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RELATIVE IMPORTANCE OF IRON-OXIDE, MANGANESE-OXIDE,
AND ORGANIC MATERIAL ON THE ADSORPTION OF CHROMIUM IN
IN NATURAL WATER SEDIMENT SYSTEMS

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RELATIVE IMPORTANCE OF IRON-OXIDE, MANGANESE-OXIDE, AND ORGANIC MATERIAL ON THE ADSORPTION OF CHROMIUM IN NATURAL WATER SEDIMENT SYSTEMS

By

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ABSTRACT

RELATIVE IMPORTANCE OF IRON-OXIDE, MANGANESE-OXIDE, AND ORGANIC MATERIAL ON THE ADSORPTION OF CHROMIUM IN NATURAL WATER SEDIMENT SYSTEMS

By

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The objective of this research was to study the adsorption of Cr by various chemical substrates that exist in soil or sediment (i.e., clays, carbonates, Mn oxides, Fe oxides, and organics).

In sediments from the Grand River, Lansing, Michigan, the relative importance of these substrates in adsorbing Cr was Fe oxides $\simeq$ organics $\gg$ Mn oxides $>$ carbonates $>$ exchangeable. When the abundance of the adsorbant is considered in the amount of metal adsorbed, the relative importance becomes: Mn oxides $>$ Fe oxides $\simeq$ organics.

Through the use of phase concentration factors and trilinear diagrams, it was concluded that Cr may exist in both +6 and +3 oxidation states in the sediment. This was supported by the partitioning results of the metals Cu, Pb, Ni, and Zn.

The partitioning of Cr and the other metals was determined by selective chemical extraction techniques. Steady state analyses were performed on each fraction to determine optimum leaching times.

Dedicated to my parents.

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INTRODUCTION

The mobility of any metal in exogenic aqueous environments is controlled by adsorption and precipitation-dissolution reactions. These properties, in turn, are controlled by the environmental parameters Eh, pH, ionic strength, temperature, and composition of the solution and by the presence of charged substrates such as clays, carbonates, Al-Fe-Mn oxides and hydroxides, and organic material. The importance of adsorption on the mobility of metals is known (Krauskopf, 1956), but the relative importance of the various substrates as controls on the adsorption of the metals in natural systems is not fully understood.

In order to study the relative importance of the various substrates on controlling the adsorption of metals in the field, there are two necessary prerequisites: 1) the metals must be in high enough concentrations to be easily measured, and 2) there must be a variety of substrates present for comparative analysis. The sediment-water system of the Grand River, Lansing, Michigan has these prerequisites. This research specifically determines the relative importance of selected substrates in the sediment of this system on the adsorption and therefore the mobility of Cr. In addition, the metals Cu, Ni, Pb, and Zn are studied.

An understanding of the chemical behavior of Cr is important if we are to accurately assess the increased additions of Cr to the environment. In addition, the fact that Cr behaves both as a toxin to man and as an essential dietary trace element suggests a need for the understanding of this metals' chemical behavior in the environment.

The selected substrates chosen for study are clays, carbonates, Mn oxides, Fe oxides, and organics. The metals associated with these substrates are determined by the method of selective chemical extractions. In addition, the metals associated with the detrital sediments will be determined. This type of an approach in examining Cr adsorption on sediments will result in the partitioning of Cr among the different chemical phases of the sediment.

Past research has indicated that Fe-Mn oxides and organic material are the two most important substrates in controlling the mobility of Cr. This research will attempt to confirm this hypothesis. The past research is limited, however, because:

1. the selective chemical extraction techniques used for Cr were not adequately evaluated,
2. the chemical partitioning results were not interpreted in terms of the chemical parameters of the system, and
3. the Cr partitioning results were not interpreted in light of the amount of substrate present. This concept is necessary if we are to predict the behavior of Cr in other types of systems (lacustrine and soil systems), where the relative amounts of phases present may differ from this system.

These problems are addressed in this study.

GOALS OF THIS RESEARCH

The overall goal of this research is to determine the relative importance of five selected substrates in the sediment on the mobility of Cr, where the addition of Cr to the environment is from an industrial source. Specific goals of this research are:

1. to determine the relative partitioning of Cr among the various chemical substrates as they are present in a water-sediment system in the Grand River, Lansing, Michigan,
2. to determine the relative partitioning of Cr among the various substrates, given that all phases are present in equal amounts. The use of phase concentration factors combined with trilinear diagrams will be introduced to determine this.
3. to provide a chemical basis for the partitioning of Cr, based on the geochemistry of this element and the chemistry of the system,
4. to determine the relative importance of Fe and Mn oxides in the sequestering of Cr,
5. to determine if the concentration of Cr associated with a particular phase is a function of the amount of that phase present,
6. to determine the oxidation state of Cr when associated with Fe oxides, and
7. to evaluate the methods of selective chemical extractions for their accuracy and repeatability.

SIGNIFICANCE OF RESEARCH

The National Academy of Sciences (1973, 1974) has outlined basic gaps in our knowledge regarding the geochemistry of Cr and other trace elements. These include:

1. a lack of basic chemical data on the behavior of solid and dissolved material, including suspended sediments, which are transported by streams to the oceans,
2. a lack of accurate background information on the "normal" concentrations of Cr in various media,
3. a general lack of understanding of the chemical interactions of Cr with the environment including 1) the fate of metal pollutants in surface waters, and 2) the diffusion of metal pollutants in and out of sediments.

These problems still have not been adequately addressed. This research will attempt to close these "gaps" by studying the behavior of Cr in natural water-sediment systems. Specifically, the fate of Cr in surface waters will be addressed.

The results of this investigation will be applicable to other areas of concern as well. For example:

1. Results of the Cr partitioning in natural water-sediment systems can also be extended to fresh water lake sediments, marine sediments, and soils. From this, a better understanding of the controls on Cr mobility in these areas would be gained.

2. Results of this study will enable us to dispose of toxic wastes more efficiently. A knowledge of the speciation of Cr in its association with certain chemical phases, as well as the stability of its oxidation states on these phases is essential for safe disposal of toxic wastes.
3. A determination of Cr partitioning will enable us to more accurately assess the long term consequences of the increased rates of the addition of Cr and other heavy metals to the environment. In addition, a better understanding of the geochemical cycling of Cr and its biologic availability in the exogenic environment will be gained.
4. Results of Cr partitioning in a natural water-sediment system can be utilized in geochemical exploration. Specifically, false anomalies can be more easily identified if it is known that Cr is selectively adsorbed to certain chemical phases of the sediment. Certainly, any geochemical sampling program should include the use of selective extraction analyses to identify any hydromorphic anomalies.

CHROMIUM: HEALTH ASPECTS AND INDUSTRIAL USES

Chromium is known to behave both as a toxin to man and as an essential dietary trace element. Hexavalent Cr is considered toxic, and has been associated with lung cancer and cardiovascular disease. It is clearly a cause of ulceration of the skin and nasal septum (Waldbott, 1978; Beliles, 1979; Schroeder, 1974; Mertz, 1971). In addition, low level Cr pollution has caused rhinitis, bronchitis, and emphysema (Mertz, 1971; Young, 1975; Waldbott, 1978). Skin injury from chromate compounds occur as corrosive reactions, including ulcers and scars, and sensitization reactions (allergenic) (National Academy of Sciences, 1974).

Chromium in the trivalent form has been recognized to be an essential dietary trace element (Hopps, 1971). It is thought that Cr forms a complex between sulfhydryl groups on the A-chain of insulin and potentiates insulin activity. In addition, it binds to plasma albumin and interacts with Mn in glucose metabolism. Symptoms of Cr deficiency in the diet mimics diabetes mellitus (Beliles, 1979). Chromium is also known to play a role in lipid metabolism (Shamberger, 1979). In rats, for example, cholesterol levels are elevated when the diet is low in Cr (Calabrese, 1978). Therefore, Cr deficiency in the diet may cause athereosclerosis and heart disease (Beliles, 1979; Schroeder, et al., 1979).

There is good evidence that part of the U.S. population may be in a marginal state of Cr deficiency (Mertz, 1978; Schroeder, 1968). Less Cr is found in the tissues of Americans than in the tissues of people living in Africa and eastern countries. Studies have shown that Americans who are known to have a high incidence of cardiovascular disease have extremely low levels of Cr in their heart tissue, while Africans and Orientals who have low incidence of cardiovascular disease have high levels of Cr in their tissues (Schroeder, 1968, 1974). According to Schroeder (1974), the low levels of Cr in the western diet may be caused by the consumption of refined sugars, since refined sugars contain almost no Cr, whereas raw and brown sugars (commonly used in other countries) have appreciable amounts of it.

Industrial uses of Cr include its addition to Fe, Ni, and other metals to increase their strength and corrosion and oxidation resistance. It is also used in primer paints, pigments, textiles, photographic supplies, and in the plating and tanning industries (Shamberger, 1979).

GEOCHEMISTRY OF CHROMIUM

Most of the Cr in the earth's crust is incorporated in the crystal lattice structure of the spinel mineral group. The common and most important ore mineral is chromite, $FeCr_2O_3$ and would theoretically contain 68% chromic oxide (Burns and Burns, 1975; Krauskopf, 1979; Hawkes and Webb, 1962). Chromium can also be incorporated into the structures of other silicates such as pyroxenes through the replacement of Fe^{3+}, Al^{3+}, and Mg^{2+} by Cr^{3+} (Hosking, 1964). A high proportion of Cr is removed from a magma in the early stages of crystal settling; therefore, Cr is often associated with ultramafic rocks.

Chromium is a constituent of the Group VIB of the periodic table and has the atomic number 24. Chromium exists in several oxidation states and forms brilliantly colored compounds (thus its name). The ground state configuration is characterized as $3d^5 4s^1$.

Generally, Cr follows Fe and Al in the exogenic cycle. Stratkov, et al. (1965) found that intensive weathering in a humid environment could free Cr from broken down rock. The freed Cr migrates in solution as the dissolved ion and on suspended sediment.

In solution Cr may exist in the +3 or the +6 oxidation state. The most common occurrence of Cr is in the trivalent state. In this state, Cr forms octrahedral complexes in solution with a variety of ligands, making it the most stable form of Cr in aqueous solution (Hueey, 1972). Griffin and co-workers (1977) studied the speciation of Cr over the pH range 1.0 to 9.0 and found that with increasing pH, the stable trivalent species are $Cr(OH)^{2+}$, $Cr_2(OH)4^{2+}$, and $Cr_6(OH)_6{}^{6+}$. Chromium (III) has a pH of hydrolysis of 5.3; therefore in natural waters with pH's ranging from 5.5 to 8.5 Cr will tend to precipitate as the hydroxide (Meyer, 1977).

The dominant hexavalent species as a function of increasing pH are H_2CrO_4, $HCrO_4^-$, and $CrO_4^=$ (Griffin, et al., 1977). Hexavalent Cr normally occurs in solution as $CrO_4^=$ under alkaline-oxidizing conditions (Hem, 1977). Robertson (1975), for example, reports concentrations of Cr^{6+} of 100 to 200 mg/l (about $10^{-5.5}$ moles/liter) from groundwaters near Pheonix, Arizona. If iron is present, however, Cr will be reduced (Schroeder and Lee, 1975). This will tend to immobilize Cr as the hydroxide.

Previous research has suggested that Cr is highly immobile in the environment (Levinson, 1980; Smith, 1972; Hawkes and Webb, 1962; Rankama and Sahama, 1950). This is a result of the tendency of the trivalent species to precipitate out of solution as the hydroxide (pH of hydrolysis for Cr(III) = 5.3). However, more recent studies have shown that Cr may become mobile in the environment under certain conditions, especially when conditions favor the stability of the hexavalent species. Schroeder and Lee (1975) found that Cr(III) and Cr(VI) are readily interconvertable in natural waters. According to Hem (1977), dissolution of trivalent minerals could occur in oxygenated groundwater or surface water, giving low, equilibrium controlled, concentrations of chromate ions. Korte and co-workers (1975) have shown that in certain types of soil, Cr has moderate to high mobility. Based on the foregoing statements, it is evident that there exists a lack of understanding on the mobility of Cr.

Organic material has been found to be an effective transporter of Cr and other metals in solution by forming organometallic complexes (Benes, et al., 1976; Udodov and Parlov, 1961; Rashid and Leonard, 1973; Andelman, 1973). Organic compounds in natural waters are known to interact with trace elements, especially through the mechanisms of complex and chelate formation (Lee and

Hoadley, 1967; Rashid, 1971; Rashid and Leonard, 1973; Jackson, 1975; Andelman, 1973). Fulvic acids play an especially important role in the transport of heavy metals in solution. This is due to their high solubility in natural waters which, in turn, is a result of their low molecular weights and the presence of many functional groups. Carboxyl, phenolic hydroxyl, and amino groups are considered to be important in complexing (Rashid, 1971). Humic acids play a more important role in the retention of trace elements in stream sediments since they are more abundant (Malcomb, 1964, In: Forstner and Wittman, 1979).

The formation of organometallic complexes makes possible extensive migration and segregation of metals, including Cr. Metals are released from soils and bottom sediments as water soluble complexes under circumstances in which they would otherwise be precipitated as sulfides, hydroxides, or carbonates (Jackson, 1975; Rashid and Leonard, 1973). Evidence of Cr migration as a result of organic complexing has been observed by DeGroot and Allersma (1963) who suggested that the high dissolved Cr content of the river downstream was caused by the mobilization of Cr from stream sediments by formation of soluble organometallic complexes. Nesterova (1960) investigated the dissolved and suspended loads of the Ob River and was able to correlate changes in the mechanism of Cr transport with changes in the organic content of the river.

PAST RESEARCH ON CHROMIUM PARTITIONING

The migration or transport of Cr is controlled by several geochemical mechanisms. Gibbs (1977) studied the trace metal content of the Amazon and Yukon Rivers to determine mechanisms of metal transport. In the suspended load he found that metals were partitioned among 1) crystalline or detrital material, 2) organic matter, 3) Fe and Mn oxides, and 4) clays. These phases are considered to be the major adsorbing phases in exogenic systems. The adsorption of a metal by one or more of these phases is an important factor in controlling the mobility of that metal. Metal partitioning studies, where the amount of metal partitioned to each phase is determined, are the basis in defining the relative importance of each phase in controlling the mobility of a metal. These studies are applicable to both sediments (marine, riverine, and lacustrine) and soils.

Little work has been done that would determine the Cr partitioning among the adsorbing phases in exogenic systems. In many of the studies, not all of the phases are studied, and some are combined. The results of past researchers are summarized in Table 1. In addition to the phases defined by Gibbs (1977), a carbonate phase is also considered.

It is generally agreed that Cr incorporated into crystalline structures is the dominant form of the element in suspended sediments and bed load sediments (DeGroot and Allersma, 1975; Kharkar, et al., 1968; Turekian and Scott, 1960; Hosking, 1968; Jankovic, 1964; Garret and Nichol, 1967; Nesterova, 1960; Gibbs, 1973, 1977; Forstner and Patchineelam, 1981; Filipek and Owen, 1979; Long and Jernigan, 1978). The low solubility of the Cr species would suggest this. In an

Table 1: Percentage of Cr associated with various adsorbing phases of sediment and soils.

		Hydromorphic Phases*					Detrital**
	Dissolved	Exch	Carb	Fe-ox	Mn-ox	Org	Res
Filipek and Owen, 1978;	-	5		13	24		60
Little Traverse Bay,							
Mich., clay size fraction							
Lake sediments							
Patchineelam, 1975;	-	8	1	33		9	49
Rhine River							
River sediments							
Gupta and Chen, 1975	-	0	0	35	3	3	60
Los Angeles Harbor							
Lake sediments							
Gibbs, 1973;	-	3	-	17		13	67
Yukon River							
River sediments							
Gibbs, 1977;	10	4	-	3		8	75
Amazon River	13	3	-	7		13	64
Yukon River							
River sediments							
Shuman, et al., 1978							
Haw River, N.C.							
River sediments							
Polluted	-	15.7	-	69.2		19.8	7.9
Control	-	2.4	-	29.2		6.8	48.3
Long and Jernigan, 1978;	-	-	-	2		7	91
Lower Barton Creek, N.C.							
River sediments							

*Hydromorphic phases:

Exch: refers to those substrates that are capable of sorbing cations from solution and releasing equivalent amounts of other cations into solution, i.e., by cation exchange (particularly clay minerals; also freshly precipitated iron oxides, amorphous silicic acids, and organic substances).

Carb: carbonates; Fe-ox: Fe oxides; Mn-ox: Mn oxides; Org: organics

**Detrital:

Res: residual material

area where the bedrock consists of ultramafic rocks, the anhydrous crystalline species Cr_2O_3 would, in part, control the solubility of Cr; its solubility is less than 10^{-8} moles/liter over the pH range 4.7 to 14 (Hem, 1977). The other species controlling the solubility of Cr in the environment is $Cr(OH)_3$. More soluble than the former (up to 10^{-2} moles/liter in the same pH range), it probably results from the release of Cr from the weathering of silicates and the disposal of wastes (Hem, 1977).

Clay minerals often contain an enrichment of metals within their structure. Hirst (1962) studied the geochemistry of sediments from the Gulf of Paria, and suggested that the elements Cr, V, Cu, Pb, and to a lesser extent Co and Ni, enter the deposition basin structurally combined in the lattices of degrated clay minerals. The differences between the ratios of these elements to Al, Mg, Fe, K, and $(Na^{+}K)$ indicate that Cr and Cu favor bonding to illite, whereas V, Co, and Ni favor montmorillonite.

One study which did not find Cr to be dominantly associated with the crystalline phase was that by Shuman, et al. (1978), which examined Cr partitioning in the Haw River, North Carolina, in both polluted and non-polluted (control) segments of the river. In the polluted sediments, the highest percentage of Cr was partitioned into the oxide fraction, however, in the control sediments, 48% of the total Cr transported was associated with the residual phase, a greater amount than was associated with any other phase. This discrepancy is explained in terms of an increase of Cr from anthropogenic inputs of metal and domestic wastes. Analytical concentrations of Cr in the crystalline form were similar for control and polluted stations, but the percentage of the total metal in this form was much smaller at polluted stations, presumably because Cr was added in other forms. Forstner and Patchineelam (1980) have shown that as the metal concentrations in the Rhine River are enriched because of pollution influences, there is a distinct increase in the association with the non-residual phases.

Chromium associated with the residual phase (detrital) is not a function of adsorption reactions, but rather of the primary incorporation of Cr into mineral structures. However, Cr association with the other phases (organic matter, Fe and Mn oxides, carbonates, and clays) is mainly caused by adsorption. These phases that commonly sequester dissolved ions by adsorption (and sometimes by coprecipitation) are termed the "hydromorphic" phases of a sediment or soil.

From the data of Table 1, it is clear that of the hydromorphic phases, the hydrous oxides and organic matter are the most efficient in scavenging Cr. Loring (1979) found that most of the nonresidual Cr in the sediment of the St. Lawrence estuary appeared to be associated with oxide grain coatings and organic matter before entry into the estuary. Few studies differentiate between Cr associated with Mn and Fe oxides. It is also seen from Table 1 that a trend in the relative importance of the various hydromorphic phases in Cr adsorption is unclear.

Caution must be used when interpreting the data from Table 1. Although all the investigators used the technique of selective chemical attacks, the methodologies differ.

Organic material is known to play an important role in various geochemical processes, such as the solubility, mobility, concentration, and accumulation of Cr and other metals (Jackson, 1975). Humic acids with lower molecular weights appear to be the most efficient in complexing metals. As the molecular weight increases, the complexing ability decreases. It is interesting to note that the metal holding capacity of various humic acids and their fractionated components is closely associated with acidic characteristics of these compounds. Those with lowest molecular weight (most efficient complexers) will possess the highest total acidity. With increasing molecular weight, acidity will decrease (Rashid, 1971). The relative amounts of metal ions complexed by organic matter is due to differences in ionic radii, structure of ionic shells, and polarization properties of metal ions (Rachid, 1974). Organic matter is an important control on the mobility of Cr (Gibbs, 1977; Cary, 1977; Casagrande and Erahill, 1976). Shimp (1971) and Shimp and Leland (1973) determined that there is a direct correlation between an increase in the organic content of Lake Michigan sediments and an increase in the concentration of Cr. The mechanism of concentration of Cr in the tops of coal beds was that of complexation to organic matter (Manskaya and Drozdova, 1968). Zubovic and co-workers (1961) demonstrated that Cr reacted with organic matter of coal to form metallo-organic complexes. Organic compounds in water and soil systems may affect the oxidation state of Cr. The reducing environment created by organic material may cause the reduction of Cr(VI) to Cr(III), thereby affecting its transport in water (Lee and Hoadly, 1967; Gloyna, et al., 1971; Andelman, 1973). Although Cr is known to concentrate in organic matter as a complex (Saxby, 1969), other information regarding the structure of the complex and the chemical behavior of it is fragmentary and incomplete.

Hydrous Fe and Mn oxides are known to behave as sinks for many heavy metals under oxidizing conditions and may keep metal concentrations in solution well below their solubilities as oxides, carbonates, sulfides, etc. Jenne (1968) proposed that the scavenging of selected trace metals by Fe and Mn oxides is an important control on the distribution of these elements in soils and water.

In aquatic systems, Fe oxides and hydroxides exist as $Fe(OH)_3$, Fe_3O_4 (magnetite), amorphous FeOOH, and FeOOH (geothite). What are usually referred to as "hydrous ferric oxides" or "ferric hydroxides" are more likely to be poorly crystalline FeOOH (Stumm and Morgan, 1970).

The mineralogy of Mn oxides is extremely varied and often confusing. It is known that MnO_2 exists in two forms: 1) $Mn_7O_{13}.5H_2O$ and 2) $Na_4Mn_{14}O_{27}.9H_2O$. MnOOH usually exists as mixtures of Mn(II) and Mn(IV) or Mn(III) (Forstner and Wittman, 1979).

The importance of Fe and Mn oxides in the adsorption of Cr has been adequately demonstrated (Turekian and Scott, 1967). Steele and Wagner (1975) concluded that the dominant transport mechanism of Cr in stream sediments of the Buffalo River, Arkansas, was by hydrous oxide coatings. The importance of this mechanism was found to increase downstream as the particle size decreased. They attributed this to an increase in surface area available for the oxide coatings. Gibbs (1977), however, demonstrated that the coating mechanism is not directly related to the surface area of the particles; the number of individual coating around the grain must also be considered. Cutshall (1967) found Fe oxides to be the most important single sediment component in the retention of ^{51}-Cr in sediments from the Columbia River (In: Forstner and Wittman, 1979). Selective chemical leaching of trace elements in sediments from the Amazon and Yukon Rivers by Gibbs (1973, 1977) indicate that 2% to 8% of Cr was present in the form of hydrous Fe-Mn oxide coatings.

