	2.3	0.3	7077
	MR	8360	572	2	6.4	148.6	8.2	12.4	13376
	οχ	274	27.8	3	21.5	19.2	2.8	2.2	16060
	RE	37650	1005	425	30	155	400	420	
JAC-19	AS	25.3	456	1	1.6	52.8	3	13.3	
	ER	325.5	2512.5	0.3	2.3	35.8	1.5	1.3	4541
	MR	9200	854	2.4	43.6	114	5.6	27.4	14720
	οχ	300	27.4	3	93.8	13.8	2.8	5.2	20680
	RE	57500	1430	555	75	165	700	395	
JAC-20	AS	27.1	1120	1.3	5.6	50.4	3.5	8.8	
	ER	277.5	2172.5	0.3	1	35.3	1.8	0.3	3920
	MR	15340	658	2.4	29.6	114.6	9.4	32.4	24544
	οχ	212	27.8	3.2	82	17.4	3	6.2	24200
	RE	29700	910	400	20	125	430	395	
JAC-21	AS	30.2	504	1.1	21.3	70.4	4.5	13.8	
	ER	452.5	2975	0	11	107.8	4.3	1	5484
	MR	10100	1344	2	203.6	197	9.8	42.2	16160
	ох	398	87	2.8	199	25.4	3.2	9.4	30800
	RE	41400	1405	485	45	115	505	400	
JAC-22	AS	196.7	2176	1.7	11.2	75.2	5.7	11.8	
	ER	220.5	1792.5	0	0.8	56.8	1	0.5	3221
	MR	10060	1032	2.2	33.8	192.4	16	31	16096
	οχ	300	47.4	4	113	23.8	4.2	9.2	35860
	RE	29700	760	350	25	145	475	465	
JAC-23	As	32.1	1968	1.3	3.9	74.4	5.3	13.4	
•	ER	307.8	3050	0.3	1	98.5	2.8	0.5	5372
	MR	10280	1226	2	47.2	189.5	18.8	29.8	16448
	ох	504	89.2	3.2	120.3	27.2	6.2	7.4	40260
	RE	28900	1370	335	55	115	405	440	
JAC-24	AS	9.8	688	1.1	1.2	31.2	2.9	9.4	
	er	86	472.5	0	0.3	14.3	0.5	1.0	894
	MR	2200	328	2	3.8	43.8	2.6	12	3520
	οχ	116	15.2	3.4	29.5	8.2	2.2	2.8	21780
	RE	19100	615	275	15	90	335	380	
JAC-25	AS	24	240	1.4	4.1	25.6	3	15.8	
	ER	187.3	927.5	0	8.8	13	1.3	1.5	1784
	MR	5600	255	2.6	16.4	20.4	3.4	17.2	8960
	οχ	190	8.6	2.8	22.8	3.6	1	2.2	14740
	RE	26800	1485	415	40	70	625	350	
JAC-26	AS	9.7	64	1.1	2	5.6	2.6	10.6	
	er	62	135.3	0.3	2.3	2	0.3	1.8	316
	MR	2620	109.6	1.8	5.6	8.6	1.4	6.2	4192
	ΟΧ	48	3.4	1.2	7	2.2	0.6	2	2860
	RE	23550	810	365	35	75	410	460	