Clays are known to play a role in the uptake of heavy metals in the environment. This is a result of the following properties that clays possess:

1. broken bonds around the edges of the silica-alumina units, which possess a negative charge. This negative charge may be balanced by the adsorption of cations.
2. their tendency to substitute Al^{3+} for Si^{4+} in the tetrahedral layer and divalent cations for Al^{3+} in the octrahedral layer. This results in an overall negative charge on the clay surface and is balanced by the adsorption of cations (metals) (Forstner and Wittman, 1979).

The pH of the environment plays an important role in the ability of clays to adsorb metals. At low pH's (below 6), Al^{+3} begins to compete with the metals for positions on the clay surface, thus there is little or no metal adsorption under these conditions. Particle size, surface area, amount of soil moisture, and degree of crystallinity are factors that affect the ability of clay minerals to adsorb metals (Levinson, 1974).

Table 1 shows that Cr is not highly associated with the clays when compared to other hydromorphic phases. The reason for this may be that other processes, such as Fe-Mn oxide adsorption, greatly reduce the heavy metal content in solution prior to clay adsorption. On the other hand, Jenne (1976) proposed that the most significant role of clay sized minerals in trace element adsorption by soils and sediment is that of a mechanical substrate for the precipitation and flocculation of organics and secondary minerals, such as Fe-Mn oxides.

Gibbs (1977) found that solid particles such as clays played a significant role in the transport of Cr, however, he recognized this mechanism as being the least important when compared to the other mechanisms. Between 7% and 14% of the total Cr transported in the Amazon and Yukon Rivers was transported as Cr adsorbed onto solid particles such as clays. The highest amount of Cr found in the exchangeable fraction was 15.7%, by Shuman and co-workers (1978). However, this occurred in the polluted segment of the Haw River, N.C., and is interpreted to be the result of anthropogenic inputs of Cr associated with this phase. In the control segment of the river, only 2.4% of the total Cr was transported by this phase.

Surbramanian and Gibbs (1975) studied the adsorption of trace metals, including Cr on clays in river water, and determined a general exchange sequence for the trace metals on clay minerals. Factors influencing this sequence are:

1. valence of the ion,
2. hydration behavior,
3. electron negativity,
4. ionization potential, and
5. the clay mineralogy

(Forstner and Wittman, 1979). This selectivitiy sequence can be written as follows:

Ca > Na > Fe > Mn > (Co, Cr) > Ni,

in which the amount of trace elements in the exchange sites decreases in the order shown. This sequence suggests that the adsorption of Ca, Na, Fe, Mn, and possibly Co will be favored over the adsorption of Cr, and therefore may account for, in part, the low adsorption of Cr by clays. Griffin and co-workers (1977) found that the amount of Cr adsorbed on clay minerals is highly dependent on the pH and oxidation state of Cr. The amount of Cr(VI) adsorbed increased as pH decreased. It was not determined, however, if at lower pH's of adsorption, the Cr was reduced prior to adsorption. No adsorption of Cr(VI) occurred at pH's where the clay surface charge is negative. As pH increased Cr(III) adsorption increased. Overall, the adsorption of Cr(VI) was very low compared to Cr(III). The effect of other competing ions, such as dissolved organics, in solution on adsorption was not investigated.

Few investigators have studied the absolute amount of Cr associated with the carbonate phase. Generally, the carbonate phase has been found to be unimportant in the sequestering of Cr (Table 1). Filipek and Owen (1978) found that the carbonate and exchangeable fractions together accounted for no more than 5% of the total Cr transported. Patchineelam (1975), who studied Cr partitioning in the Rhine River, found only 1% of the total Cr was transported by the carbonate phase. Gupta and Chen (1975) found no Cr associated with carbonates in the Los Angeles Harbor, CA.

CONCEPT OF PHASE CONCENTRATION FACTOR

A limitation of the past work on determining the partitioning of Cr in sediments and soils is that few consider the effects of the amount of phase present when estimating the importance of the particular phase in sequestering a metal. For example, much of the variation seen in Table 1 could be simply a function of the amount of phase present.

For some of the studies, not considering the amount of phase present is valid. For example, if the question addressed by the study was, "How much metal is transported by a particular phase?" or "Which phase in this system is most responsible for the sequestering of metals?", then consideration of the amount of phase present is not necessary.

On the other hand, in studies which attempt to determine the relative importance of the phases and interpret the results chemically, this type of an approach is not valid. The amount of the individual phases must be considered in the interpretations. For example, the relative importance of organic material in sequestering Cr may simply be a function of the amount of organic material present. This idea needs to be tested and will be addressed in this study by the following technique.

Forstner and Patchineelam (1980) developed the concept of phase concentration factor (PCF) to determine the relative importance of the chemical phases in sequestering a metal which is independent of the amount of phase present. The PCF is defined as the ratio of the percentage of the total metal concentration in a sediment associated with a certain phase to the percentual content of phase with respect to the other phases present. If the computed PCF for a metal in a phase is greater than 1, than an enrichment of the metal has occurred in that phase. If the PCF is less than 1, then the phase is not an important adsorber of the metal. For example, Forstner and Patchineelam (1980) determined that the PCF for Cr in the residual phase was greater than 1. They concluded that a high percentage of Cr in inert associations with the crystal lattices probably reflects the lithogenic influences from the drainage basin of the Rhine River.

The PCF is especially useful in understanding the mobility of a metal, since it is a relative value that is not influenced by the total amount of phase present. It is especially suited for comparison of samples with large differences in total metal concentrations. Forstner and Patchineelam found that PCF values of Cr were greater than 1 in both the easily and moderately reducible fractions. In addition, they computed this value to be significantly higher for the silt size particles than for the fine-grained sediments.

OXIDATION STATES OF CHROMIUM AND ADSORPTION ONTO MN OXIDES, FE OXIDES, AND ORGANIC MATTER

An estimation of the Cr oxidation state associated with the various chemical phases is necessary in order to 1) assess the stability of the adsorbed species, and 2) make predictions about the behavior of Cr upon mobilization from a specific phase. If Cr is releasd as the hexavalent species, then it will likely remain in solution, whereas trivalent Cr would readily precipitate out of solution as the hydroxide.

When Cr is complexed to organic materials, it probably is in the +3 oxidation state. These complexes are relatively inert and thermodynamically metastable, and can exist for long periods of time (Cotton and Wilkenson, 1972; in Filipek and Owen, 1979). That Cr is in the +3 oxidation state on organics may be supported by the following reasons:

1. Organic material is most stable in reducing environments. Under these conditions it is likely that Cr will exist as the reduced species, with an oxidation state of +3.
2. Organic colloids are usually negatively charged species, due to the presence of carboxyl and hydroxyl groups. Therefore, these species would adsorb positively charged ions. When Cr exists as a cation, it is in the +3 oxidation state ($Cr(OH)^{2+}$ and $Cr(OH)_2{}^{+}$).

Bartlett and James (1979) have concluded that Cr exists in the +6 oxidation state when adsorbed on Mn oxides. Their study suggests that Mn can exist as the electron acceptor in soil systems in which Cr(III) is being oxidized to Cr(VI). It was concluded that Cr is adsorbed onto the negatively charged Mn oxide surface as the trivalent cation, and then is oxidized by Mn to the hexavalent species. Now unstable on the Mn oxide surface, this species is released into solution as Cr(VI).

Although researchers have defined the oxidation state of Cr adsorbed onto Mn oxides and organic material, little is known about Cr speciation when adsorbed onto Fe oxides. Since Fe oxides play an important role in Cr mobility, a knowledge of the Cr oxidation state associated with them is needed. Consider the following argument.

An understanding of the mechanism for the sequestering of trace metals by Fe and Mn oxides is necessary if we are to understand the importance of this process in determining the fate of Cr in the environment. It is believed that one or more of the following mechanisms may be responsible for the sequestering ability of Fe-Mn oxides; coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the crystal lattice (Chao and Theobald, 1976; Loganathon and Bureau, 1973; Murray and Dillard, 1979). Hem (1977), using theoretical equilibrium models has shown that a ferrous-ferric oxidation reaction coupled with the reduction of Cr could cause the precipitation of Cr with the formation of the hydrous Fe oxide. The reduction of Cr by the oxidation of Fe was experimentally demonstrated by Schroeder and Lee (1975). The surface of Mn oxides is thought to be more reactive than that of Fe oxides and, therefore, should be able to sequester more metals (Stumm and Morgan, 1970). The pH's of hydrolyses of the two oxides are 8.6 for Mn(II) and 5.5 and 2.0 for Fe(II) and Fe(III) respectively. In natural water systems with pH's below 8.6 little Mn(II) would be expected to precipitate. However, Fe has been suggested to be a catalyst for the oxidation of Mn(II) and thereby cause the precipitation of the Mn oxide (Hem, 1975, 1977; Chao and Theobald, 1976). The Mn oxide with a pH at zero point charge (ZPC) of 3-4 would have a negative surface in the pH range 5.5

to 8.5 and therefore would attract the positive surfaced Fe oxide ($pH_{zpc} = 8.6$). Although the Fe has a lower pH of hydrolysis, it probably exists in solution as the colloidal form and thereby is able to react with the Mn surface. The "new" Fe surface could then cause more Mn to precipitate. This process would continue to build up a complex mixed Fe-Mn oxide system.

If the solution is oxidizing, then the Cr species is anionic ($Cr_2O_7^=$ or $CrO_4^=$), and might be expected to be sequestered by the positive surface of the iron phase of the Fe-Mn oxide system. On the other hand, if the cationic species is present due to the reduction of Cr by Fe(II), Cr might be expected to be sequestered by the Mn phase. These arguments need to be tested and are addressed in this study.

EFFECTS OF GRAIN SIZE ON THE SEQUESTERING AND PARTITIONING OF CHROMIUM

The partitioning of Cr among the various chemical fractions does not vary significantly with grain size, however, the concentration of Cr sequestered by the various fractions does (Gibbs, 1977; Filipek and Owen, 1978; Forstner and Patchineelam, 1980).

Filipek and Owen (1978) examined the effects of grain size on trace metal partitioning from Little Traverse Bay, Michigan, and determined that actual concentrations of metals increase by 2 to 20 fold from the sand to the clay fraction. In comparison, the total surface area increases by a factor of at least 10^5 in these fractions. They emphasize that this is a much greater magnitude than that of the change in metal concentrations, and, since the increase in metal concentrations from sand to clay is small, the metals are primarily of detrital origin. If the origin of these metals were hydromorphic, then the metal concentrations would be more surface area-dependent.

Gibbs (1977) examined the concentration of Cr in various transporting phases for various particle sizes for the Amazon and Yukon Rivers (Figure 1). The concentration of Cr associatd with crystalline material increased as grain size decreased. This increase was of much lower magnitude than the increase in surface area associated with decreasing grain size. The behavior of Cr here was attributed not to an increase in surface area, but to a changing mixture of clay minerals, quartz, and feldspar. Clay minerals are usually rich in the transition metals, while the larger grained quartz and feldspars are poor in transition metals.

Figure 1: Concentration of chromium in various transporting phases for various particle sizes for Amazon and Yukon Rivers (Gibbs, 1977).

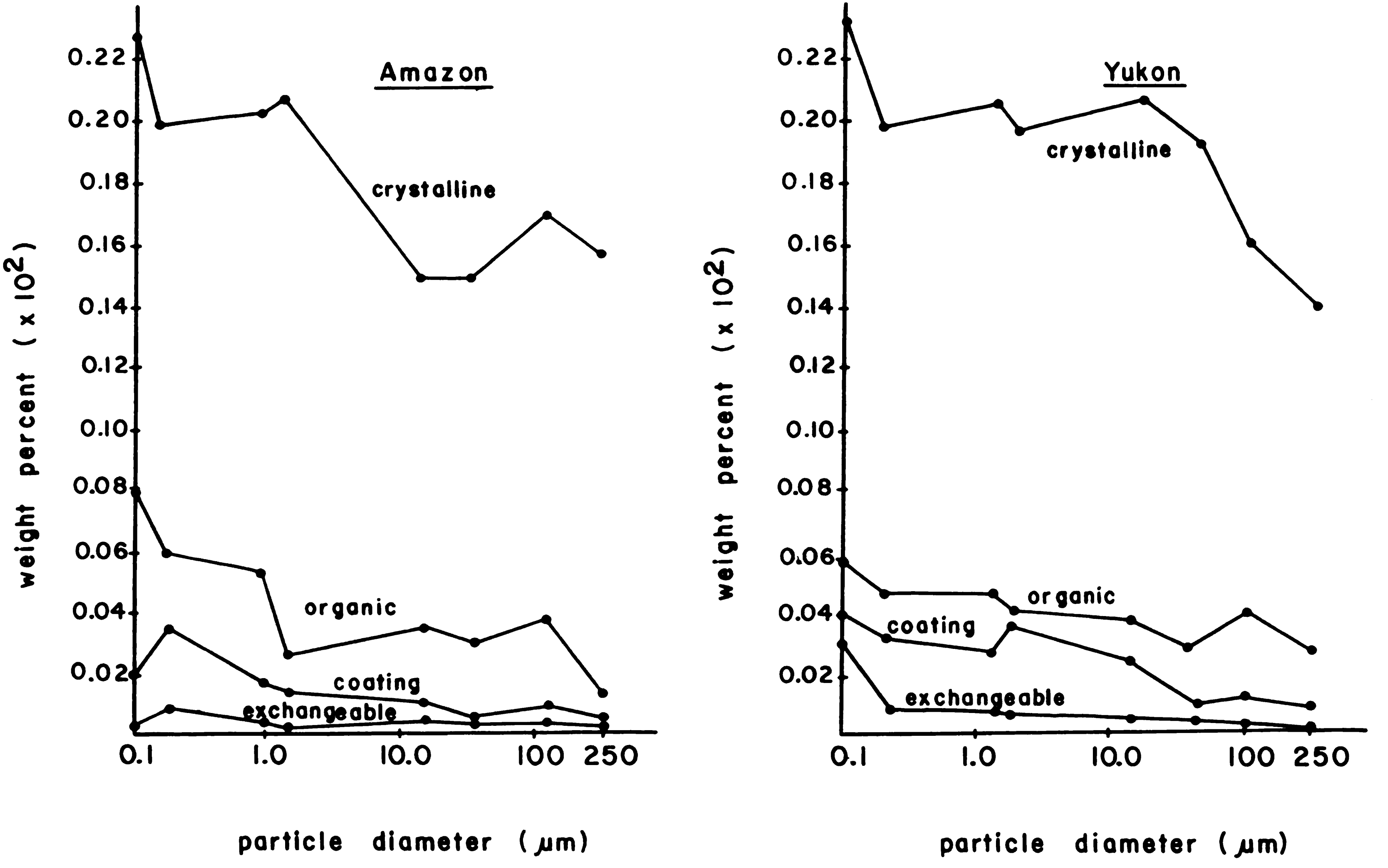

Amazon
crystalline
organic
coating
exchangeable
weight percent (x 10^2)
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.1
1.0
10.0
100
250
particle diameter (μm)
Yukon
crystalline
organic
coating
exchangeable
weight percent (x 10^2)
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.1
1.0
10.0
100
250
particle diameter (μm)

Figure 1.

Chromium concentrations in the oxide phase increases as grain size increases (Forstner and Patchineelam, 1980; Gibbs, 1977). Gibbs (1967) attributed this to a greater supply of metals to a larger grained materials. The coarser material would have a higher permeability, thus would allow a greater supply of precipitating ions to filtrate through the soil. The fine-grained material would have a lower permeability, which, in turn, would decrease the availability of precipitating metals to the oxide coatings.

Chromium concentrations in both organic and exchangeable phases increased with decreasing grain sizes (Gibbs, 1977; Forstner and Patchineelam, 1980; Filipek and Owen, 1978). This may be attributed to an increase in surface area available for precipitation of metals. The effect of grain size on Cr sequestering by carbonates has not been examined, however, other metals such as Mn, Cu, and Zn are more concentrated in the fine-grained sediment fractions than in silt size materials (Forstner and Patchineelam, 1980).

The mass transport of a metal in a riverine system is a function of 1) the concentration of the element present, and 2) the size distribution of the phases times the mass transportation rate of each (Gibbs, 1977). Although smaller particles have higher Cr concentrations, particles of intermediate size are more abundant, and therefore sequester a greater amount of Cr.

A more thorough investigation of the mass transport of Cr would require a knowledge of the size distribution of each of the various phases. Since the size distribution between phases differs, a single value for the size mode cannot be obtained. Gibbs found that the transportation mode for Cr in the various phases ranged between 2 and 15 μm.

Past research has indicated that the relative importance of chemical phases in sequestering Cr does not appear to be affected by the grain size of the sediment. This study will examine different grain size fractions (> and < 0.21 mm) to confirm this hypothesis.

SUMMARY OF PAST RESEARCH

It is generally agreed that the greatest percentage of Cr in a system is associated with the residual phase. The Cr associated with this phase, however, is not present as a result of adsorption processes. On the other hand, the Cr associated with the hydromorphic phases occurs as a result of various adsorption processes. The relative importance of the hydromorphic phases in sequestering Cr is not well understood, however, it appears that either the organic material or the hydrous oxide coatings may be responsible for adsorbing the greatest percentage of Cr. It would be useful to understand the relative importance of the phases on Cr adsorption in terms of the geochemistry of Cr and the chemistry of the system so that the results may be extended to other systems. Previous research, however, has not attempted this.

Although past research has indicated that the Fe-Mn oxide coatings are important adsorbers of Cr in a riverine system, it is not known which phase (Fe oxides or Mn oxides) is mostly responsible for this.

Most of the past research does not consider the effects of the phase concentrations when determining the relative importance of the phases in sequestering Cr. In studies where the goal is to provide a chemical explanation for the relative importance of the phases, this aspect must be considered.

A knowledge of the oxidation state of Cr when complexed to the various chemical phases is a requirement for assessing the stability of this metal in association with a phase. It has been determined that Cr is in the +3 oxidation state when complexed to organic material. It has been suggested that Mn oxides adsorb Cr as the trivalent cation, but then oxidize it to the hexavalent ion. The degree to which this process occurs has not been investigated. Also the oxidation state of Cr when associated with Fe oxides has not been examined.

Although little research has been focused on the effects of grain size on the partitioning of Cr, it is generally agreed that grain size does not affect the relative partitioning of Cr. However, absolute concentrations of Cr sequestered are very dependent on the grain size available for adsorption. With the exception of the hydrous oxides, smaller sized particles tend to sequester a greater amount of Cr than larger grained particles, due to a greater surface area available for adsorption. Although smaller particles sequester a greater amount of Cr per gram sediment, intermediate sized particles are responsible for sequestering the greatest percentage of Cr, simply because this size is most abundant.

One must be cautious in comparing the various partitioning studies. Although the technique used is the same (selective chemical extractions), the methodologies differ.

In conclusion, the major gaps in our knowledge that prevent an understanding of the relative importance of the hydromorphic phases in sequestering Cr are:

1. the relative importance of Fe-Mn oxides and organics in sequestering Cr,
2. the relative importance of Mn and Fe oxides,
3. the effects of phase concentrations on Cr partitioning,
4. the oxidation state of Cr on Fe oxides, and the extent to which Mn oxides are capable of oxidizing Cr from the +3 and +6 state, and
5. a theoretical understanding of the adsorption processes by the various phases.

This study will specifically focus on these problems.

LOCATION AND DESCRIPTION OF THE STUDY AREA

The area of investigation is the Grand River located in the south-central portion of Michigan's Lower Peninsula (Figure 2). It includes the western edge of Ingham County. The City of Lansing, with a population of 137,000, lies in the northwest corner of Ingham County and is the center of industrial and commercial activity in the region.

The Grand River enters Ingham County from the south and flows through Lansing, and then westward through Grand Ledge and into Lake Michigan. Within the study area, the Grand River drains Clinton, Eaton, and Ingham Counties, whose combined population is 410,000. Its drainage above Lansing is approximately 12,300 sq. miles which represents 22% of its total drainage area (Firouzian, 1963). In the northwest corner of Ingham County, the Red Cedar River enters the Grand River from the east. Major tributaries of the Red Cedar include the Sycamore Creek, Deer Creek, Doan Creek, and Sloan Creek (Radfar, 1979). The amount of base flow for the Grand River south of Lansing is 3×10^{-4} CMS per sq. km., while that for the Red Cedar in East Lansing is 2×10^{-4} CMS per sq. km. (Firouzian, 1963). With an annual flow of 23.5 CMS at Lansing, the Grand River has an average width of 45 meters and is up to 3 meters deep.

Climate

The study area is a humid environment, with an average precipitation of 78.7 cm. The wettest month of the year is May, averaging 10.2 cm of rain. The months of April and June through September average 7.62 cm (The Weather

Figure 2: Study area and sampling locations.

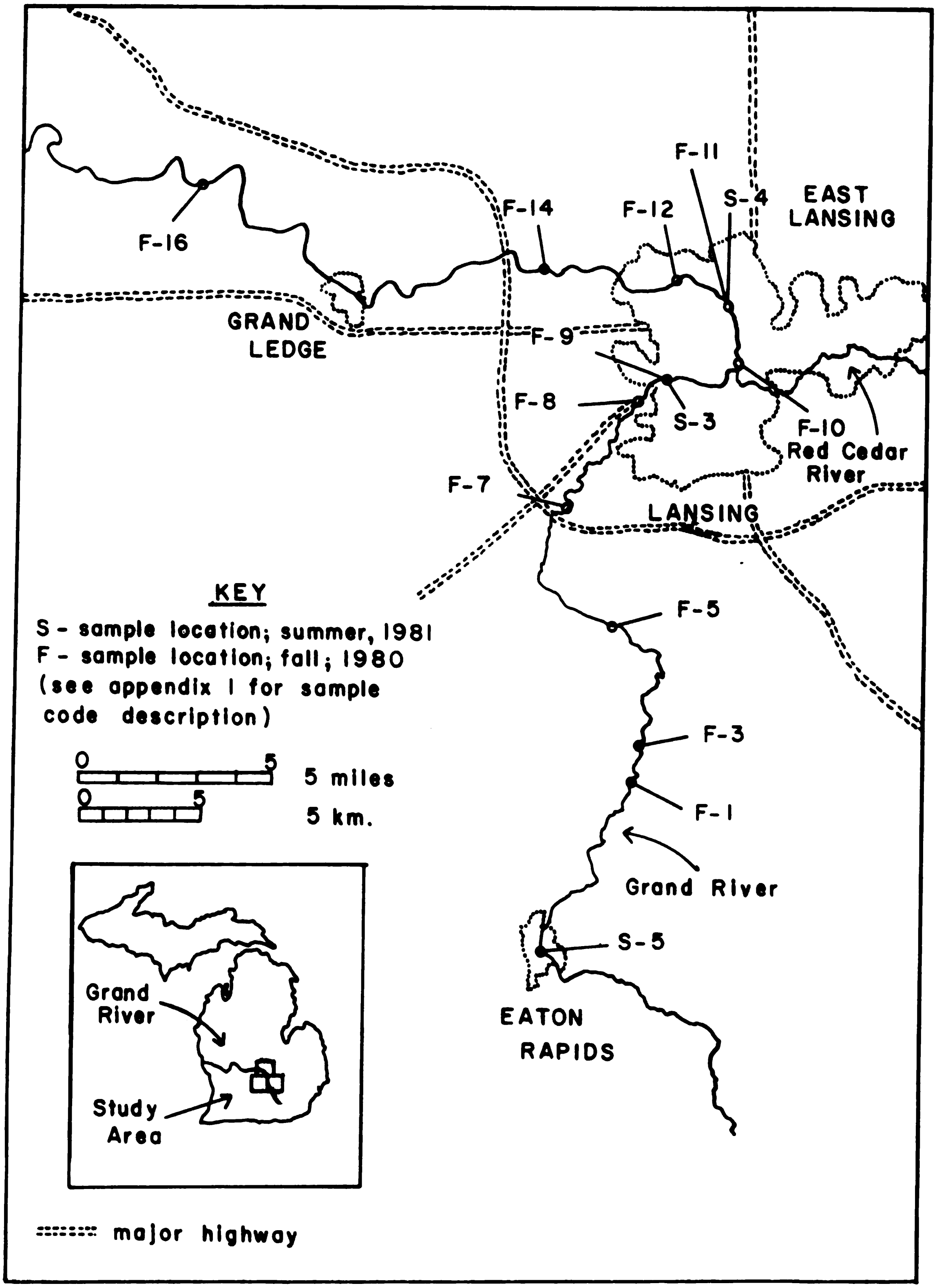

F-11
S-4
EAST LANSING
F-14
F-12
F-16
GRAND LEDGE
F-9
F-8
S-3
F-10
Red Cedar River
F-7
LANSING
KEY
S - sample location; summer, 1981
F - sample location; fall; 1980
(see appendix I for sample code description)
F-5
F-3
F-1
0 5 5 miles
0 5 5 km.
Grand River
S-5
EATON RAPIDS
Grand River
Study Area
major highway

Figure 2.

Handbook, 1974). Twenty percent of the annual precipitation falls as snow, mainly during the months November through March. Table 2 shows the average monthly temperatures (maximum and minimum) and total monthly precipitation for the City of Lansing. Almost 65% of Lansing's total annual precipitation is lost to transpiration (U.S. Dept. of Commerce, 1976).

Vegetation

Most of the study area is contained within Ingham County, which is 15% covered by forest. The forest includes various association of hardwoods, principally oak, hickory, beech, and ash. Most of the county is covered by grass and non-cultivated crops with the rest used for the production of cultivated crops (Veatech, et al., 1961).

Geology of the Area

The topography of Ingham County is characterized by gently rolling morainic hills and flat undulating ground moraine. Pleistocene glacial drift, which ranges from 0 to 36 meters in depth, covers the bedrock. The drift comprises unconsolidated clay, silt, sand, and gravel. The bedrock is composed of alternating beds of sandstone and shales with thin beds of coal and limestone representing the Saginaw Formation of Pennsylvanian Age. The bedrock forms the southern edge of the Michigan Basin and dips about one degree north. As mentioned earlier, ultramafic rocks are the primary source of naturally occurring Cr. Since this type of rock is not abundant in the study area, the bedrock and glacial drift are not expected to be a dominant source of Cr to the area.

Table 2: Average monthly temperatures (°C) and precipitation (cm) for Lansing, MI (The Weather Handbook, 1974).

	TEMPERATURE			PRECIPITATION	
	Ave.	Max.	Min.	Total	Snow
Jan.	-4.4	-0.6	-8.3	5.1	27.9
Feb.	-4.4	0.0	-8.9	5.1	22.9
Mar.	0.0	5.0	-4.4	5.1	20.3
Apr.	7.8	13.3	1.7	7.6	7.6
May	13.9	20.0	7.8	10.2	t
June	19.4	25.6	13.3	7.6	0.0
July	22.2	28.3	15.6	7.6	0.0
Aug.	21.1	27.8	15.0	7.6	0.0
Sept.	16.7	22.8	10.6	7.6	t
Oct.	10.6	16.1	5.0	5.1	2.5
Nov.	3.3	7.2	-1.1	5.1	15.2
Dec.	-2.8	1.1	-6.1	5.1	25.4
Yearly	8.9	13.9	3.3	78.7	121.9

PRELIMINARY RESEARCH

Preliminary research was initiated in order to determine if the Lansing environment acts as a point source for Cr, as well as for Pb, Mn, Fe, Cu, Zn, and Ni, and thereby provide a suitable field area for further studies. It was concluded that the Grand River sediments in Lansing provide concentrations of these metals at high enough values for their study and that Lansing is a point source for these metals.

Methodology

Sediment samples were collected by hand at the water-sediment interface along the bank, and temporarily stored in polyethylene bags. Within three hours after collection, the samples were centrifuged at 28,000 RPM and then dried for at least 48 hours at $50^{\circ}C$.

An indication of the amount of "mobile" (or hydromorphic) metal was obtained by treatment of the sediment with an acid-reducing solution. Five gram sediment samples of the less than 80 mesh were leached with 1N hydroxylamine hydrochloride in 25% (v/v) acedic acid. Reaction time was six hours with continuous agitation at room temperature. The leachates were separated from the sediment by centrifugation at 28,000 RPM and stored in polyethylene bottles.

Since organic material is also responsible for the sequestering of Cr and other metals, the amount of Cr in this fraction was spot checked in three of the samples. This was done by leaching 2 grams of each sample with 3 ml of 0.02M HNO_3 and 15 ml of 30% H_2O_2 (adjusted to a pH of 2 with HNO_3). The H_2O_2 was added in increments of 5 ml, 15 minutes apart with the solution maintained at a temperature of 85 ± 3.2M NH_4OAc (in 20% (v/v) HNO_3) was added to each sample, followed by dilution to 100 ml.

Results

Although not enough data was collected to establish real background concentrations for the area, significant increases of the metals studied were detected in the stream sediments to suggest that Lansing is acting as a point source for these metals (Table 3). The greatest increase occurs between sites 9 and 10. Siges 1 through 9 can be considered as one population and sites 10 through 18 as another population. Between the two populations, the concentration of Pb differs the greatest by a factor of 37 followed by Zn (7.4), Ni (4.4), Cr (4.4), Cu (2.9), Fe (1.5), and Mn (1.5).

The amount of Cr liberated by the oxidizing attack on samples 8, 15, and 17 was 0, 25, and 43 in ppm whole rock respectively. Comparing these values to the "acid reducing" fraction for the same sites shows that more Cr may be associated with the Fe-Mn oxides than with organics. The limited data, lack of statistical data analyses, and the nature of the chemical attacks used make interpretations on the chemical partitioning of Cr or other elemental associations tenuous. However, a comparison of the preliminary data with results of Long and Jernigan (1978) indicate that the relative partitioning of Cr is different between area in which Cr is being added naturally and one in which it is being added as a pollutant (Table 4). These results stimulated further work.

Table 3: Acid-reducing leach attack on preliminary samples along the Grand River, MI.

SITE	Fe	Mn	Cu	Pb	Zn	Ni	Cr
1*	22400**	3589	4.3	71	214	40.8	12
2	27800	4552	5.9	150	712	59.8	14
3	26200	4662	13.9	161	724	179	15
4	16600	3538	4.6	66	208	51.3	6
5	13000	3214	318	80	104	62.1	4
6	9600	3429	30.7	203	100	35.2	3
7	8100	1266	27.4	33	33	20.9	2
8	32700	2037	123	142	65	76.0	6
9	9200	1807	51.7	368	227	82.7	3
10	31000	4721	151	5584	2104	400	33
11	25600	4640	94.5	2312	1657	101	30
12	27600	4737	233	2040	1640	391	26
13	29200	4830	196	2264	1833	399	36
14	26700	4763	203	2848	1768	327	36
15	21200	4583	107	1152	1094	156	15
16	21600	3981	145	1432	1350	261	24
17	29100	4700	469	12832	1771	499	57
18	28700	4576	116	15920	1447	128	26

* Sites 1-9 are located along the Grand River south of Lansing at approximately equal intervals. Sites 10-14 are located within the City of Lansing, and sites 15-18 are north of Lansing.

** ppm whole rock.

Table 4: Chromium partitioning in stream sediments*.

Fraction	Lower Barton Creek, NC	The Grand River, MI
oxidizing (organic)	2.86	24**
acid reducing (Fe-Mn oxides)	0.60	36

* In ppm whole rock

** Oxidizing values for the Grand River based on three samples

METHODOLOGY

Selective Chemical Extractions

An assessment of the bioavailability of an element from sediment or soil and the controls on its concentrations in solution dictates that one study the amount of metal associated with the hydromorphic phases rather than the total metal concentration. The determination of the hydromorphic states of a trace metal in the soil or sediment is accomplished by the method of selective chemical attacks or by statistical inference. The method of selective chemical attacks is most often used. The rationale of the method is that selected chemicals will react preferentially with certain phases of the soil or sediment and can cause dissolution of this phase, along with the mobilization of the metals that are associated with it.

The attacks can be done separately on sub-splits of a sample or sequentially on one split of a sample. Because of this difference in technique (sequential analysis or separate analysis) and the variety of experimental procedures chosen for the attacks, it is often difficult to compare absolute results among the investigators. Regardless of the technique, however, the method of selective chemical attacks do indicate the relative importance of chemical fractions in the soils or sediments and their association with trace metals and as such, is an important tool in determining the behavior of those metals. The methodology, however, must be well defined before any interpretation can be made.

Procedure of Selective Chemical Attacks Used in this Study

Two sampling periods were chosen for this study: Fall of 1980 and Summer of 1981. Sampling locations are depicted on Figure 2.

A. Collection of Samples:

1. Water samples: The samples were collected at the water-sediment interface with a Van Dorn water sampler. The parameters Eh, pH, and temperature were recorded in situ, and alkalinity was determined within two hours of collection.
2. Sediment samples: The Fall, 1980 samples were collected using waders and a polyethylene scoop near shore. In the Summer of 1981, the samples were collected from a canoe, with a bottom grab sampler. Samples were collected from the thalwig or in cross section as indicated (in results, Appendix 1).

B. Preparation of Samples:

1. Water samples: The samples were filtered through a 0.45 µm millipore filter and acidified to a pH of < 2. Polyethylene bottles were used for storage.
2. Sediment samples: The sediments were oven dried at 30-40°C and sieved into the > 0.21 mm and < 0.21 mm size fractions. Wax cartons were used for storage.

C. Water Analysis:

All water parameters were determined within 18 days of sample collection. Concentrations of Na, Ca, and Mg were measured by flame atomic adsorption spectrophotometry. A graphite furnace was used to measure Cr. Sulfate concentrations were determined by a method using atomic adsorption spectrophotometry (Dunk, et al., 1969). A chloride electrode was used to determine chloride. Alkalinity was determined by potentiometric titration. Table 5 summarizes the results of the water analysis.

D. Sediment Mineralogy:

X-ray diffraction analyses were performed on the whole sediment as well as on their clays (clay mineralogy analysis methodology, Jackson, 1958). The whole sediment is composed mostly of quartz, with lesser amounts of calcite and dolomite. Albite was also detected in small amounts. The clays present are mostly illite and kaolinite, with some vermiculite and minor amounts of smectite and chlorite. Clay minerals were found to make up a very small percentage of the bulk samples. A low abundance of clay minerals is expected in river sediments from the thalwig. The sample mineralogy is consistent with what would be expected in river sediments in this area (Balkumar, 1971). The amount of Cr detected in the samples (Appendix 1) is consistent with normal background concentrations for unconsolidated sediments and soils (Connor and Shacklett, 1975), suggesting that there is no unique source for anomalous concentrations of Cr in this area.

E. Selective Chemical Attack Procedure:

In this study, six fractions were defined in the partitioning of Cr. The fractions chosen were those most likely to be affected by various environmental conditions. They include exchangeable, carbonates, Mn oxides, Fe oxides, Organics, and Residual. The procedure used is a combination of attacks used by Tessier (1979), Chao and Theobald (1976), and Gupta and Chen (1975) and is summarized below:

1. Exchangeable: 5 grams of dry sediment was extracted at room temperature with 40 ml of 1M $MgCl_2$, pH 7, with continuous agitation for 1 hour (Tessier, 1979).

Table 5: Results of the water analysis*

Location	Cr	Ca	Mg	Na	K	SO_4	Cl	Alk[1]	pH	Eh[2]	T[3]
Eaton Rapids	N.D.	72.0	23.0	22.6	3.2	—	34	158.0	7.3	-6	19
Maple	N.D.	79.0	24.0	21.4	5.8	61	680	156.6	7.4	179	21
pre- Moor	N.D.	68.4	22.2	18.4	3.8	47	25.5	153.8	7.5	101	19
Moor	N.D.	68.4	22.0	17.8	3.4	47	27.0	156.6	7.4	174	20
Grand Ledge	N.D.	70.4	22.4	22.4	4.4	63	34.0	156.6	7.55	189	21
Dimondale	N.D.	78.4	24.2	19.0	4.8	47	720	159.4	7.2	259	19

* concentrations in ppm

[1] alkalinity

[2] values in mv

[3] temperature in °C

N.D. - None detected

2. Carbonates: The residue from (1) was leached with 40 ml of 1M NaOAc (pH 5 with HOAc) at room temperature with continuous agitation for 5 hours (Tessier, 1979).
3. Mn oxides: The residue from (2) was leached with 125 ml of 0.1M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc at room temperature for 30 minutes with continuous agitation (Chao and Theobald, 1975).
4. Fe oxides: The residue from (3) was leached with 100 ml of 0.04M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc at $96^\circ \pm 3^\circ C$ with occasional agitation for 6 hours (Tessier, 1979).
5. Organics: The residue from (4) was leached with 15 ml of 0.02M HNO_3 and 25 ml of 25% H_2O_2 (pH 2 with HNO_3) at $85^\circ \pm 2^\circ C$ for 2 hours with occasional agitation. A second aliquot of 15 ml of 30% H_2O_2 (pH 2 with HNO_3) was added and the sample was heated to $85^\circ \pm 2^\circ C$ for 3 hours with occasional agitation. After cooling, 25 ml of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 100 ml and agitated continuously for 30 minutes. The addition of NH_4OAc is designed to prevent adsorption of the metals onto the oxidized sediment (Gupta and Chen, 1975).
6. Residual: 0.2000 grams of dry residue (5) was fused with 1.000 grams of $LiBO_3$ and 15 minutes at $1000^\circ C$. The fused sample was immediately dissolved in 5 ml HCl and approximately 50 ml of double distilled water. Upon dissolution, the sample was diluted to 100 ml. Triplicate fusions were run for each sample (Perkin Elmer Atomic Adsorption Instruction Manual, 1973).

All extractions, except the determination of the residual fraction, were done in 250 ml polyethylene centrifuge tubes. Between extractions, each sample was centrifuged for 12 minutes at 15,000 RPM. The

Table 6. Chemical Characteristics of Phases

Phase Extracted	Chemical Characteristic
Clays	Exchangeable
Carbonates	Easily acid-soluble
Mn oxides	Easily reducible
Fe oxides	Moderately reducible
Organics	Oxidizable
Resisual	Resistant

Table 7: Chemicals utilized in the extraction of metals associated with different chemical phases in sediments*.

Chemical phase	Extraction methods	Authors
Adsorption and cation exchange	(a) $BaCl_2$; (b) $MgCl_2$ (c) NH_4OAc	Jackson, 1958; Gibbs, 1973
Detrital/authigenic phases	EDTA treatment	Goldberg and Arrhenius, 1958; Gad and Le Riche, 1966
Hydrogenous/lithogenous phases	(a) 0.1M HCl (b) 0.3M HCl (c) 0.1M HNO_3	Piper, 1971; Malo, 1977 Jones, 1973
Reducible phases	1M $NH_2OH \cdot HCl$; 25% v/v acetic acid	Chester and Hughes, 1967
Moderately reducible phases (hydrous Fe oxides)	Reduction with sodium dithionite complexing with sodium citrate	Aguilera and Jackson, 1953 Holmgren, 1967
Easily reducible phases (Mn-oxides and amorphous Fe oxides)	0.1M $NH_2OH \cdot HCl$; 0.01M nitric acid	Chao, 1972

* Forstner and Wittman, 1979

Table 7: Continued.

Chemical phase	Extraction methods	Authors
Carbonates	(a) CO_2 treatment (b) Exchange columns	Patchineelam, 1975; Deurer, et al., 1978
Organics, sulphides	30% H_2O_2 at 95°C, extract with (a) 1N NH_4OAc or (b) 0.01M HNO_3, fat solvents: e.g., chloroform, ether, gasoline, benzene, carbon disulfide	Jackson, 1958; Engler, et al., 1974; Gupta and Chen, 1975; Bergmann, 1963; Welter, 1969; Cooper and Harris, 1974
Humic and Fulvic acids	0.5N NaOH; 0.1N $NaOH/H_2SO_4$	Rashid, 1971; Volkov and Fomina, 1974
Solid organic material	Na hypochlorite, dithionite/ citrate	Gibbs, 1973
Detrital silicates	Digestion with $HF/HCLO_4$;	
	Lithium metaborate (1000°C)	Bennet and Hawley, 1965

supernatant was removed with a pipet and stored in a polyethylene bottle for analysis. Each sample was then washed with 25 ml double distilled water and centrifuged at 15,000 RPM for 10-12 minutes. The supernatant was discarded. The solutions to be analyzed were acidified to pH of less than 2. This step was found to be important, especially for the exchangeable and carbonate leaches. The supernatants from each selective chemical attack were analyzed by flame atomic adsorption spectrophotometry.

Although it is implied that selective chemicals are specific for dissolving specific phases, this is not exactily correct. The chemicals used in the attacks are specific for a certain chemical characteristic in the sediment or soil. For example, H_2O_2 is used to dissolve organic material, however, it will also dissolve any other portion of the sediment that will undergo dissolution when oxidized. Table 6 lists the chemical characteristic of each phase. Chemicals chosen to attack a certain phase actually attack all portions of the sediment with the specified chemical characteristic of that phase.

Discussion of Selective Chemical Attacks

A. Choice of Chemical Reagents:

It was mentioned earlier that differences in selective chemical attack procedures make it difficult to compare absolute results among investigators. One variable often encountered between selective chemical attack procedures is the choice of chemicals used in attacking a certain phase. Table 7 summarizes the variety of chemicals that have been used in the past for selective extraction procedures (Forstner and Wittman, 1979). The reagents chosen for use in this study were chosen on the basis of 1) their known selectivity to attack a specific phase, and 2) the ease to which they lend themselves to atomic absorption analysis.

Several reagents have been used to extract exchangeable metals, including $MgCl_2$, $BaCl_2$, NH_4OAc, and NaOAc. Although NH_4OAc has been most extensively used, several investigators claim that it may also attack the carbonate phase (Tessier, et al., 1977). In this study $MgCl_2$ was chosen for the exchangeable attack because 1) it does not appear to attack the carbonate fraction, and 2) it has been found to be an effective reagent for desorbing specifically adsorbed trace metals (Tessier, et al., 1979; Gibbs, 1973).

The reagent most often used for the dissolution of the carbonate phase is Na acetate. Usually it is acidified to a pH of 5 with HOAc. Lower pH's have been shown to partially attack Fe and Mn oxides. Grossman and Millet (1961) determined that the use of NaOAc to selectively attack the carbonate phase had no affect on organic carbon or free ion concentrations in noncalcareous soil samples.

Few investigators have attempted to differentiate between Mn and Fe oxides by selectively dissolving one group of oxides without seriously attacking the other. Chao and Theobald (1976) concluded that Mn oxides are selectively dissolved when leached with 0.1M hydroxylamine hydrochloride for 30 minutes at room temperature. Under these conditions, Fe oxides are not dissolved. A harsher attack with hydroxylamine hydrochloride will result in the dissolution of Fe oxides, such as that proposed by Tessier and co-workers (1979), in which the sediment is extracted with 0.04M $NH_2OH \cdot HCl$, but under a temperature of 95^oC, and with a reaction time of six hours.

Sodium dithionite-citrate is often used in dissolving Fe oxides. However, Tessier and co-workers (1979) observed a substantial precipitation of leached metals during the attack, presumably due to the formation of sulfide as a result of the disproportionation of dithionite. Other problems in the utilization of dithionite are 1) contamination with Zn, and 2) clogging of the burner in atomic absorption analysis. For these reasons hydroxylamine hydrochloride in HOAc was chosen for the Fe oxide attack, with the concentrations proposed by Tessier and co-workers (1979).

Hydrogen peroxide is usually utilized in selectively attacking organic matter. Although oxidation of all forms of organic material may not be complete, more efficient methods (e.g., concentrated nitric acid with or without hydrochloric or perchloric acid) may partially attack silicate lattices (Tessier, et al., 1979). This study attempts to selectively attack the organic fraction by leaching with H_2O_2 and HNO_3, as proposed by Tessier and co-workers (1979).

Procedures for dissolving primary and secondary minerals (residual phase) usually involve fusion with lithium metaborate or dissolution with mixtures of hydrofluoric and perchloric or nitric acids. Both procedures are effective. The lithium metaborate fusion procedure has been utilized in this study.

B. Steady State Analysis

A second variable encountered with selective chemical extraction procedures is the reaction time alloted for each of the specific attacks. To determine the optimum time of leaching for each of the selective chemical attacks, steady state experiments were conducted. These experiments were designed to show when steady state conditions are reached between the leaching solution and the sediment. This type of experimentation would also show if other phases of the sediment are attacked too long. The reaction time necessary to reach a steady state condition for each phase was determined by sampling the reacting sediment-solution system at selected time intervals. A steady state condition occurs when the amount of metal leached does not increase with an increase in reaction time. Three metals were studied: Cr, Fe, and Mn.