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SAMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE Conc.
JAC-27	AS	39.3	416	1.2	6.1	45.6	4.2	15.5	
	ER	215	1052.5	0.3	3.3	18.8	1.5	0.8	2028
	MR	10380	774	2.2	34	61	6	19.2	16608
	ΟΧ	430	31	3.4	98.8	10.2	2.8	4	29920
	RE	37900	1475	425	45	105	445	405	
JAC-28	AS	44.8	752	1.3	6.3	57.6	6	15.4	
	ER	665	8200	0	2.8	85	6.8	1	14184
	MR	18820	1600	4.2	82.8	147	11.8	33.4	30112
	οχ	616	95.6	4.2	97.3	11.8	3.4	10	33880
	RE	39200	1690	420	50	125	525	405	
JAC-29	AS	53.3	1680	1.4	5.4	28.8	3.8	9.6	
	ER	296.5	11175	0	0.5	21.8	3.5	1.3	18354
	MR	21800	4460	4.4	54.8	128.6	22	44	34880
	OX	486	194.8	4	71	9.4	4.6	15.4	28380
JAC-30	AS	163.2	144	1.7	1 3	53 6	3 7	15 4	20000
	EP	241 3	35	0 3	<u> </u>	13 3	0 3	1	442
	MD	9740		3	1 6	113 4	4	13	15584
		480	9 7	J 4 2	13	12 8	36	13	27720
	DF	29650	705	400	55	105	510	415	21120
120-21		1 4 3	A16	1 1	71	50 4	2 4	16 4	
JAC-JI	rd Fd		410 5275	1.1	7.1	50.4	J. 4 2 2	17.4	9996
	er Md	204.0	52/5	0.3	277	125 2	3.3	25	0030
		11000	1000	J.2 E A	102 0		7 0	JJ 11 C	21240
		432	9/.9	J.4 A16	102.0	14.4	475	11.0	31240
	RE	29550	1000	412	07	100	4/3	430	
JAC-32	A 5	37.3	97.0	1.3	2.3	0.4	3	14.2	
	B R	125.5	287.5	0.3	1	1.5	0.8	0.5	661
	MR	5680	108.2	6	8	20.2	4.8	16.2	9088
	OX	176	10.6	7	16.3	5.8	3.4	4.4	10560
	RE	32600	620	435	30	135	600	380	
JAC-33	AS	41.2	1584	1.3	6	62.4	5.3	10.8	
	ER	405	21550	0.3	0.5	128.8	14	0.5	35128
	MR	10380	2940	2.6	37.4	218.8	33.4	23	16608
	ΟΧ	676	171.8	2	70.3	13.8	4.6	9.8	22660
	RE	42150	1205	420	35	120	380	400	
JAC-34	AS	29	568	1	1.5	30.4	3.7	13.2	
	ER	307.8	6600	0.3	0	30.5	3	0.5	11052
	MR	10180	1078	2.2	3.2	66.2	7.8	14.6	16288
	ΟΧ	416	59.6	2.6	20.3	9	3	3.8	25520
	RE	21177	723	345	29	96	416	349	
JAC-35	AS	17.8	304	1.3	6.8	21.6	3	12.6	
	ER	154.5	827.5	0	1.5	7.5	0.8	0.5	1571
	MR	4060	268	3	29.6	28	5.4	13.6	6496
	οχ	198	22	3.2	80.3	8.2	3.2	3.6	20240
	RE	31700	1110	405	45	115	410	495	

SAMPLE	EXTR	FE	MN	CR	CU	ZN	NI	PB	PHASE Conc.
JAC-36	AS	33.4	144	1.2	1.8	11.2	3.3	11.9	
	ER	141.3	540	0	0	2	0.8	0.8	1090
	MR	3720	113.8	2.2	1	17	7	8.6	5952
	ох	198	13.6	3	13.5	7.2	3.4	2.2	23100
	RE	26550	835	370	25	105	465	495	
JAC-37	AS	25.5	176	1.5	1.2	9.6	2.7	9.4	
	ER	86	104.8	0	0.5	2	0.3	1	305
	MR	3400	87.6	2.4	0.8	16	3.4	5.2	5440
	OX	128	8.6	3.6	13.3	6.4	3.4	2.8	22220
	RE	25300	720	370	55	115	575	360	
JAC-38	AS	12.2	528	1.3	2	12	2.7	9.9	
	ER	83.3	332.5	0	1.3	4.3	0.8	1.8	665
	MR	6640	330	2.8	7	25.2	3	10.2	10624
	ox	120	22.2	2.8	17	7.6	2.2	3.8	13860
	RE	27800	855	390	10	105	420	365	
JAC-39	AS	23.7	216	1.4	1.5	12	2.5	11.7	
	ER	183.5	1110	0.3	0.3	3.3	0.3	1.5	2070
	MR	7860	245.2	3.2	3.2	20	3.2	11.2	12576
	0X	202	16.4	2.8	8	6.8	1.8	2.8	14740
	RE	29250	980	380	25	110	530	450	2
JAC-40	AS	13.6	512	1.1	2.7	13.6	2.6	13	
•	ER	78.8	365	0	0.8	4	0	0.8	710
	MR	6040	388	28	12 6	26 R	3.8	11 2	9664
	07	180	28	2 6	21 8	6 8	2 2	3	15180
	RE	30544	816	381	25	105	423	285	T ATAA

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Parameters measured from Maine water samples.