Two different procedures were utilized in determining when steady state conditions were reached for each phase. Both approaches utilize the previously described selective chemical attack procedure to selectively attack each phase. The two approaches in determining steady state conditions for each phase differ in the way the leachate extracted from each phase attack was obtained.

In the first approach, six subsplits of a main sample were utilized; each split corresponding to a specific reaction time to be studied. Care was chosen to randomly mix the splits between different phase attacks to prevent any bias; i.e., split A was not always selected for examining the shortest reaction time. All reaction times examined for each of the chemical attacks were done in triplicate.

The results of this first approach demonstrate the difficulty in obtaining homogeneous splits from a main sample. Specifically, the variation between the metal concentrations within the splits in triplicate at times made it difficult to draw conclusions as to when steady state conditions were reached. For this reason, a second approach to determining steady state conditions was attempted.

The procedure for the second approach involved the use of five splits from the main sample, each split corresponding to a steady state analysis for each of the five phases. This procedure does not encounter the problem of obtaining homogeneous splits from a main sample, since the same split was used in studying all reaction times for a given phase attack. The removal of solution from a split at selected reaction times resulted in a change in the ratio of metal concentration to solution; however, it was assumed that the alliquots removed were small enough that a large change in this ratio did not occur. The effects of this ratio change are not known and represents a weak point in the procedure. However, replacement of the alliquot removed with additional attacking chemical most likely would result in a greater amount of metal leached, since fresh attacking chemical would be available for leaching.

Of the two approaches, the first is a more ideal procedure, since the metal concentration - solution ratio is not altered. However, the second approach was utilized in this study, since the difficulty in obtaining homogeneous splits from a main sample prevented accurate conclusions as to when steady state conditions were reached. The results of the steady state analysis, approach II, are plotted in Figure 3, and are summarized below:

1. Exchangeable (Figure 3a): No Cr is leached. Both Fe and Mn reach a steady state plateau after one hour of reaction. Both Fe and Mn show a change in slope after one hour. This implies that a new chemical phase is being attacked. This experiment was repeated three times with smaller results.
2. Carbonates (Figure 3b): Both Cr and Fe reach a steady state plateau before the five hour recommended reaction time of Tessier (1979). Mn did not reach a steady state, even after seven hours of reaction. The behavior of Mn during this attack needs further investigation.
3. Mn oxides (Figure 3c): Cr, Mn, and Fe reach steady states before the recommended 30 minute reaction time (Chao and Theobald, 1976). It appears that Fe and Mn are leached from another phase after 30 minutes and 75 minutes, respectively.

Figure 3: Steady state analyses showing the amount of Fe, Mn, and Cr leached from the hydromorphic phases as a function of time. 3a) Exchangeable attack, 3b) Carbonate attack, 3c) Mn oxide attack, 3d) Fe oxide attack, 3e) Organic attack.

Exchangeable

Exchangeable

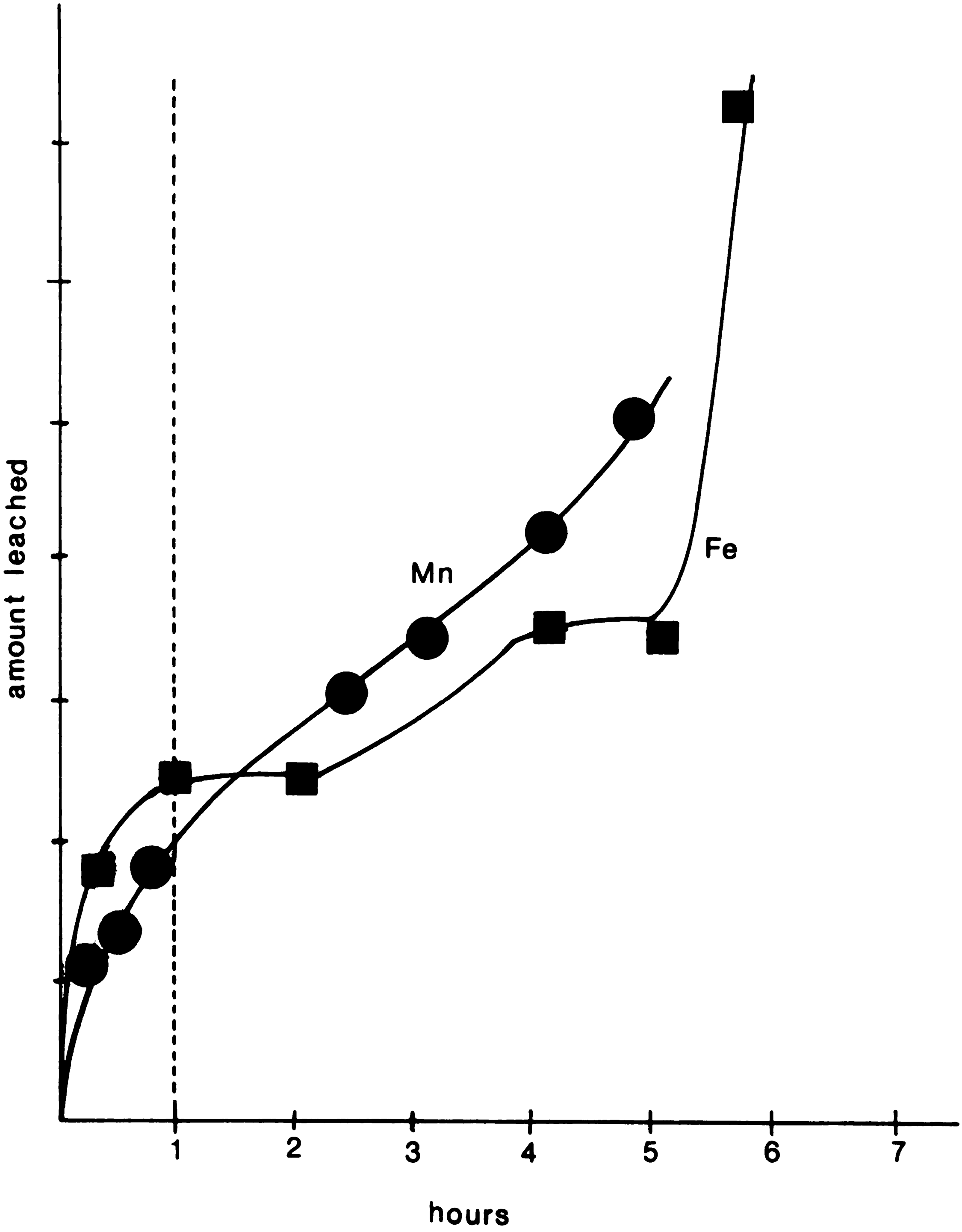


Figure 3a.

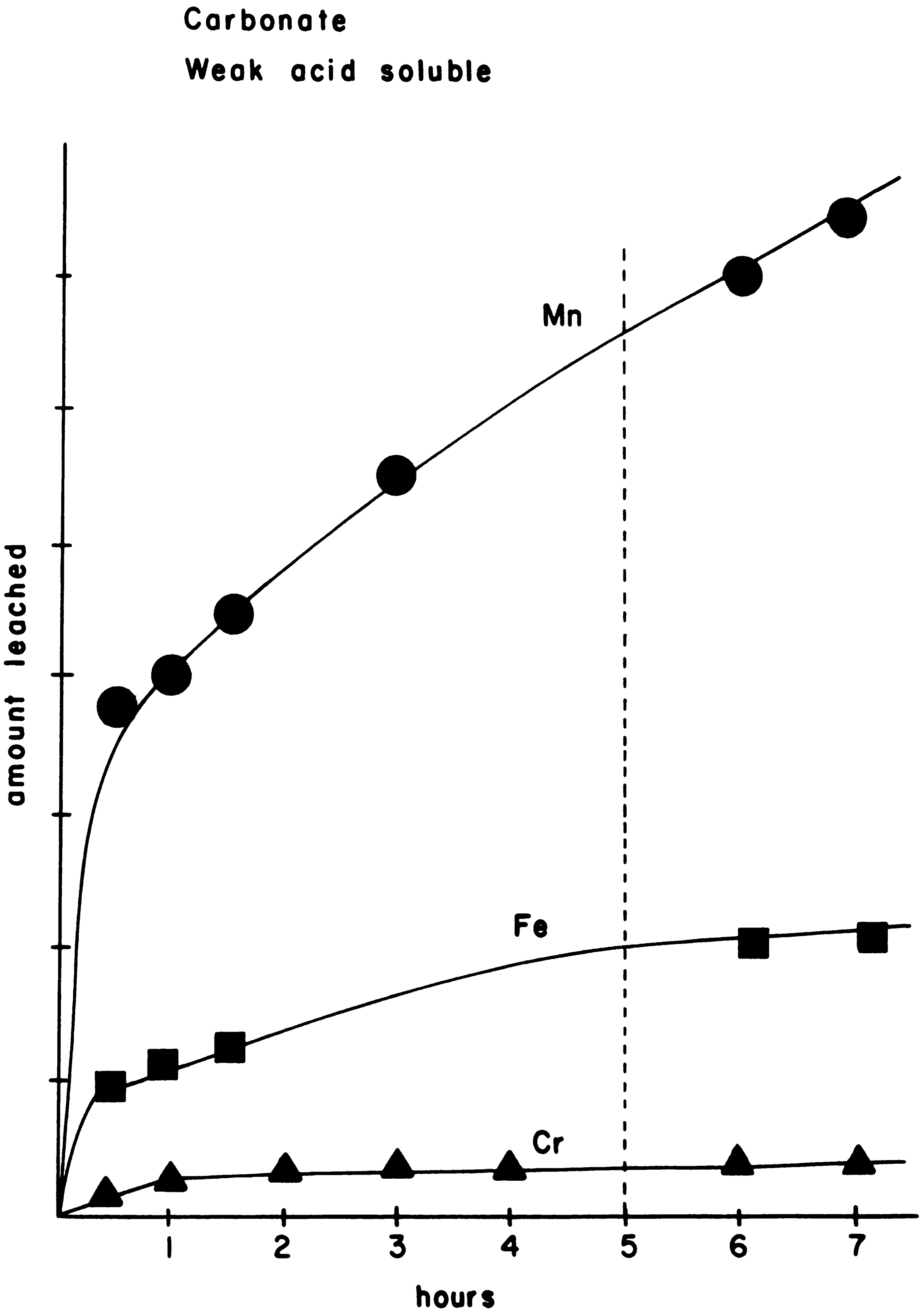

Carbonate
Weak acid soluble
Mn
Fe
Cr
amount leached
1
2
3
4
5
6
7
hours

Figure 3b.

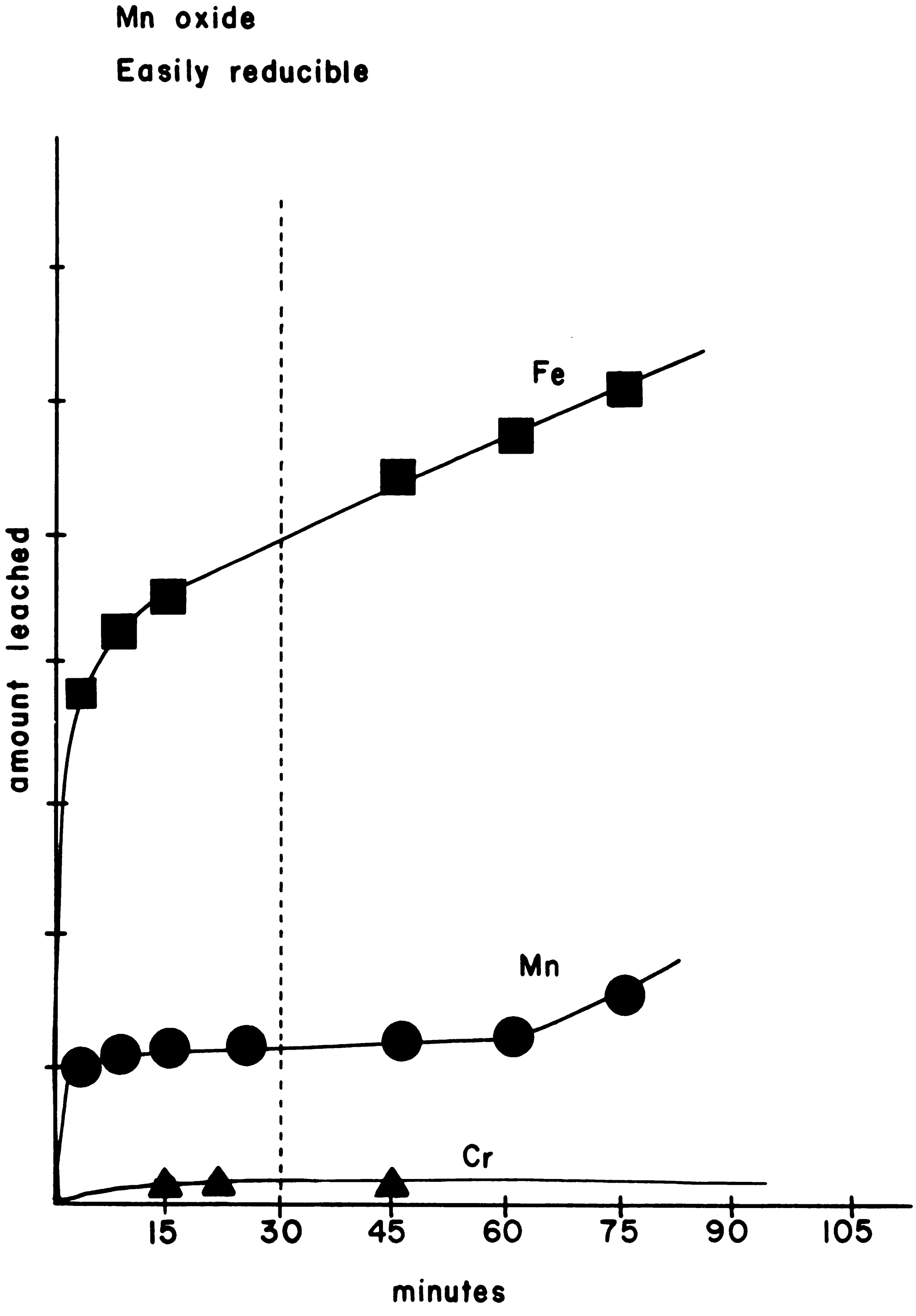

Mn oxide
Easily reducible
Fe
Mn
Cr
amount leached
15
30
45
60
75
90
105
minutes

Figure 3c.

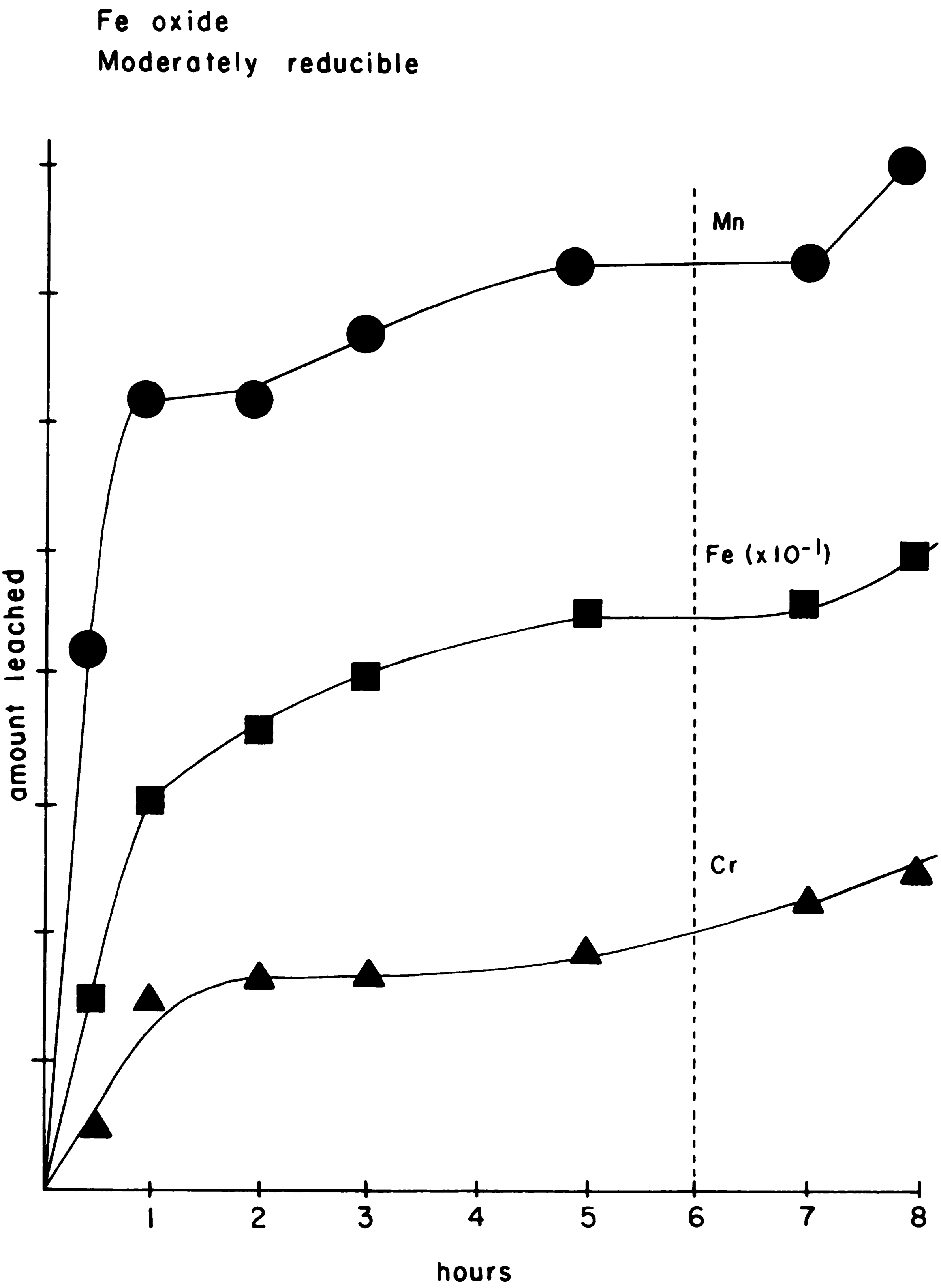

Fe oxide
Moderately reducible
amount leached
hours
Mn
Fe (x 10⁻¹)
Cr
1
2
3
4
5
6
7
8

Figure 3d.

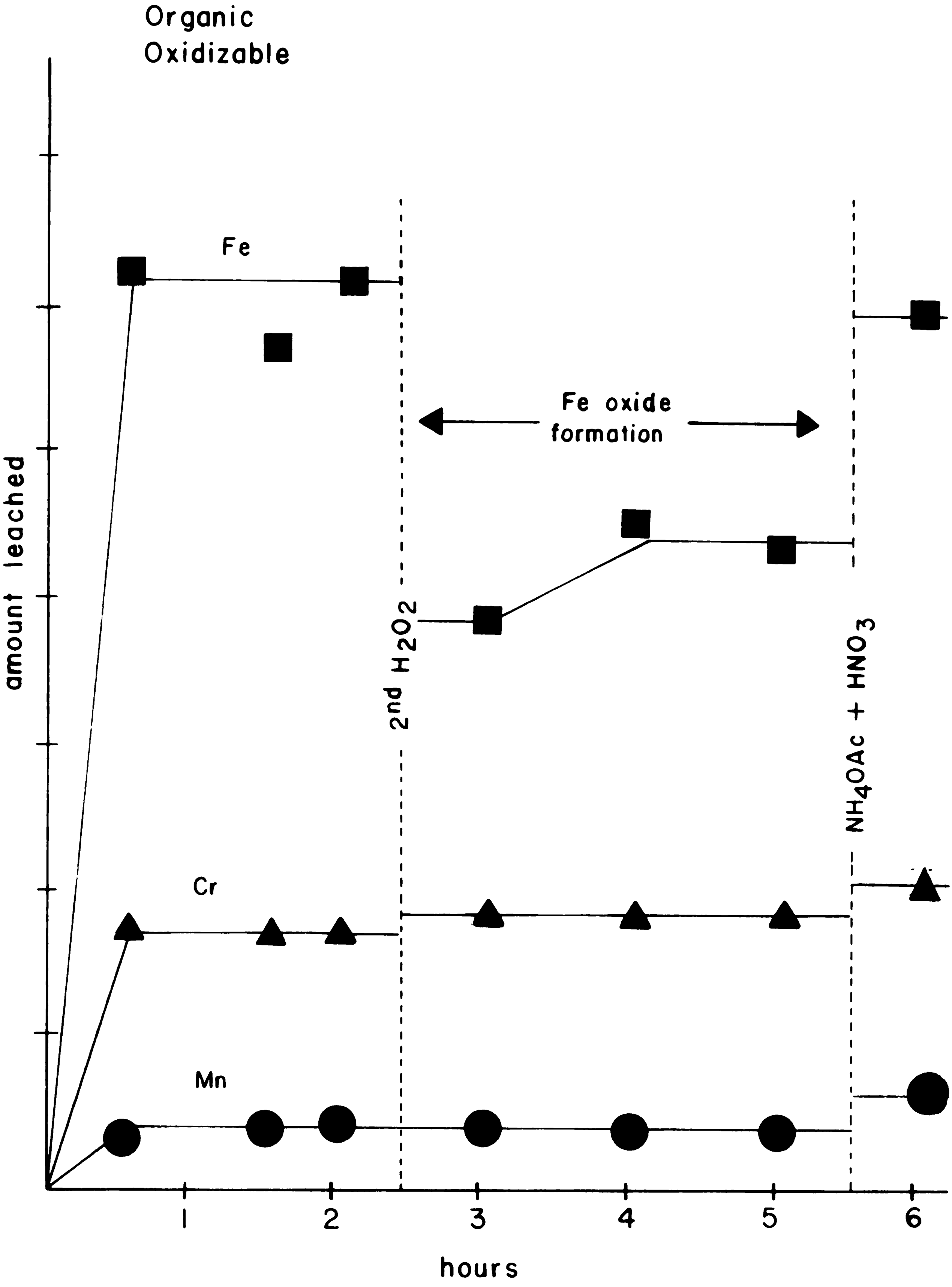

Organic
Oxidizable
Fe
Fe oxide formation
Cr
Mn
2nd H_2O_2
$NH_4OAc + HNO_3$
amount leached
1
2
3
4
5
6
hours

Figure 3e.