Sample	Na	К	Ca	Mg	<u>c1</u>	Alk	T	<u>pH</u>
Cal-4	4.04	0.37	3.46	0.82	6.35	8.9	19.0	5.9
Cal-5	2.70	0.48	5.02	0.91	3.85	17.8	19.0	6.2
Cal-6	2.06	0.26	2.70	0.50	2.80	8.9	24.0	5.5
Cal-7	2.44	0.29	2.38	0.44	3.25	4.4	24.0	5.5
Cal-8	4.23	0.65	4.97	1.19	4.35	26.6	26.0	6.2
Cal-9	1.93	0.36	1.98	0.38	3.00	4.4	25.0	5.7
Tom-9	1.48	0.36	2.49	0.51	2.05	4.4	19.0	5.8
Tom-10	1.52	0.40	2.84	0.60	1.80	4.4	20.0	5.8
Tom-11	1.49	0.39	2.38	0.55	2.00	8.9	21.0	5.8
Tom-12	1.88	0.55	2.58	0.58	3.65	8.9	21.0	5.8
Tom-13	1.59	0.37	1.66	0.32	2.90	8.9	21.0	5.8
Tom - 14	1 72	0.73	0 85	0.20	2 85	4 4	22 0	5 5
Tom-15	1 59	0.75	1 66	0.27	2 90	4 4	22.0	6 8
T_{Om-16}	1 51	0.37	1 84	0.32	A 70	7.7 8 9	21 0	6 A
	1 22	0.30	2 63	0.41	1 45	67	14 0	5 5
	1.2J	1 02	2.0J A QQ	1 10	1.13	12 2	12.0	5.5
	2.11	1.03	4.JJ 2.25	1 02	0.33	12.2	14 0	5.1
Jac-J	2.20	0.40	J.JJ 5 47	2.07	0.0J		14.0	J./ C E
Jac-6	2.12	0.00	J.4/	2.07	5.00	24.4	14.0	0. 0
Jac-o	2.0/	0.50	3.33	1 70	0./0	10.0	15.0	5.0
Jac-y	3.8/	0.5/	5.07	1.76	***	7.8	15.0	5.2
Jac-13	1.71	0.38	3.35	1.19	2.55	10.0	13.5	6.2
Jac-14	1.14	0.60	2.75	1.03	1.65	4.4	19.5	5.6
Jac-15	1.47	0.37	1.96	0.55	3.10	3.3	20.0	5.8
Jac-20	0.84	0.38	2.84	0.84	***	6.7	20.5	6.1
Jac-22	0.99	0.34	3.68	0.91	***	8.9	20.0	5.8
Jac-24	1.00	0.48	2.79	0.87	***	13.3	22.0	5.7
Jac-26	1.32	0.48	5.20	0.75	2.75	2.2	17.5	5.3
Jac-29	0.98	0.36	1.41	0.68	***	2.2	20.0	5.8
Jac-38	1.02	0.41	3.19	1.00	***	8.9	15.0	5.7

Elemental data in ppm. Temp. in ^oC. Alk in mg/l CaCO₃. *** = non-determinable due to titration interferences. APPENDIX 4: Statistical Data for Phase Concentration Distributions for the Grand River, Michigan and for the Streams in Three Areas of Maine Test for goodness of fit of phase concentration data to a normal distribution (confidence level = 95).

A. Chi-squared Test for Log oxidizable phase concentrations in Grand River sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq. <u>Value</u>
- •	· · · balan	3 4 4	7	6	2449
at	or below	3.44	/	0	. 2440
	3.44	3.76	5	5	.0276
	3.76	4.08	3	6	1.5558
above	4.08		12	10	.5280

Chi-square = 2.35624 with 1 d.f. Sig. level = 0.125

B. Chi-squared Test for Log moderately reducible phase concentrations in Grand River sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq. <u>Value</u>
at	or below	3.57	9	6	1.1457
	3.57	3.73	2	6	2.9925
	3.73	3.89	7	7	.0156
above	3.89		9	8	.2393

Chi-square = 4.39308 with 1 d.f. Sig. Level = 0.036

C. Chi-squared Test for Log easily reducible phase concentrations in Grand River sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq <u>Value</u>	
at	; or below	2.26	5	6	.05257	
	2.26	2.58	9	8	.19239	
	2.58	2.90	8	8	.00187	
above	2.90		55	6	.11157	

Chi-square = 0.358401 with 1 d.f. Sig. level = 0.549

D. Chi-squared Test for Log oxidizable phase concentrations in Maine stream sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq. <u>Value</u>
at	; or below	3.97	4	6	.941
	3.97	4.19	9	11	.292
	4.19	4.30	9	8	.296
	4.30	4.41	15	8	5.803
	4.41	4.52	6	8	.444
	4.52	4.63	8	7	.209
	4.63	4.74	3	5	.975
above	4.74		7	8	.169

Chi-square = 9.12822 with 5 d.f. Sig. level = 0.104

E. Chi-squared Test for Log moderately reducible phase concentrations in Maine stream sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq. <u>Value</u>
at	; or below	3.73	8	8	.02831
	3.73	3.90	10	10	.00814
	3.90	3.98	5	6	.32735
	3.98	4.07	4	7	1.23351
	4.07	4.15	6	7	.13916
	4.15	4.23	11	6	3.29784
	4.23	4.32	7	5	.47684
above	4.32		10	11	.19549

Chi-square	=	5.76164	with	5	d.f.	Sig.	level	=	0	. 3	3	0
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F. Chi-squared Test for Log easily reducible phase concentrations in Maine stream sediments.

	Lower Limit	Upper Limit	Observed Frequency	Expected Frequency	Chi-sq. <u>Value</u>
at	t or below	2.33	3	7	2.231
	2.33	2.67	15	8	6.439
	2.67	2.83	8	5	1.419
	2.83	3.00	9	6	1.641
	3.00	3.17	2	6	2.826
	3.17	3.33	5	6	.189
	3.33	3.50	2	6	2.310
	3,50	3.83	6	9	.862
above	3.83		<u> </u>	8	.776

Chi-square = 18.6934 with 6 d.f. Sig. level = 4.714E-3

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