4. Fe oxides (Figure 3d): Cr, Mn and Fe reach steady states before the six hour recommended reaction time (Tessier, et al., 1979). Another phase appears to be attacked after eight hours.
5. Organics (Figure 3e): The nature of the organic attack does not easily lend itself to steady state analysis. However, the results do show that a steady state condition appears to be reached by the end of the six hour recommended reaction time (Tessier, et al., 1979). The second addition of H_2O_2 only liberates minor amounts of additional metals. The experiment demonstrates the importance of the additions of NH_4OAc and HNO_3 to recover any liberated metal that might precipitate as an oxide during the reaction. Fe is a good example.

Summary

Few investigations report a steady state analysis of the selective chemical attacks they use. These results confirm, in part, the previously run steady state analyses by Tessier and co-workers (1979). The results also suggest that the recommended reaction times for the other attacks (exchangeable, carbonate, and organic) are reliable. The behavior of some metals in certain attacks (Mn for example in the carbonate attack) needs further investigation.

The results also show that different metals behave differently during the attacks. This suggests that a steady state analysis should be done on all metals to be studied by this method.

Selectivity of Extractants

A knowledge of the selectivity of a certain chemical in attacking a specific phase is essential in the determination of the chemical partitioning for a metal. The degree of selectivity exhibited by a certain chemical must be evaluated on the basis of 1) the degree of completeness in dissolving a specific phase, and

2) its ability to resist attacking other phases. Tessier and co-workers (1979) have evaluated the selectivity of the chemicals used in this study. Theire results are as follows:

1. Exchangeable: An analysis of the exchangeable leachate resulted in low levels of Si, Al, S, Fe, and organic carbon. This implies that $MgCl_2$ does not affect the silicates, sulfides, Fe-Mn oxides, or organic material. A higher metal concentration than expected was found in the leachate from the carbonate phase, thus it is possible that the $MgCl_2$ does not completely desorb the "exchangeable" metals. Decreasing the pH from 7 to 5, however, may result in the release of metals from the carbonate fraction.
2. Carbonates: Low levels of Si, S, Al, and organic carbon material in NaOAc-HOAc leachate imply minimal dissolution of silicates, sulfides, and organic material. Higher concentrations of Fe and Mn present were attributed to a dissolution of divalent salts, namely ferrous and manganous carbonates. Complete dissolution of the carbonate phase is evidenced by the disappearance of the dolomite X-ray diffraction peak following treatment with the acetate buffer (pH 5.0).
3. Mn-Fe oxides: The amounts of Si and Al found in the leachate suggest that only a slight attack of the silicate lattices occur. X-ray diffraction results indicate a loss of smectite, suggesting partial attack of these minerals. Low levels of organic carbon imply that the organic fraction is not attacked. The completeness of $NH_2OH \cdot HCl$ in dissolving the oxide fraction is evidenced by the low levels of Fe and Mn in the organic leachate.

   Chao (1972), on the basis of differential response of Mn oxides and Fe oxides to chemical reduction and solution in acid medium, determined that a 0.1M solution of $NH_2OH{\cdot}HCl$ at room temperature selectively dissolved the Mn oxides when reacted with the sediment for only 30 minutes. Apparently, the degree of dissolution of Fe and Mn oxides is determined by, among other factors, the mineralogical structure of these oxides.

4. Organics: It was mentioned earlier that the dissolution of organics by H_2O_2 is incomplete, but that stronger oxidizing solutions result in the dissolution of silicate minerals. According to Jackson (1958), the remaining organic matter should consist of parifin-like material and resistant structural (nonhumified) organic matter residues. Low levels of Si and Al in the organic leachate suggest that the attack of silicate minerals is minimal.
5. Residual: Fusion of the sediment with lithium metaborate results in complete dissolution.

REPEATABILITY ANALYSIS

Selected samples were analyzed repeatedly over a period of eight months. Two aspects were studied: 1) the repeatability of leaching results for splits of the main sample, and 2) the effect of sample storage on leaching results. Table 8 summarizes the results for Cr. The following observations and conclusions were made:

1. The absolute value of the amount of Cr leached may change between different splits of the main sample. This demonstrates the difficulty of obtaining a totally homogeneous sample for analysis.
2. Even though the absolute values for the leachings are different between splits, interpretations of the relative partitioning of Cr between the fractions remains the same.
3. Sample storage does not appear to affect the relative partitioning of Cr between the chemical fractions. The effect of sample storage on the absolute amount of Cr leached cannot be differentiated from the variance noted in Table 8 for splits of the main sample.

Table 8: Repeatability analysis.

Sample	Date of collection	Date of leaching	Exch*	Cr concentration (ppm whole rock)				Res	TOC
				Carb	Mn-ox	Fe-ox	Org		
1. Size fraction: < 0.21 mm									
S-4, Maple	summer, 1981	summer, 1981	N.D.**	1.20	0.50	38.4	52.8	57	1.17
S-1, Maple	fall, 1980	summer, 1981	N.D.	1.44	0.50	24.8	34.8	47	0.79
F-11, Maple	fall, 1980	fall, 1980	N.D.	1.20	0.75	19.5	22.0	43	0.79
S-2, Holt	fall, 1980	summer, 1981	N.D.	1.20	0.75	16.4	31.2	40	0.85
F-5, Holt	fall, 1980	fall, 1980	N.D.	1.20	1.50	12.4	20.3	37	0.85
2. Size fraction: > 0.21 mm									
S-1, Maple	fall, 1980	summer, 1981	N.D.	1.52	0.50	25.2	42.6	32	1.14
F-11, Maple	fall, 1980	fall, 1980	N.D.	1.20	0.75	16.2	28.8	28	1.14
S-2, Holt	fall, 1980	summer, 1981	N.D.	1.12	0.50	18.4	39.2	32	1.09
F-5, Holt	fall, 1980	fall, 1980	N.D.	1.20	1.00	16.5	28.6	32	1.09

*Exch - exchangeable
Carb - carbonate
Mn-ox - Mn oxide
Fe-ox - Fe oxide
Org - organic
Res - residual
TOC - total organic carbon

**none detected

RESULTS AND DISCUSSION

Partitioning results for the metals Fe, Mn, Cu, Zn, Ni, and Pb are listed in Appendix I. The results of this research may be presented by two approaches. The first approach does not consider the amount of phase present, while the second does. The former approach (considered here as the traditional approach) asks the question, "Which of the adsorbing substrates in a particular environment sequesters the most metal?". This approach will be discussed first.

The second approach to be discussed asks the question, "Which of the potential adsorbing substrates is chemically more important for the adsorption of a metal (i.e., which substrate adsorbs more metal, given equal amounts of substrate)?".

Traditional Approach

The pi diagrams in Figure 4 summarize the mean Cr concentrations in each of the chemical phases for all phases for all samples, including fall and summer sampling periods. These diagrams indicate the relative importance of each of the phases in sequestering Cr, without considering the total amount of phase present. More Cr is associated with the < 0.21 mm size fraction than with the > 0.21 mm size fraction, but more "hydromorphic" Cr exists in the > 0.21 mm size fraction.

The greatest percentage of Cr is associated with the residual fraction. Of the hydromorphic phases, Fe oxides and organics appear to be equally important in the sequestering of Cr. The carbonate, Mn oxide, and exchangeable fractions

Figure 4: Summary pi diagram of chromium partitioning in the chemical phases. Results represent all samples from fall, 1980 and summer, 1981, sampling periods. Amount of phase present was not considered in constructing the diagrams.

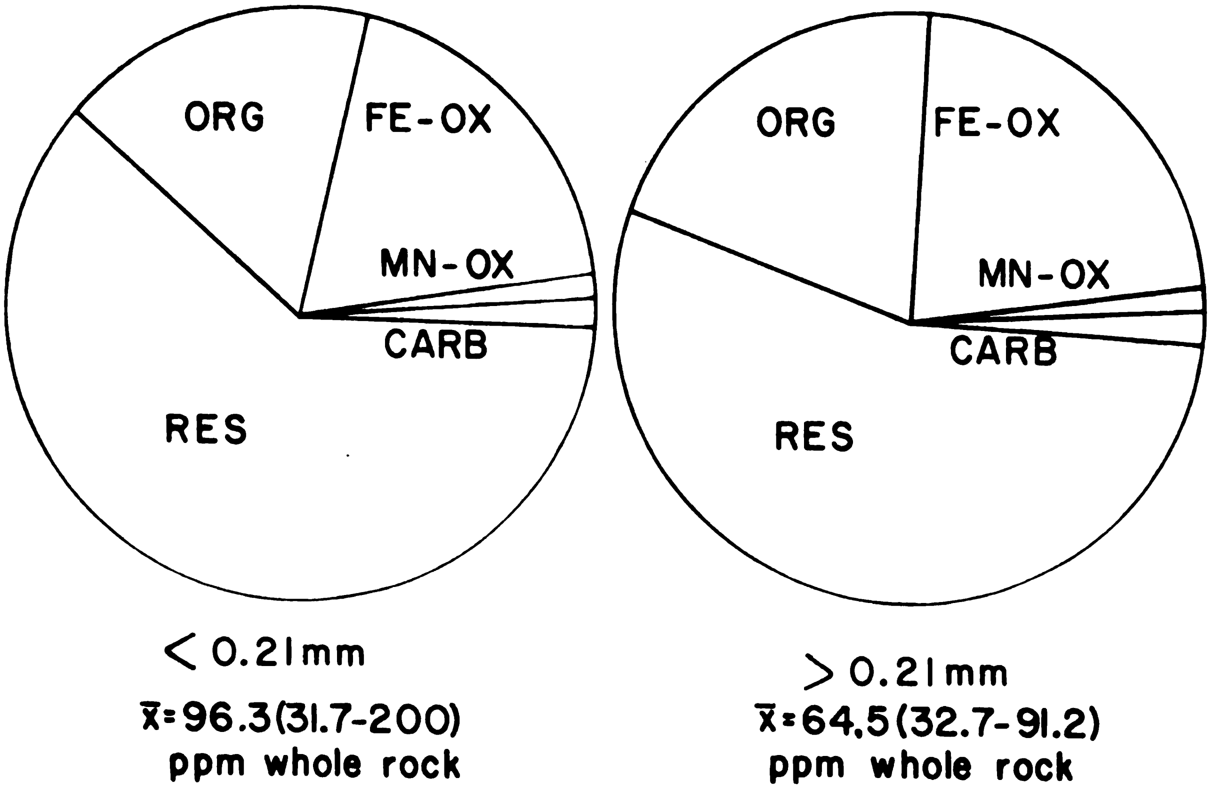

ORG
FE-OX
MN-OX
CARB
RES
< 0.21mm
$\bar{x}$=96.3(31.7-200)
ppm whole rock
ORG
FE-OX
MN-OX
CARB
RES
> 0.21mm
$\bar{x}$=64.5(32.7-91.2)
ppm whole rock

Figure 4.

appear to adsorb relatively little amounts of Cr compared to Fe oxides and organics. No Cr was detected in the dissolved fraction.

Specific partitioning results for each sample are depicted through the use of pi diagrams (Figure 5, see back inside cover). These pi diagrams indicate that the relative importance of Fe oxides and organics is variable. They also illustrate the unimportance of the Mn oxide, carbonate, and exchangeable fractions in adsorbing Cr. No trends in the relative importance of the chemical phases in sequestering Cr are observed as a function of sample location. In other words, the presence of Lansing does not appear to affect the partitioning behavior of Cr. A change in Cr partitioning results from the presence of Lansing might have been expected, since increased amounts of Cr, Fe, and organic material are introduced into the system.

The results of this research are consistant with Cr partitioning studies previously done. Specifically, both past research and this research conclude that:

1. the greatest percentage of Cr is associated with the residual phase,
2. of the hydromorphic phases, Fe oxides and organic fractions sequester the most Cr,
3. Mn oxide, carbonate, and exchangeable fractions sequester little Cr, and
4. more Cr is associated with the < 0.21 mm size fraction than with the > 0.21 mm size fraction.

The results of the Cr partitioning behavior handled in this manner may be explained on a chemical basis, since they are similar to what would theoretically be expected. However, because the amounts of phases present were not considered by this approach, chemical interpretations of the results are not valid.

Chromium Partitioning as a Function of Phase Concentration

A. Effect of Absolute Abundance of Substrates on Chromium Partitioning

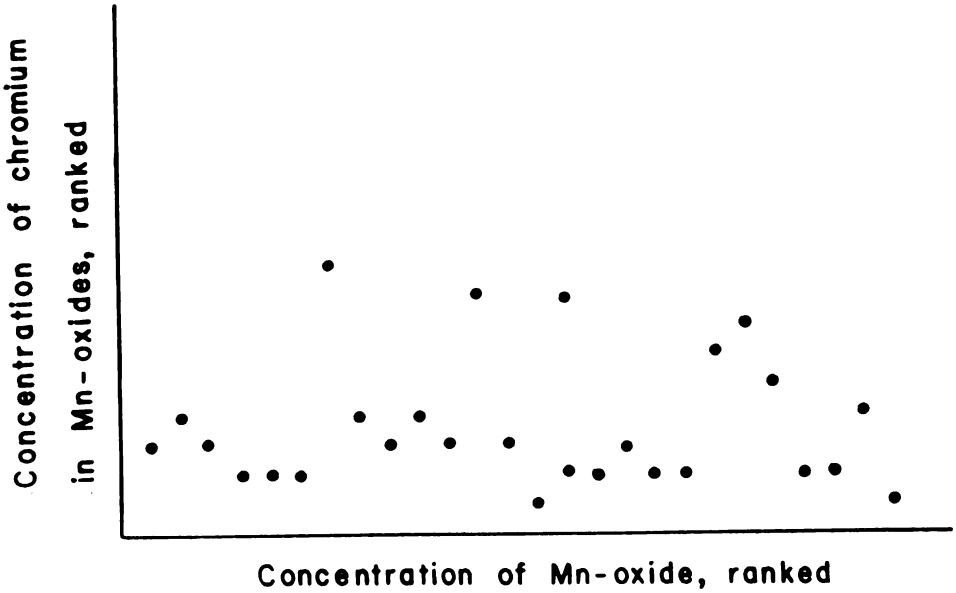
If one is to interpret Cr partitioning using phase concentration factors, then it must be demonstrated that the absolute abundance of substrates controls the partitioning of Cr.

If the concentration of a chemical phase is important in controlling the partitioning of an element, then there should be a correlation between the concentration of the chemical phase and the concentration of the element in that phase. An estimate of the concentrations of the Fe oxide, Mn oxide, and organic phases in the sediments was made by measuring the concentrations of a) the total organic carbon content for the organic phase, b) the Fe concentration mobilized by the "moderately reducing attack" for the Fe oxide phase, and c) the Mn mobilized by the "easily reducing attack" for the Mn oxide phase.

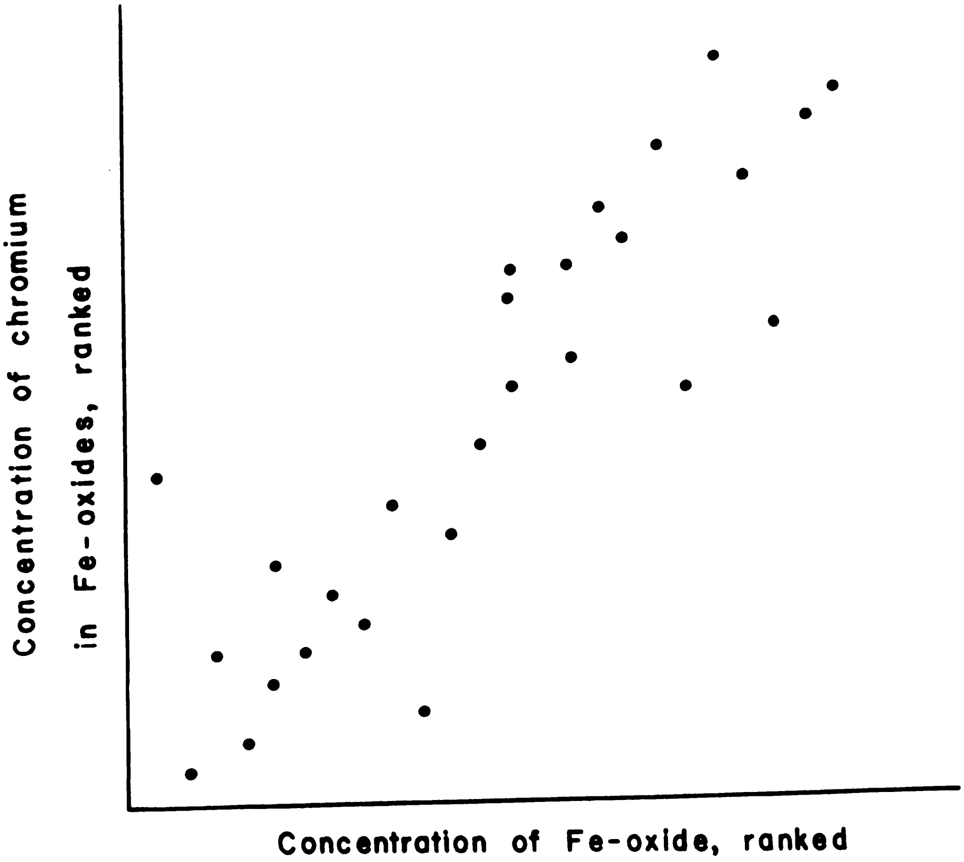
The concentrations of Cr in these three phases (organic, Mn oxide, and Fe oxide) were plotted against total organic carbon (TOC), Fe in Fe oxides, and Mn in Mn oxides (Figure 6). These diagrams demonstrate that the concentration of Cr is positively correlated with both Fe oxides and TOC (correlation coefficient). The correlations were determined using non-parametric statistics (Till, 1974). Rank order was used rather than absolute concentrations because a parametric relationship between the amount of adsorbed Cr and the amount of adsorbing substrate does not exist. These results imply that phase concentration factors (PCF) can be used in interpreting Cr partitioning in this study area.

No correlation is indicated between the concentration of Mn oxides and the concentration of Cr associated with them. Although the magnitude of Cr concentration associated with Mn oxides was within detection limits

Figure 6: Rank correlation diagrams of chromium concentration versus concentration of a) Mn oxides, b) Fe oxides, and c) total organic carbon.



a



b

Figure 6a and b.

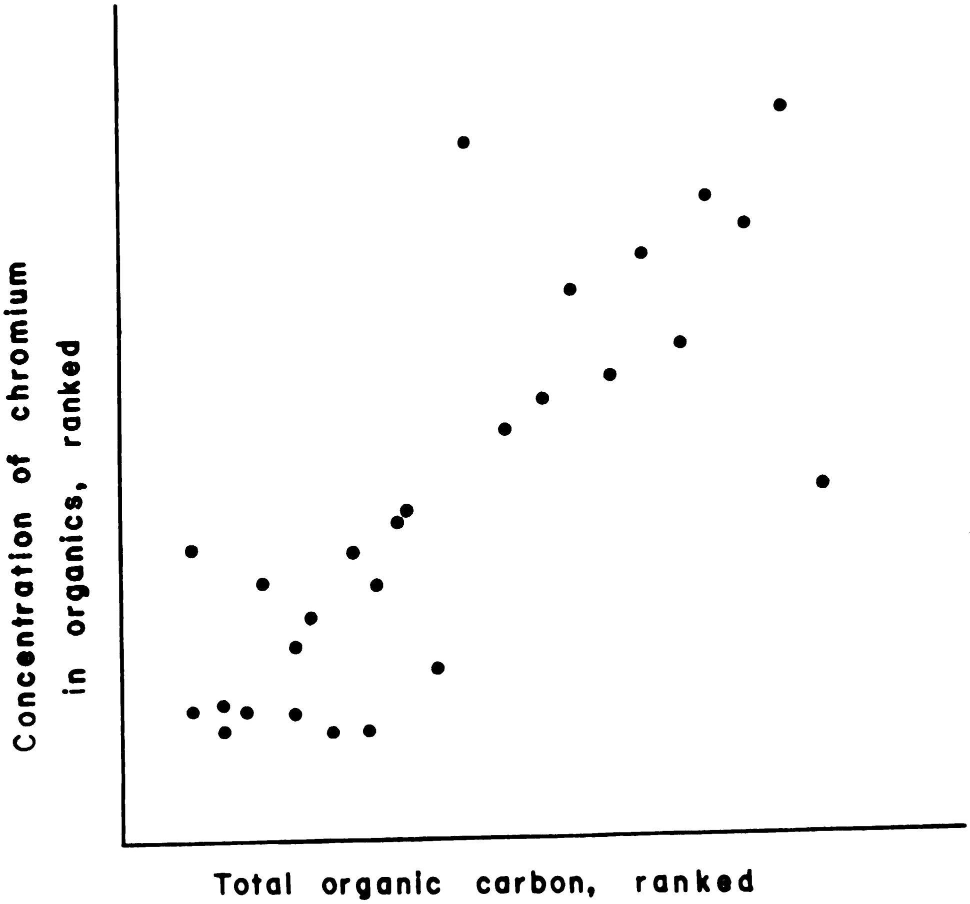

Concentration of chromium
in organics, ranked
Total organic carbon, ranked

Figure 6c.

for atomic adsorption analysis, subtle changes between samples in the amount of Cr associated with this phase may be masked by the error that exists when the metal concentration is near detection limits, as it is in this situation. As a result, trends that exist in the data may be masked. It cannot be concluded, therefore, that the concentration of Cr associated with Mn oxides does not increase as the amount of Mn oxides increase. PCF's will be utilized to interpret Cr partitioning among Mn oxides, as well as among Fe oxides and organics.

B. The Use of Phase Concentration in Determining Cr Partitioning:

In order to define the substrate which is chemically most important in adsorbing Cr, the relative partitioning must be determined amongst phases that are present in equal amounts. One method of determining this is through the use of PCF's. PCF's, as defined by Forstner and Patchineelam (1981), however, were not used in this study because absolute phase concentrations for exchangeable, carbonate, and residual phases were not determined. However, this study obtained relative Cr concentrations in the phases Fe oxide, Mn oxide, and organic by: 1) normalizing Cr concentrations to 1 gram of phase present, and 2) utilizing a modified phase concentration factor (m-PCF), according to a similar procedure developed by Filipek and co-workers (1981). m-PCF's for the metals Ni, Zn, Cu, and Pb were also calculated.

1. Normalization of Chromium Concentrations fo 1 Gram of Each Phase:

Normalizing Cr concentrations to 1 gram gives the concentration of Cr associated with each phase, assuming that all phases exist in equal amounts (1g). The results of this study indicate that of the three chemical phases of interest, the relative importance is Mn oxides (Mn-ox) > Fe oxides (Fe-ox) > organics (org) (Table 9). In other words, given equal amounts of the three phases, Mn oxides sequester the most Cr, followed by Fe oxides, while organic material sequesters the least.

Forstner and Patchineelamn (1981), who developed the concept of PCF, determined the relative importance of the three phases to be Fe-ox $<$ Mn-ox $>$ org for the sequestering of Cr by sediments in the Rhine River. Although the methods of calculating relative order of phase importance in this study differs from that of Forstner and Patchineelam's one would expect similar results, since both methods are based on normalizing phase concentrations.

The disagreement between this study and Forstner and Patchineelam's study (1981) may be attributed to the following:

a. The concentration of $NH_2OH{\cdot}HCl$ used by Forstner and Patchineelam in the Fe oxide attack was greater than that used in this study (1M $NH_2OH{\cdot}HCl$ vs. 0.04M $NH_2OH{\cdot}HCl$). Steady state analyses (Figure 7) demonstrate that more Cr was leached out using the 1M $NH_2OH{\cdot}HCl$. Therefore, the disagreement in the relative importance of Fe and Mn oxides between the two studies may result from the fact that more Cr was leached out in the Fe oxide attack by Forstner and Patchineelam. Further research is necessary to determine which attack is more selective in attacking Fe oxides.

b. The amount of Fe mobilized during the Mn oxide attack (see partitioning results, Appendix I) suggests that, in this study, a partial dissolution of the Fe oxide fraction may have occurred at this time. If this is true, a significant amount of Cr analyzed in the Mn oxide leachate could have been associated with Fe

Figure 7: Steady state analysis for chromium in the Fe oxide phase. The effect of leaching with 1M $NH_2OH{\cdot}HCl$ vs. 0.04M $NH_2OH{\cdot}HCl$ on chromium mobilization from sediment.

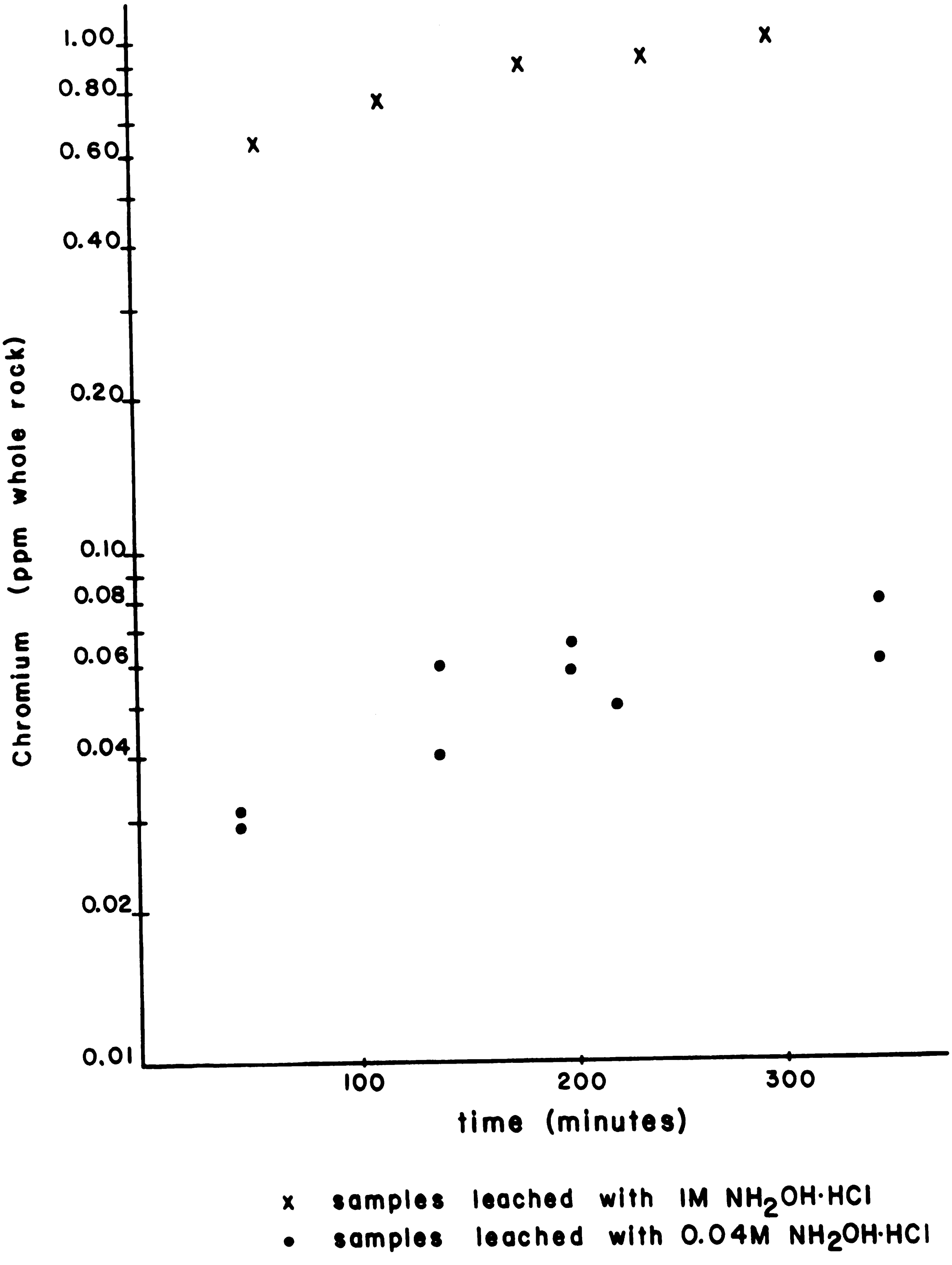

Chromium (ppm whole rock)
1.00
0.80
0.60
0.40
0.20
0.10
0.08
0.06
0.04
0.02
0.01
100
200
300
time (minutes)
x samples leached with 1M $NH_2OH \cdot HCl$
• samples leached with 0.04M $NH_2OH \cdot HCl$

Figure 7.

Table 9: Concentrations of Cr in 4 chemical phases, when normalized to 1 gram of phase.

A. Samples leached in fall, 1980

	ppm Cr in 1 gram of:			
Sample	Fe ox	Org	Mn ox	Res
Size fraction: < 0.21 mm				
F-1, Bunder	7.27	0.50	12.2	192
F-3, Riverside	11.1	3.48	72.3	65
F-5, Holt	6.39	2.39	25.1	37
F-7, Waverly	10.7	2.76	47.9	40
F-8, Riverside	6.41	0.00	50.0	33
F-9, Elm	5.00	0.00	154.	43
F-10, Kalamazoo	6.02	0.00	100.	32
F-11, Maple	10.5	2.78	9.89	43
F-12, Tecumseh	2200.	0.43	285.	47
F-14, Delta	10.2	1.33	6.80	97
F-16, Jones, bank	8.46	1.83	32.1	42
F-16, Jones	6.87	0.10	35.2	75
Size fraction: > 0.21 mm				
F-1, Bunker	8.46	0.00	7.32	25
F-5, Holt	9.03	2.62	26.6	32
F-9, Elm	19.1	0.00	47.2	33
F-11, Maple	8.70	2.53	19.9	28
F-14, Delta	12.2	0.00	33.1	33

B. Samples leached in summer, 1981

	ppm Cr in 1 gram of:			
Sample	Fe ox	Org	Mn ox	Res
Size fraction: < 0.21 mm				
S-1, Maple	4.44	0.44	6.50	47
S-5, Eaton Rapids	5.98	9.08	4.35	35
S-3C, Moor, center	4.27	4.56	1.76	53
S-3B, Moor, ¼	4.63	4.19	4420.	52
S-3A, Moor, shore	2.76	-	120.	25
S-4, Maple	5.02	4.51	3.33	57
Size fraction: > 0.21 mm				
S-1, Maple	4.52	3.74	6.45	32
S-2, Holt	2.49	3.60	7.14	32

oxides. As a result, the relative importance of the two phases would be incorrectly biased toward Mn oxides.

c. Forstner and Patchinnelam consider the carbonate phase in addition to the organic, Mn oxide, and the Fe oxide phases. This, however, probably has little or no affect, since carbonates are not important substrates for Cr adsorption.

2. Modified Phase Concentration Factor (m-PCF):

The second method used in defining relative Cr concentrations given equal amounts of phase concentrations involved the use of m-PCF's. The m-PCF is defined as the % metal of the total metal scavenged by a particular phase divided by the percent, by weight, that the particular phase comprises within the sediment. The m-PCF considers only the Mn oxide, Fe oxide, and organic phases because the concentrations of the carbonate and exchangeable phases were not determined.

The method used in calculating m-PCF's is found in Appendix II. Two types of m-PCF's were utilized, so called m-PCF$_A$ and m-PCF$_B$. The two differ in their calculation of phase concentrations present in the sediment. Specifically, m-PCF$_A$ calculates the phase concentrations assuming Fe oxides are present at FeOOH, Mn oxides as MnO_2, and organics as the total organic carbon material (determined as a function of total organic carbon). m-PCF$_B$ calculates the phase concentrations as the concentration of Fe in Fe oxides, of Mn and Fe in Mn oxides, and the total organic carbon for the three phases Fe Oxide, Mn oxide, and organic, respectively.

Values for m-PCF's are only approximations, since several sources of error exist:

a. It is assumed that only a single phase was attacked in each extraction step. This is least likely to be true for the easily reducible attack. In addition to Mn oxides, amorphous Fe oxides and easily hydrolyzable organics may be leached from the sediment. m-PCF$_B$ recognizes the possibility of attacking amorphous Fe oxides.

b. In calculating m-PCF's, concentrations of the organic, Fe oxide, and Mn oxide phases were obtained. The results indicate that the concentrations of organic and Fe oxide phases are of the same magnitude, but that these two phases are on the magnitude of 100 x's more abundant than Mn oxides. As a result of low Mn oxide concentrations, the amount of Cr associated with this fraction is also small, and exists at the detection limits for atomic absorption analysis. Such low concentrations may obscure trends that exist in the data.

Results

m-PCF's for the metals Cr, Cu, Ni, Zn, and Pb are plotted as percents on a trilinear diagram (Figure 8). The use of a trilinear diagram enables one to interpret the data visually, whereas the presentation of this data via a table does not allow for an easy interpretation of the partitioning results. Each point on the diagram depicts a single sample and represents the relative importance between equal amounts of organics, Fe oxides, and Mn oxides in scavenging a particular metal. Specifically, each point represents the m-PCF value of each phase in a particular sample as a percent of the sum of m-PCF's for all three phases. The following is a summary of the results of each metal studied:

Figure 8a:
Mn oxide,
in PCF_A va

Figure 8a: Trilinear diagram expressing the competition between equal amounts of Mn oxide, Fe oxide, and organic phases in sequestering chromium. Results based on PCF_A values.

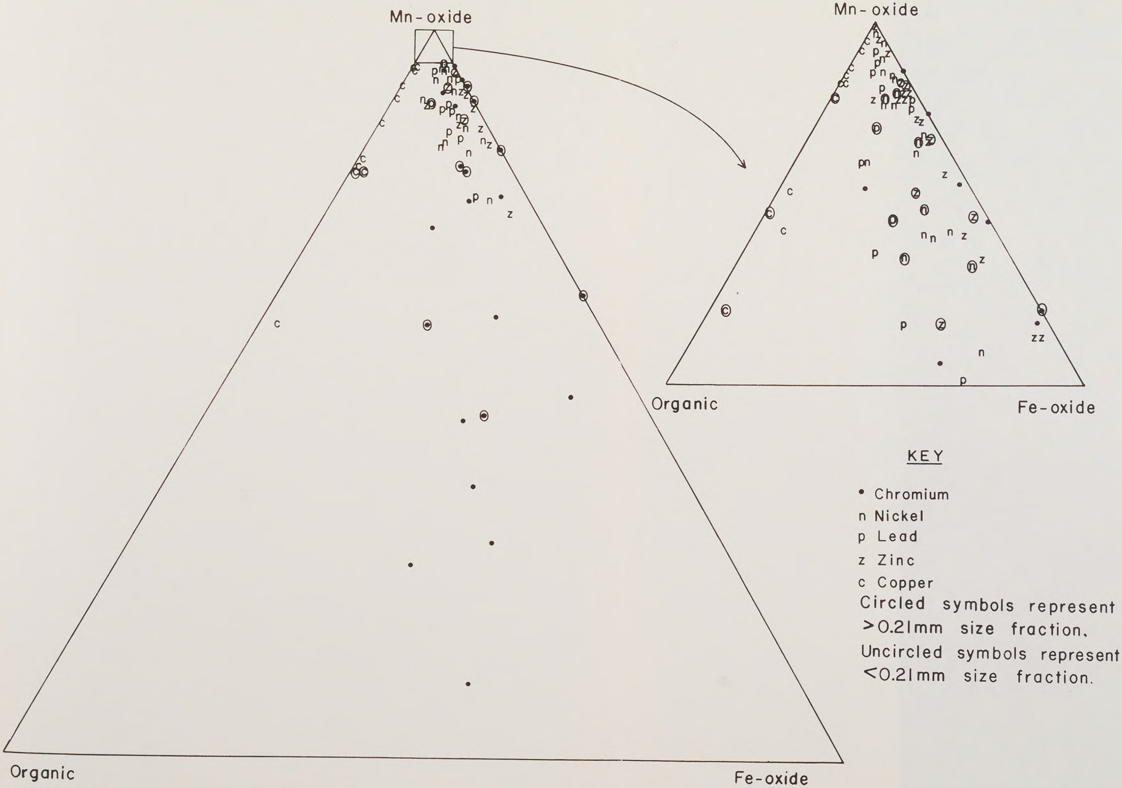
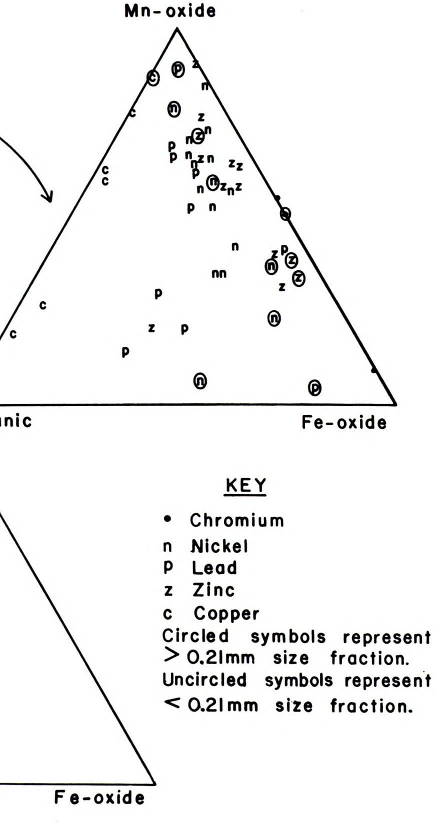

Mn-oxide
Organic
Fe-oxide
Mn-oxide
Organic
Fe-oxide
KEY
• Chromium
n Nickel
p Lead
z Zinc
c Copper
Circled symbols represent >0.21mm size fraction.
Uncircled symbols represent <0.21mm size fraction.

Figure 8a.

Figure 8b: Trilinear diagram expressing the competition between equal amounts of Mn oxide, Fe oxide, and organic phases in sequestering chromium. Results based on PCF_B values.

Figure 8b.


Mn-oxide
nic
Fe-oxide
KEY
• Chromium
n Nickel
p Lead
z Zinc
c Copper
Circled symbols represent > 0.21mm size fraction.
Uncircled symbols represent < 0.21mm size fraction.
Fe-oxide

Chromium: All three phases appear to be important in scavenging Cr. With the exception of Cu, organic material appears to be more important for Cr than for the other metals (Ni, Pb, Zn).

Copper: Organic material and Mn oxides are responsible for the scavenging of almost all of the Cu. Fe oxides appear to be insignificant in removing this ion from solution.

Lead: Mn oxides appear to be the most important scavenger for Pb. Both organic material and Fe oxides appear to be of minor importance in the removal of Pb from solution.

Zinc: Mn oxides appear to be the most important scavenger of Zn. Organics have little association with this metal. Only a small percentage of Zn was found to be associated with Fe oxides.

There appears to be no difference in the partitioning of the >0.21 mm and <0.21 mm size fractions, based on observation of the trilinear diagrams (Figure 8).

It should be noted that the use of m-PCF's changes the relative importance of the chemical phases in sequestering for all of the metals studied (Table 8). However, the relative phase importance based on m-PCF$_A$ does not differ from the relative importance based on m-PCF$_B$. This suggests that either method can be used to calculate the m-PCF's.

From Table 8, one can see that normalizing the phase concentrations results in a much greater importance of Mn oxides in the scavenging of metals than when normalizing is not done. This suggests that the high percentage of metal associated with the organic and Fe oxide phases occurs because these phases are present in much higher concentrations than Mn oxides, and thus are more readily available for adsorption.

Table 10: Average changes in the relative importance of the chemical phases in sequestering metals when utilizing m-PCF's.

	Relative importance of chemical phases before normalizing phase concentrations	Relative importance of chemical phases after normalizing to phase concentrations
Cr	(Fe-ox, Org) > Mn-ox	Mn-ox > (Fe-ox, Org)
Ni	Fe-ox > Mn-ox*	Mn-ox ≫ Fe-ox > Org
Pb	Fe-ox > Mn-ox*	Mn-ox ≫ (Fe-ox, Org)
Zn	Fe-ox > Mn-ox > Org	Mn-ox ≫ Fe-ox > Org
Cu	Org > Mn-ox > Fe-ox	Mn-ox > Org > Fe-ox

*The importance of the organic phase varies between samples.

Discussion of Results

The results of this study show that Cr is associated with Fe oxide, Mn oxide, and organic phases. This can be explained on a chemical basis if Cr exists in both the +3 and +6 oxidation state in the sediments. Consider the following discussion as an explanation of this:

Hydrous Mn oxides have extremely high adsorption capacities and high adsorption affinities for heavy metals (Drever, 1982). δMnO_2 has a zero-point charge of 2.8 in the absence of adsorbed ions other than OH^- and H^+. At higher pH values normally found in surface waters, the δMnO_2 has a negative surface charge and therefore is capable of adsorbing positively charged ions. The cation exchange capacity of δMnO_2 increases with increasing pH (Drever, 1982). Murray (1975) suggested that the adsorption mechanism for δMnO_2 is:

$$\text{Mn-OH} + M^{2+} = \text{Mn-OM}^+ + H^+$$

However, Hem (1978) argued that the scavenging of metals by Mn oxides is more complicated than simple adsorption processes. Specifically, he suggested that the scavenging of metals involves phase transformations among the Mn oxides and the catalysis of redox reactions by the Mn^{2+}-Mn oxide system.

The Eh-pH diagram showing Cr speciation (Figure 9) shows that Cr in the (III) oxidation state exists as a positive species in solution, and therefore should be adsorbed on negatively charged surfaces. Chromium in the (VI) oxidation state exists as a negative species in solution and conversely, should be adsorbed onto positively charged surfaces. Based on the pH at zero point charge (pH_{ZPC}) for Mn oxides and clays (approximately 3-4 and 2-4 respectively; Figure 10), both substrates would tend to adsorb trivalent Cr species. This conclusion is supported by the work of Griffin and co-workers (1977), who found that trivalent Cr is readily adsorbed onto clays, whereas the adsorption of hexavalent Cr does

Figure 9: Eh-pH diagram showing stable species of chromium (Hem, 1977). Approximate field of study area water denoted by dotted enclosure.

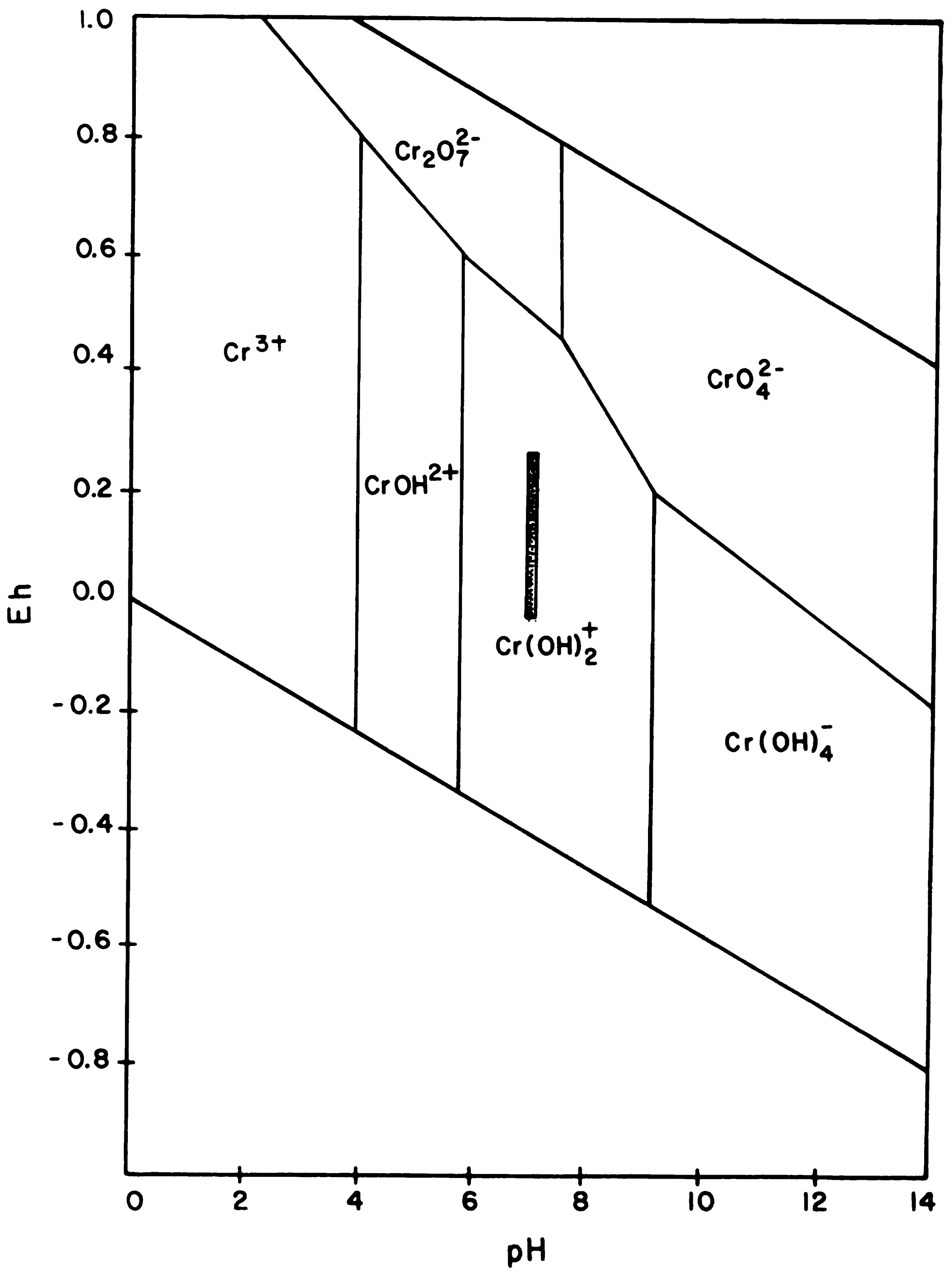

1.0
0.8
0.6
0.4
0.2
0.0
- 0.2
- 0.4
- 0.6
- 0.8
Eh
0
2
4
6
8
10
12
14
pH
Cr^{3+}
$Cr_2O_7^{2-}$
$CrOH^{2+}$
CrO_4^{2-}
$Cr(OH)_2^+$
$Cr(OH)_4^-$

Figure 9.

Figure 10: Surface charge of clays, Mn oxides, and Fe oxides as a function of pH (modified from Stumm and Morgan, 1981).

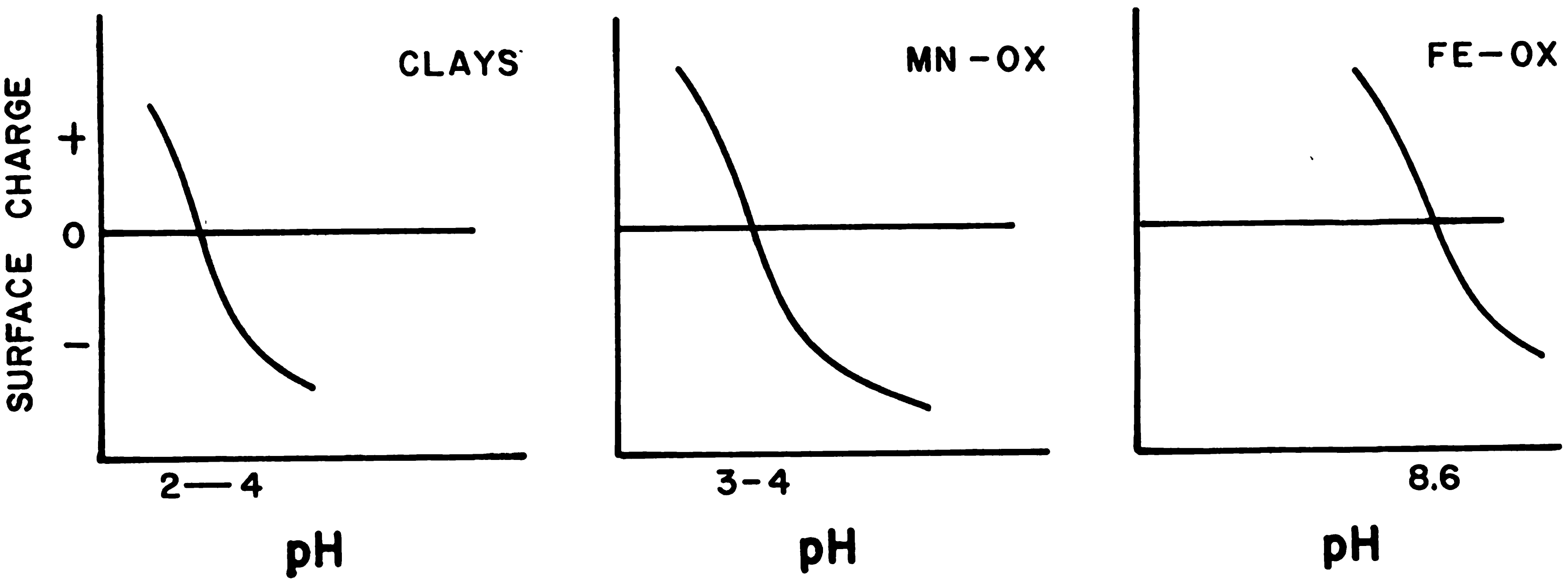


Figure 10.

not occur (Figure 11). The presence of trivalent Cr in this system is indicated by its association with Mn oxides.

Cr(III) in association with Mn oxides is known to be oxidized to Cr(VI); however, the extent of this process was not determined (Bartlett and James, 1979). The oxidized Cr, now existing as a anionic species in solution, would tend to be adsorbed onto positively charged surfaces. Fe oxides, with a pH_{ZPC} of 8.6 (generally; Figure 10), would have a positive surface charge given the pH conditions of the river (pH_{river} = 6-8; Figure 9). Thus, the oxidation of Cr(III) by Mn oxides to the negatively charged hexavalent species would result in adsorption of Cr by Fe oxides. The presence of hexavalent Cr in this system is indicatd by the association of Cr with Fe oxides.

The fact that Cr exists as both an anion and a cation in the sediment is supported by the behavior of the other metals studied. Specifically, past research has indicated that the metals Cu, Ni, Zn, and Pb exist as cations in the sediment. If this is true, a high association of them with Mn oxides should be expected, since Mn oxides have a negative surface charge. Conversely, a low association with positively charged Fe oxides should also be observed. These metals did, indeed, show a high association with Mn oxides and a low association with Fe oxides. Along the same reasoning then, the association of Cr with Mn oxides suggests its presence as a cation - Cr(III). Cr behaves differently from the other metals, however, in that it is also associated with Fe oxides. This suggests that Cr is also present as an anion - Cr(III).

The association of Cr with organic material is supported by the behavior of Cu. Previous research has shown that organic material is an important scavenger for Cu (Jackson, 1975; Rashid and Leonard, 1973; Rashid, 1974; Gibbs, 1973, 1977; Andelman, 1973). Rashid (1974) suggested that the high association between Cu and organic material results from the formation of a strong bond

Figure 11: Chromium adsorption onto clays as a function of pH and oxidation state (modified from Griffin, et al., 1977).

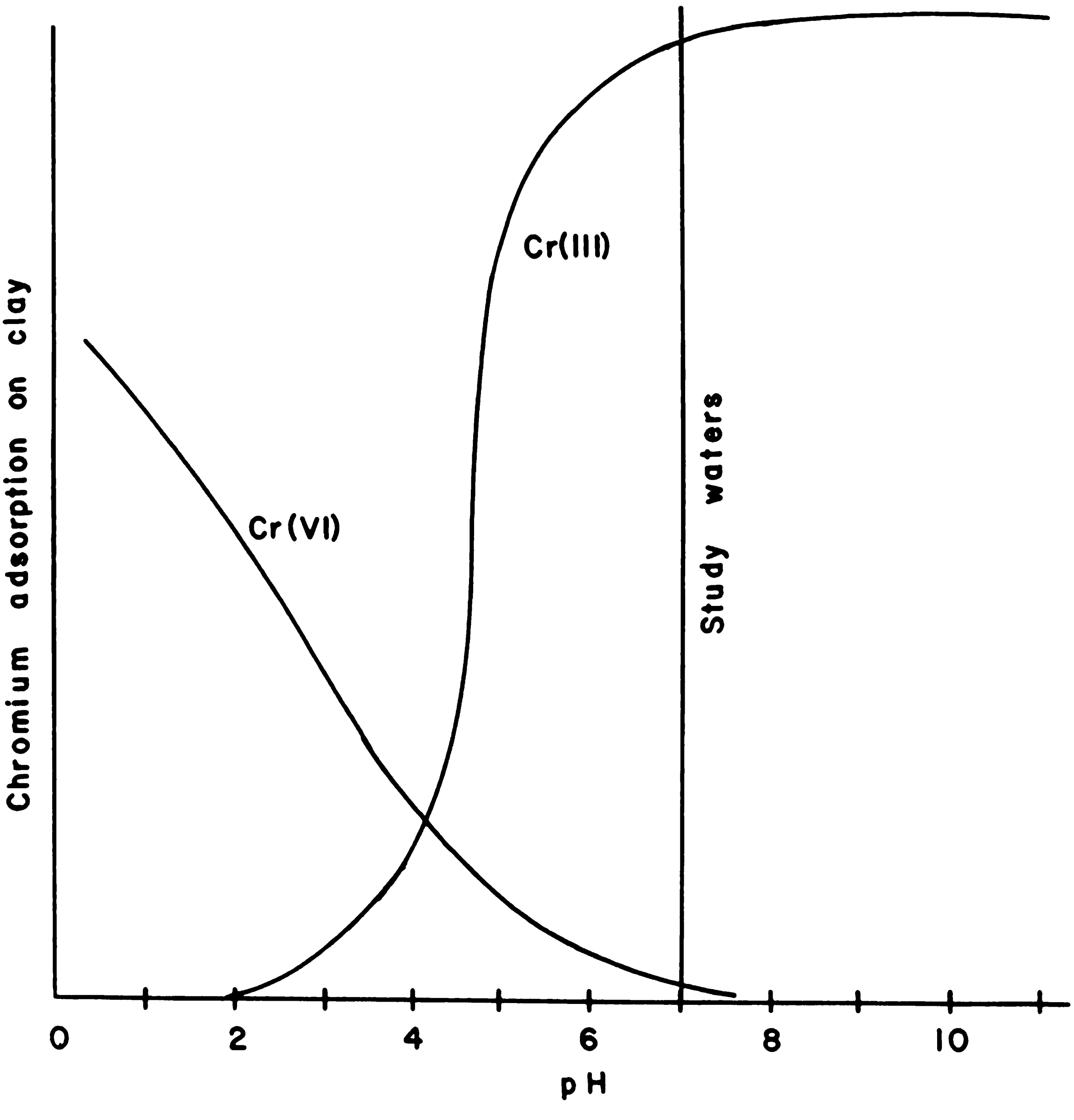

Chromium adsorption on clay
Cr(III)
Cr(VI)
Study waters
0
2
4
6
8
10
pH

Figure 11.

between them. Desorption studies indicated that this bond is stronger than the bond that forms between organic material and other metals, such as Co, Mn, Ni, and Zn. These metals were easily dislodged from organics with solutions of ammonium acetate and Fe^{+3}. Nikitina (1973) suggested that some complexes may be of zero-point charge. The trilinear diagrams based on the results of this study show that a high association of Cu with organic material does indeed exist. Like Cu, Cr also appears to be associated with organic material, based on an observation of the trilinear diagrams. This suggests that, as is true for Cu, organic material is an important substrate for Cr adsorption.

In conclusion, an outline for Cr behavior is as follows: Chromium enters the river in the (VI) state (industrial source) and is converted to Cr(III). (Cr in solution is stable as the (III) species; see Figure 9.) The Cr is adsorbed by organic material and is electrostatically attracted to the Mn oxide surface where it is subsequently converted to Cr(VI). Now unstable on the Mn oxide surface, Cr is released from this phase and is adsorbed by Fe oxides. It appears, however, that the oxidation of Cr(III) to Cr(VI) by Mn oxides and subsequent adsorption onto Fe oxides is not complete. This is indicated by the association of a significant amount of Cr with Mn oxides. The concentration of Cr in both the carbonate and exchangeable fractions was small. This low concentration in the exchangeable fraction would be expected, since the concentration of clay minerals in the samples was low (see methodology section, D. Sediment analysis). This outline suggests that Cr exists in both the (III) and (VI) oxidation states in the sediment. This is in disagreement with Meyer (1977), who suggests that in natural waters with pH's ranging from 5.5 to 8.5 Cr will tend to accumulate in solution if it occurs in the +6 state, and in the sediments if it occurs in the +3 state.

It appears that the use of m-PCF's and trilinear diagrams is an important tool in studying the partitioning behavior of the metals. This method provides a visual presentation of the data, and compared to the presentation of the data via tables, it is a much easier method for interpreting the results.

CONCLUSIONS

This research examined the partitioning of Cr among six chemical phases within the sediment. The technique used to determine the relative importance of the six chemical fractions was that of selective chemical extractions. An evaluation of this methodology indicated that absolute concentrations of elements in a particular phase will vary between splits of the same sample, however, the relative partitioning of an element among the chemical phases will remain the same. The chemical used in the attacks were chosen on the basis of their selectivity and completeness in the attack. For each specific attack, a steady state analysis was performed to determine a reaction time that would completely dissolve the phase, but not attack another.

The partitioning results of this study indicate that:

1. more Cr is associated with the < 0.21 mm size fraction in the sediment than with the > 0.21 mm fraction.
2. when considering only the hydromorphic phases, more Cr exists in the > 0.21 mm size fraction than in the < 0.21 mm fraction.

These results are consistent with past research.

In examining the relative importance of the six geochemical phases in the sequestering of Cr, it was found that the greatest percentage of Cr was associated with the residual phase. However, since the association of Cr with this phase does not occur as a result of adsorption processes, the relative partitioning of Cr amongst the hydromorphic phases was examined. The association of Cr with these phases do result from adsorption processes.

Of the hydromorphic phases, the greatest percentage of Cr was associated with the Fe oxide and organic phases. However, if equal amounts of phases are considered, Mn oxides become the most important substrate for the adsorption of Cr. It was concluded that the high percentage of Cr associated with Fe oxides and organic occurs because these phases were, by far, the most abundant phases present. Both carbonate and exchangeable phases were unimportant in the sequestering of Cr in this study.

PCF's were utilized to determine the relative partitioning of Cr when equal amounts of phases are present. However, in order to utilize PCF's in interpreting the partitioning results it was necessary to show that the amount of Cr associated with a particular phase is dependant on the concentration of that phase in the sediment. If this is true, one should observe a direct correlation between the phase concentration and the concentration of Cr adsorbed by that phase. The results of this study did, indeed, show a positive correlation between the amount of Fe oxide and the concentration of Cr associated with this phase. This also held true for the organic phase. This trend was not observed for the Mn oxide phase, however, this may be a result of such low concentrations of Cr in that phase, resulting in a relatively large error factor and a masking of any trends in the data. Although the concentration of Cr in the Mn oxide fraction was small, enough was present to determine PFC's.

The use of trilinear diagrams in this study proved to be an important tool for interpreting the partitioning results based on PCF's. By observing these diagrams it was concluded that all three phases (Mn-ox, Fe-ox, org) are important in sequestering Cr (given equal amounts of phases). This suggests that Cr is present in both the +3 and +6 oxidation states in the sediment, based on zero-point charge theory and the relative partitioning of Cr amongst the substrates. Through the use of PCF's and trilinear diagrams, the relative partitioning of the metals Cu, Pb, Ni, and Zn was used to support this conclusion.

Finally, a outline of Cr behavior in this system was developed. Hexavalent Cr, introduced into the river by an industrial source, is immediately reduced to its trivalent form, a positively charged species. Cr is then adsorbed by both organic material and Mn oxides. The Cr attracted to the negatively charged Mn oxide surface is oxidized and released as an anionic species. An association of Cr with Mn oxides, however, suggests that this oxidation process is not complete. The oxidized Cr may now become adsorbed onto the positively charged Fe oxide surface. No adsorption onto clay minerals was observed since they were present in such low concentrations. This outline suggests that Cr exists in both the (III) and (VI) oxidation states in the sediment.

SUGGESTIONS FOR FURTHER RESEARCH

Results of this research suggest that future research should be directed toward I) the improvement of selective chemical extraction procedures, and II) a better undersatnding of the adsorption processes and speciation of Cr in natural systems.

I. Continued investigation of selective chemical extraction procedures and techniques is necessary to improve their accuracy and repeatability. The following suggestions are made for the improvement of this technique.

   1. Additional steady state analyses are necessary. Results of this study indicate that different metals require different reaction times for their dissolution within a specific phase. A steady state analysis was performed on the metals Cr, Mn and Fe; however, several areas still remnain vague (i.e., behavior of Mn in the carbonate attack). Therefore, these analyses should be repeated and the results confirmed.
   2. A technique for the differentiation of organic and sulfidic metal associations should be investigated. Presently, current methodology results in the dissolution of the sulfide phase simultaneously with that of the organic fraction.
   3. Further investigation on the separation of hydrous Fe and Mn oxides is necessary. In this study, an analysis of the Mn oxide leachate yielded a significant concentration of Fe (see

Appendix II), suggesting that amorphous Fe oxides may also have undergone dissolution in this attack.

4. Further investigation on the choice of chemical reagents utilized in the attacks is necessary. The choice of a chemical reagent should be a function of 1) its selectivity in dissolving a single, specific phase, and 2) the ease to which it lends itself to atomic adsorption analysis. These aspects need to be investigated.

II. This study has attempted to gain an understanding on the relative importance of various chemical phases in the sediment on the adsorption of Cr. Major conclusions of this study are based on the utilization of Eh-pH diagrams and theoretical calculations. It was assumed that the solubility of Cr is controlled by $Cr(OH)_3$, a realistic species for the systems in which Cr is introduced by disposal of industrial waste. However, the complexation of Cr to other ions was not investigated, which may significantly alter its solubility. Studies directed toward understanding the solubility of Cr in natural waters are necessary, and should include an examination of potential Cr complexes as well as the oxidation state of dissolved Cr in natural systems.

This study estimated the oxidation state of Cr when adsorbed onto Fe oxides. Again, this estimation was determined using Eh-pH diagrams that were based on the solubility of Cr being controlled by $Cr(OH)_3$, and did not consider the effects of complexation on Cr solubility. An accurate determination of the speciation of Cr as it is adsorbed on both Fe oxides and organic material is necessary.

The use of trilinear diagrams should be included in other partitioning studies to exhibit the competition between phases in the sequestering of metals. If PCF's are determined the results could be extended to other environments where relative concentrations of phases differ.

Future research on investigating the behavior of Cr might be focused on understanding its remobilization from sediments. Factors such as redox changes, pH changes, biological interferences, and salt concentration effects should be considered.

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Appendix I: Partitioning results of the metals Cr, Mn, Fe, Zn, Cu, Pb, and Ni (ppm whole rock). All samples were collected in thalwig of river unless indicated otherwise.

A. Leach attacks performed in fall, 1980:

Sample		Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1.	Size fraction: >0.21 mm							
F-1	Bunker	N.D.	0.72	0.50	6.48	0.00	25.0	0.06
F-5	Holt	N.D.	1.20	1.00	16.5	28.6	32.0	1.09
F-9	Elm	N.D.	1.12	0.50	11.8	0.00	33.0	0.09
F-11	Maple	N.D.	1.20	0.75	16.2	28.8	28.0	1.14
F-14	Delta	N.D.	1.04	1.00	11.7	0.00	33.0	0.06
F-16	Jones	N.D.	0.72	0.50	8.55	0.00	33.0	0.04
2.	Size fraction: <0.21 mm							
F-1	Bunker	N.D.	-	1.25	6.48	0.80	192.0	0.16
F-3	Riverside	N.D.	2.32	3.00	20.6	14.6	65.0	0.42
F-5	Holt	N.D.	1.20	1.50	12.4	20.3	37.0	0.85
F-7	Waverly	N.D.	1.76	2.25	16.1	13.8	40.0	0.50
F-8	Riverside	N.D.	-	0.50	5.31	0.00	33.0	0.12
F-9	Elm	N.D.	0.40	1.00	5.22	0.00	43.0	0.09
F-10	Kalamazoo	N.D.	0.80	0.75	4.59	0.00	32.0	0.13
F-11	Maple	N.D.	1.20	0.75	19.5	22.0	43.0	0.79
F-12	Tecumseh	N.D.	4.40	4.50	67.7	17.0	47.0	4.00
F-14	Delta	N.D.	1.20	1.00	8.82	2.00	97.0	0.15
F-16	Jones, bank	N.D.	0.96	1.75	9.54	4.20	42.0	0.23
F-16	Jones	N.D.	0.72	0.75	6.57	0.20	75.0	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix I: Continued.

B. Leach attacks performed in summer, 1981:

Sample		Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1.	Size fraction: >0.21 mm							
S-1	Maple[2]	N.D.	1.52	0.50	25.2	42.6	32.0	1.14
S-2	Holt[2]	N.D.	1.12	0.50	18.4	39.2	32.0	1.09
2.	Size fraction: < 0.21 mm							
S-1	Maple[2]	N.D.	1.44	0.50	24.8	34.8	47.0	0.79
S-2	Holt[2]	N.D.	1.20	0.75	16.4	31.2	40.0	0.85
S-3A	Moor, shore[3]	N.D.	0.40	0.75	4.20	1.40	25.0	0.00
S-3B	Moor, 1/4	N.D.	1.12	0.50	35.0	56.6	52.0	1.35
S-3C	Moor, center	N.D.	1.04	0.25	31.4	50.6	53.0	1.11
S-4	Maple	N.D.	1.20	0.50	38.4	52.8	57.0	1.17
S-5	Eaton Rapids	N.D.	2.0	0.25	33.2	41.8	35.0	0.46

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] sample collected in fall, 1980

[3] S-3A,B,C represent a traverse sampling of the river.

Appendix I: Continued.

IRON

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	7.20	82.6	175	1680	126	7400	0.06
F-5 Holt	1.76	31.3	357	4320	1195	18100	1.09
F-9 Elm	3.68	123	162	1372	38.8	11000	0.09
F-11 Maple	3.28	27.8	445	4140	1124	17500	1.14
F-14 Delta	2.72	60.1	130	2142	71.8	14800	0.06
F-16 Jones	3.68	55.7	94.5	2052	50.6	17100	0.04
2. Size fraction: <0.21 mm							
F-1 Bunker	23.8	126	242	1980	230	50200	0.16
F-3 Riverside	11.7	346	1721	4120	879	13100	0.42
F-5 Holt	9.12	526	899	4320	1171	6500	0.85
F-7 Waverly	6.56	80.7	613	3332	715	8300	0.50
F-8 Riverside	6.56	99.7	218	1840	185	9500	0.12
F-9 Elm	12.5	164	185	2324	234	9500	0.09
F-10 Kalamazoo	5.20	83.1	186	1688	259	13000	0.13
F-11 Maple	10.1	13.9	436	4120	775	41600	0.79
F-12 Tecumseh	7.68	45.9	404	6224	1891	11600	4.00
F-14 Delta	6.48	48.5	240	1940	506	34900	0.15
F-16 Jones, bank	8.64	26.5	368	2504	351	11100	0.23
F-16 Jones	4.16	56.4	262	2124	139	10300	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix I: Continued.

IRON

B. Leach attacks performed in summer, 1981:

Sample		Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1.	Size fraction: >0.21 mm							
S-1	Maple[2]	1.12	9.60	18.8	5568	1170	22600	1.14
S-2	Holt[2]	1.28	4.00	44.8	7368	1380	18300	1.09
2.	Size fraction: <0.21 mm							
S-1	Maple[2]	1.44	49.6	23.8	5584	690	42300	0.79
S-2	Holt[2]	2.08	441	52.8	6176	670	13500	0.85
S-3A	Moor, shore[3]	3.53	142	8.75	1520	70.0	9200	0.00
S-3B	Moor, 1/4	1.68	41.6	20.5	7552	2310	26500	1.35
S-3C	Moor, center	1.52	24.0	21.3	7352	1960	28400	1.11
S-4	Maple	1.44	41.6	25.0	7648	1790	40500	1.17
S-5	Eaton Rapids	4.00	154	498	5648	520	8000	0.46

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] sample collected in fall, 1980

[3] S-3A,B,C represent a traverse sampling of the river.

Appendix I: Continued.

MANGANEESE

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	6.40	122	68.3	30.2	3.60	140	0.06
F-5 Holt	8.72	114	37.6	32.8	12.4	75.0	1.09
F-9 Elm	4.64	45.4	10.6	32.4	3.60	125	0.09
F-11 Maple	8.96	126	37.6	33.6	11.8	80.0	1.14
F-14 Delta	4.96	74.2	16.2	56.0	6.20	190	0.06
F-16 Jones	10.32	77.4	15.1	51.5	9.6	235	0.04
2. Size fraction: <0.21 mm							
F-1 Bunker	7.60	188	102	30.1	4.00	802	0.16
F-3 Riverside	5.76	200	41.5	39.2	7.80	232	0.42
F-5 Holt	26.1	262	59.8	37.0	10.2	122	0.85
F-7 Waverly	4.48	166	47.0	54.1	8.80	110	0.50
F-8 Riverside	3.92	59.0	10.0	12.7	2.2	235	0.04
F-9 Elm	4.64	95.0	6.50	14.7	3.60	150	0.09
F-10 Kalamazoo	4.64	63.0	7.50	19.8	3.40	145	0.13
F-11 Maple	6.08	139	75.8	41.2	10.6	145	0.79
F-12 Tecumseh	19.4	69.0	15.8	35.8	14.8	155	4.00
F-14 Delta	9.44	110	147	39.1	9.20	753	0.15
F-16 Jones, bank	5.76	78.0	54.5	26.1	8.80	188	0.23
F-16 Jones	19.3	122	21.3	21.7	3.60	177	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix I: Continued.

MANGANEESE

B. Leach attacks performed in summer, 1981:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
S-1 Maple[2]	11.9	91.2	77.5	63.8	12.2	80.0	1.14
S-2 Holt[2]	63.5	374	70.0	88.2	10.0	115	1.09
2. Size fraction: < 0.21 mm							
S-1 Maple[2]	9.44	165	76.5	67.0	10.2	175	0.79
S-2 Holt[2]	51.4	323	54.0	68.0	6.40	120	0.85
S-3A Moor, shore[3]	3.92	67.2	6.25	14.4	1.60	160	0.00
S-3B Moor, 1/4	17.4	365	113	164	22.0	150	1.35
S-3C Moor, center	7.44	371	142	151	17.0	160	1.11
S-4 Maple	6.3	510	150	161	23.4	180	1.17
S-5 Eaton Rapids	7.84	224	57.5	59.4	4.20	80.0	0.46

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] sample collected in fall, 1980

[3] S-3A,B,C represent a traverse sampling of the river.

Appendix I: Continued.

NICKEL

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	NP[2]	2.64	1.75	4.41	1.40	N.D.	0.06
F-5 Holt	NP	9.20	5.00	9.36	9.60	N.D.	1.09
F-9 Elm	NP	1.36	1.25	2.25	1.20	N.D.	0.09
F-11 Maple	NP	9.12	5.50	17.7	9.00	N.D.	1.14
F-14 Delta	NP	2.32	2.25	11.9	1.80	N.D.	0.06
F-16 Jones	NP	2.40	2.25	13.1	2.20	N.D.	0.04
2. Size fracation: < 0.21 mm							
F-1 Bunker	NP	5.44	3.00	4.50	1.40	N.D.	0.16
F-3 Riverside	NP	16.4	8.25	7.92	5.00	N.D.	0.42
F-5 Holt	NP	16.2	9.25	8.28	8.40	N.D.	0.85
F-7 Waverly	NP	14.2	7.50	11.5	9.00	N.D.	0.50
F-8 Riverside	NP	4.72	2.75	3.87	1.60	N.D.	0.12
F-9 Elm	NP	3.20	1.25	3.15	0.80	N.D.	0.09
F-10 Kalamazoo	NP	2.96	1.50	2.70	1.20	N.D.	0.13
F-11 Maple	NP	9.12	6.75	10.4	7.60	N.D.	0.79
F-12 Tecumseh	NP	8.24	5.75	10.3	5.60	N.D.	4.00
F-14 Delta	NP	5.76	4.50	7.29	2.60	N.D.	0.15
F-16 Jones, bank	NP	7.20	6.00	8.37	3.20	N.D.	0.23
F-16 Jones	NP	4.80	3.75	4.77	1.40	N.D.	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] NP - Analysis of leachate not performed

Appendix I: Continued.

NICKEL

B. Leach attacks performed in summer, 1981:

Sample		Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1.	Size fraction: >0.21 mm							
S-1	Maple[2]	1.76	6.00	4.74	20.6	10.0	N.D.	1.14
S-2	Holt[2]	1.92	13.4	7.50	23.2	9.40	N.D.	1.09
2.	Size fraction: < 0.21 mm							
S-1	Maple[2]	1.28	9.44	4.50	16.8	7.40	N.D.	0.79
S-2	Holt[2]	1.68	12.6	8.50	15.4	5.40	N.D.	0.85
S-3A	Moor, shore[3]	0.24	1.76	0.50	2.20	0.80	N.D.	0.00
S-3B	Moor, 1/4	2.00	13.2	4.75	36.8	25.0	N.D.	1.35
S-3C	Moor, center	1.44	12.4	5.00	33.0	21.0	N.D.	1.11
S-4	Maple	1.04	10.1	4.00	26.4	14.2	N.D.	1.17
S-5	Eaton Rapids	1.20	11.8	10.0	16.8	6.60	N.D.	0.46

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] sample collected in fall, 1980

[3] S-3A,B,C represent a traverse sampling of the river.

Appendix I: Continued.

ZINC

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	0.24	7.84	3.75	9.54	1.40	15.0	0.06
F-5 Holt	1.28	81.2	37.5	74.4	33.4	35.0	1.09
F-9 Elm	0.80	34.0	6.00	23.1	1.80	35.0	0.09
F-11 Maple	1.12	81.0	41.8	77.4	32.0	35.0	1.14
F-14 Delta	1.92	9.50	5.00	35.7	1.00	30.0	0.06
F-16 Jones	0.72	9.50	4.50	38.8	2.80	25.0	0.04
2. Size fraction: <0.21 mm							
F-1 Bunker	0.72	1.06	4.50	9.90	2.60	35.0	0.16
F-3 Riverside	1.36	52.7	12.5	21.8	6.60	20.0	0.42
F-5 Holt	0.64	55.0	25.0	35.4	11.8	15.0	0.85
F-7 Waverly	0.80	50.6	12.3	25.7	6.60	30.0	0.50
F-8 Riverside	1.52	34.3	4.50	12.2	2.20	15.0	0.09
F-9 Elm	1.52	25.0	6.50	9.63	1.80	20.0	0.12
F-10 Kalamazoo	3.36	31.2	8.75	63.0	4.60	30.0	0.13
F-11 Maple	7.84	85.0	61.5	83.3	19.4	40.0	0.19
F-12 Tecumseh	0.80	94.6	87.0	94.5	39.2	25.0	4.00
F-14 Delta	0.56	33.1	11.3	34.7	6.20	40.0	0.15
F-16 Jones, bank	5.12	53.3	23.0	41.7	5.60	20.0	0.23
F-16 Jones	5.20	26.6	8.50	15.8	2.60	15.0	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix I: Continued.

ZINC

B. Leach attacks performed in summer, 1981:

Sample		Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1.	Size fraction: >0.21 mm							
S-1	Maple[2]	4.40	67.7	49.0	129	22.0	35.0	1.14
S-2	Holt[2]	0.96	58.0	20.5	59.0	7.20	35.0	1.09
2.	Size fraction: <0.21 mm							
S-1	Maple[2]	2.72	88.9	7.65	104	12.6	35.0	0.79
S-2	Holt[2]	0.80	51.2	18.8	40.2	4.00	20.0	0.85
S-3A	Moor, shore[3]	0.32	8.64	2.00	5.40	1.60	15.0	0.00
S-3B	Moor, 1/4	0.88	58.4	27.8	173	21.1	50.0	1.35
S-3C	Moor, center	1.28	72.2	28.5	119	14.0	55.0	1.11
S-4	Maple	1.76	87.9	39.0	179	26.8	70.0	1.17
S-5	Eaton Rapids	1.04	69.1	30.0	51.4	3.20	15.0	0.46

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

[2] sample collected in fall, 1980

[3] S-3A,B,C represent a traverse sampling of the river.

Appendix I: Continued.

COPPER

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	0.08	0.64	1.00	0.36	2.20	10.0	0.06
F-5 Holt	1.20	3.12	0.75	1.53	71.6	30.0	1.09
F-9 Elm	0.16	1.20	1.25	0.72	11.2	25.0	0.09
F-11 Maple	1.28	3.52	0.50	1.53	71.4	25.0	1.14
F-14 Delta	0.24	1.76	2.00	0.45	2.00	20.0	0.06
F-16 Jones	0.08	0.96	1.25	0.54	2.40	15.0	0.04
2. Size fraction: <0.21 mm							
F-1 Bunker	0.56	6.00	3.75	0.99	10.4	15.0	0.16
F-3 Riverside	0.40	0.88	1.50	0.63	9.80	15.0	0.42
F-5 Holt	0.40	0.32	0.50	0.63	21.8	15.0	0.85
F-7 Waverly	0.40	0.72	1.25	0.54	9.00	20.0	0.50
F-8 Riverside	0.32	4.40	3.00	0.63	5.80	15.0	0.12
F-9 Elm	0.40	3.92	2.50	0.63	5.00	15.0	0.09
F-10 Kalamazoo	0.80	10.3	5.25	1.08	21.0	20.0	0.13
F-11 Maple	1.04	5.04	0.75	1.80	71.6	40.0	0.79
F-12 Tecumseh	3.12	11.4	6.25	1.17	107	25.0	4.00
F-14 Delta	0.88	6.40	5.50	0.63	23.6	15.0	0.15
F-16 Jones, bank	1.04	5.28	6.50	1.44	14.0	20.0	0.23
F-16 Jones	0.80	4.88	4.50	0.90	8.60	15.0	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix I: Continued.

LEAD

A. Leach attacks performed in fall, 1980:

Sample	Exch[1]	Carb	Mn-ox	Fe-ox	Org	Res	TOC
1. Size fraction: >0.21 mm							
F-1 Bunker	N.D.	3.92	2.25	3.51	1.00	40.0	0.06
F-5 Holt	N.D.	31.5	3.00	40.7	63.4	45.0	1.09
F-9 Elm	N.D.	94.0	14.8	39.6	6.20	65.0	0.09
F-11 Maple	N.D.	29.4	3.00	42.5	57.0	60.0	1.14
F-14 Delta	N.D.	10.6	5.00	22.7	6.40	50.0	0.06
F-16 Jones	N.D.	5.70	2.25	4.59	1.20	45.0	0.04
2. Size fraction: <0.21 mm							
F-1 Bunker	N.D.	1.20	2.00	3.24	1.80	50.0	0.16
F-3 Riverside	N.D.	1.68	2.50	4.50	8.00	55.0	0.42
F-5 Holt	N.D.	6.48	1.75	7.02	12.8	70.0	0.85
F-7 Waverly	N.D.	4.08	3.25	6.48	13.4	55.0	0.50
F-8 Riverside	N.D.	4.48	3.25	4.50	3.00	50.0	0.12
F-9 Elm	N.D.	61.4	13.3	22.3	9.80	60.0	0.09
F-10 Kalamazoo	N.D.	23.0	7.75	13.5	8.00	55.0	0.13
F-11 Maple	N.D.	42.6	4.75	58.8	61.8	95.0	0.79
F-12 Tecumseh	N.D.	29.4	14.8	101	58.8	65.0	4.00
F-14 Delta	N.D.	82.2	41.8	33.8	17.0	55.0	0.15
F-16 Jones, bank	N.D.	6.48	10.0	10.7	12.8	60.0	0.23
F-16 Jones	N.D.	10.2	5.50	7.02	4.20	55.0	0.21

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[1] Exch - exchangeable; Carb - carbonate; Mn-ox - Mn oxide; Fe-ox - Fe oxide; Org - organic; Res - residual; TOC - total organic carbon

Appendix II: Calculation of Modified Phase Concentration Factor

Filipek, et al. (1981) analyzed the relative importance of phases using a PCF approach, which, in this study, is referred to as m-PCF_A. This parameter and a variation of it (m-PCF_B) were utilized in this study. The main difference between these two methods of calculating m-PCF is in their method of computing phase concentrations. The partitioning results obtained by the two methods were similar. The procedure for calculating m-PCF_A and m-PCF_B is described below and an example follows.

I. PCF_A (Filipek, et al., 1981)

A. Calculation of concentration of phase present:

1. Fe oxides: It is assumed that Fe oxides are present as FeOOH. Fe in FeOOH, by weight, is 62% of FeOOH. Multiplying the concentration of Fe leached in the moderately reducing attack by 1.6 yields the total FeOOH (62.5% x 1.6 ≈ 100%).

2. Mn oxides: It is assumed that Mn oxides are present as MnO_2. Mn in MnO_2, by weight is 63.2% of MnO_2. Multiplying the concentration of Mn leached by the easily reducible attack by 1.6 yields the total MnO_2 present (63.2% x 1.6 ≈ 100%).

3. Organic material: Organic material is estimated by multiplying total organic carbon by 2.2, the factor most commonly given for C in living organic material (i.e., Emory, 1960; In: Filipek, et al., 1981).

B. The percent, by weight, of the various fractions in the sediment is determined (Fe-ox, Mn-ox, org only).

C. The concentrations of the metals to be studied in each of the three phases are listed as percents of the total metal concentration in the three substrates.

D. The m-PCF_A for a metal is determined by dividing the percent metal in a particular phase by the percent that the particular phase makes up of the total substrate (i.e., step C/step B for each phase).

E. The m-PCF for a particular metal and phase is plotted as a percent of the total PCF values.

Appendix II: Continued.

II. PCF_B

A. PCF_B is computed exactly as PCF_A with the following modification:

1. The concentration of each phase present in a sample is determined as follows:

   a. Fe-oxide: This phase concentration is equal to the concentration of Fe released by the sediment in the moderately reducible attack.

   b. Mn-oxide: This phase concentration is equal to the concentration of Mn and Fe in the easily reducible attack.

   c. Organic: This phase concentration is equal to the total organic carbon content.

The Calculation of m-PCF$_A$ and m-PCF$_B$ for Cr

Sample: 5-Holt; < 0.21 mm fraction, fall leach attack

A. m-PCF$_A$

1. Calculation of Phase Concentrations

1. Calculation of Phase Concentrations	2. Phase Percent of Total Sediment
a. Fe-ox, present as FeOOH; 4320 ppm Fe x 1.6 = 6912	27
b. Mn-ox, present as MnO$_2$; 959.8 ppm x Mn 1.6 = 95.7	0.37
c. Org, 0.85TOC x 10,000 x 2.2 = 18700	73

3. Chromium concentration in each phase, as a percent

	Mn-ox	%	Fe-ox	%	Org	%
Cr	3.00 ppm	7.8	20.6	54	14.6	38

4. Calculation of m-PCF$_A$ (step C/step B)

	Mn-ox	Fe-ox	Org
m-PCF$_A$	21.1	2.0	0.53
as a %	89	8.5	1.5

(this value to be plotted on a trilinear diagram)

B. m-PCF$_B$

1. Calculation of Phase Concentrations	2. Phase percent of Total Sediment
a. Fe-ox, equal to concentration of Fe in moderately reducible attack = 4320	33
b. Mn-ox, equal to concentration of Fe + Mn in easily reducible attack = 96.8	0.75
c. Org, equal to TOC = 8500	66

Steps 3 and 4 are equivalent to those for calculating m-PCF$_A$.

3. Chromium concentration in each phase, as a percent

	Mn-ox	%	Fe-ox	%	Org	%
Cr	3.00 ppm	7.8	20.6	54	14.6	38

4. Calculation of m-PCF$_A$ (step C/step B)

	Mn-ox	Fe-ox	Org
m-PCF$_B$	10.4	1.64	0.58
as a %	82	13	5

Figure 5: Results of chromium partitioning in Grand River sediments illustrated through pi diagrams.

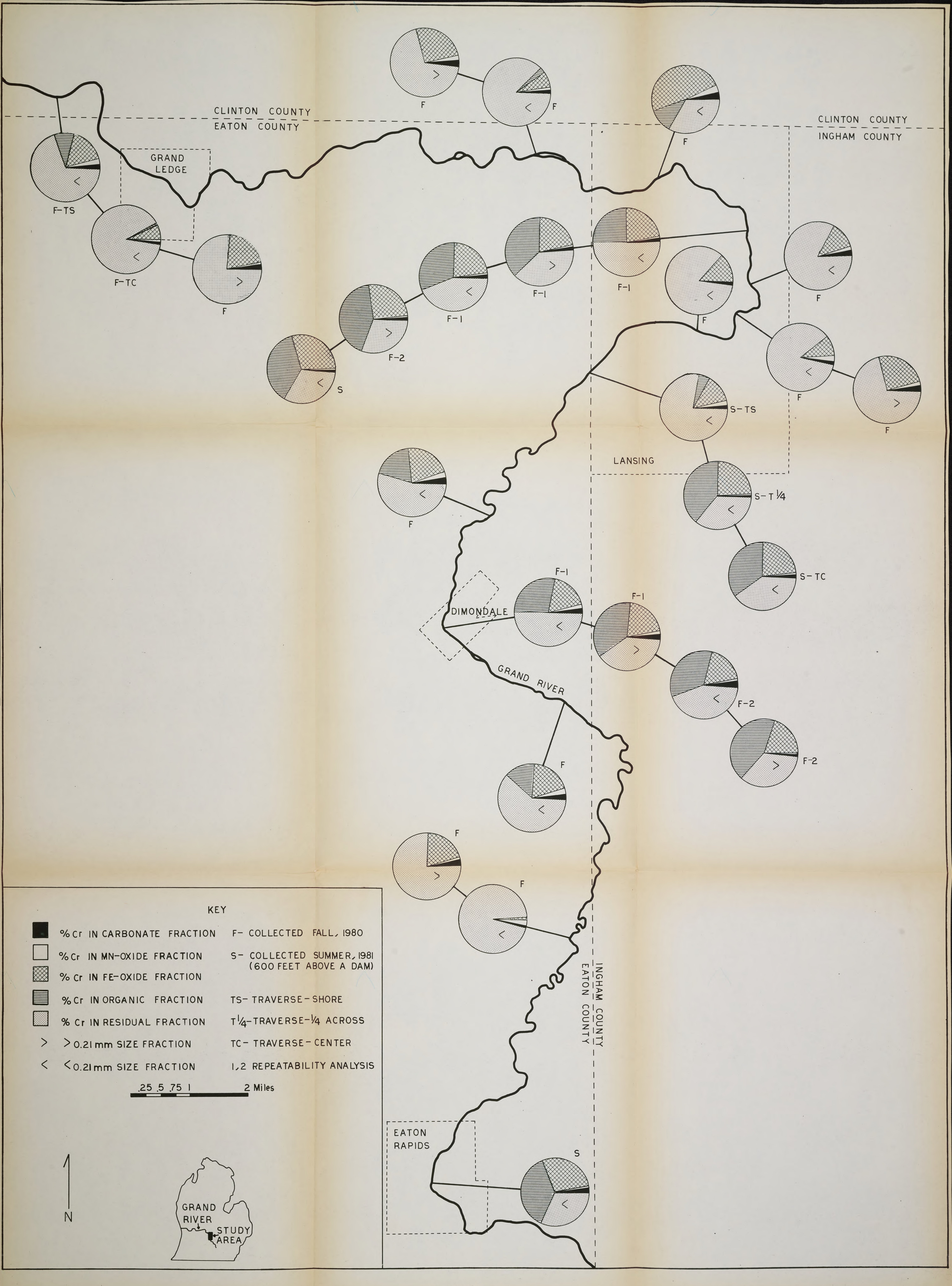
CLINTON COUNTY
EATON COUNTY
CLINTON COUNTY
INGHAM COUNTY
GRAND LEDGE
LANSING
DIMONDALE
GRAND RIVER
EATON RAPIDS
INGHAM COUNTY
EATON COUNTY
F-TS
F-TC
F
F-1
F-2
S
S-TS
S-T 1/4
S-TC
KEY
% Cr IN CARBONATE FRACTION
% Cr IN MN-OXIDE FRACTION
% Cr IN FE-OXIDE FRACTION
% Cr IN ORGANIC FRACTION
% Cr IN RESIDUAL FRACTION
> >0.21 mm SIZE FRACTION
< <0.21 mm SIZE FRACTION
F- COLLECTED FALL, 1980
S- COLLECTED SUMMER, 1981 (600 FEET ABOVE A DAM)
TS- TRAVERSE-SHORE
T 1/4-TRAVERSE-1/4 ACROSS
TC- TRAVERSE-CENTER
1,2 REPEATABILITY ANALYSIS
.25 .5 .75 1 2 Miles
N
GRAND RIVER
STUDY AREA

FIGURE 5